Development and application of a complex polymer coating to ensure high corrosion resistance of the outer surface of steel pipes of urban heating networks

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Various approaches and materials are used in the development of corrosion-resistant coatings. Polymer-based coatings have already proven their durability and ease of use and are promising materials for the development of corrosion-resistant protection. In comparison with metallized coatings, they are not subjected to constant destruction, and, unlike ceramic coatings, have sufficient plasticity to withstand mechanical loads and impact during transportation and installation. This paper presents the results of a study on the development of a corrosion-resistant polymer coating based on epoxy and polyurethane enamels, proposed for protecting the outer surface of a hot water supply pipeline with non-insulated insulation during channel-free laying. Polyurethane and epoxy enamels have their pros and cons. The idea of the work is to use a combined two-layer coating of polyurethane and epoxy enamel for corrosion protection in order to combine the positive properties of these polymers in a single complex.
The effectiveness of protecting the pipe surface from corrosion damage using a combined coating is reduced by poor adhesion of the coating material to the steel pipeline surface. For better adhesion to the metal, the pipe surface was pre-treated using a laser unit to obtain a developed relief and a preset roughness. Laser treatment is offered as an alternative to surface preparation instead of sandblasting.
Key words: corrosion protection, adhesion of polymer coating, increased adhesion, preparation of steel surface, increasing corrosion resistance of steel
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Introduction

The cities with the million-plus population have widely spread structure of underground hot water supply pipelines. It determines high dependence of the service life of steel pipelines on such indicators as acidity, humidity and biological activity of soil, ground currents, temperature and stresses in a pipe. All of them decrease potentially possible duration of the service life of steel hot water supply pipelines, mainly due to their corrosion destruction. Direct influence of the environment on duration of the service life of a pipeline during operation is noted. Additionally, it depends also on other factors. Analysis of this problem is presented by the works of I. L. Moskalev [1], L. A. Goldobina [2], N. A. Gromova [3]. Transporting medium is also related to the influencing factors on pipeline metal, it is true both for water supply [4] and other [5–7] systems, as well as quality of a pipeline manufacturing, its transportation and mounting [8, 9].

The following basic causes of pipe corrosion in heat supply pipelines are noted: soil corrosion [10–12], which s determined by soil humidity and pH, with protection methods presented in the researches of domestic and foreign researchers [13–15]; corrosion cracking under stress [16]; electrochemical corrosion owing to presence of ground currents from tram and trolley-bus electric power supply networks as well as underground railway electric power supply networks. Metal corrosion process in the field of ground currents is considered as an electrochemical process, caused by forming of galvanic pairs and electrolysis process in the places of delamination of protective coatings. Speed of corrosion process, according to the Faraday law, is determined by amount of electricity between anodes and cathodes of a steel pipeline, which is laid in a soil, and depends on soil electric resistance and nature of the processes taking place in anode and cathode areas on metal surface. Respectively, if a pipeline is subjected to additional effect of ground current (in addition to soil corrosion), sharp increase of the speed of corrosion processes both outside and inside a pipe can occur in the areas where electrolytic effect of these currents summarized with the current of galvanic pairs [17]. Total part of steel pipelines, which were rejected due to corrosion destruction of pipes, exceeds 85 %, what requires applying of the complex measures for their protection, including active and passive methods. Active methods of electrochemical protection [18–20] are implemented with use of galvanic anodes (protectors) having more negative electrochemical potential than that of a pipeline metal. Use of artificial decrease of soil specific electric resistance in the mounting places of protectors is also possible. Passive protection of the outer surface of steel pipes in heat supply pipelines concludes in use of special metallic and polymer coatings. At present time, different variants of such coatings were suggested and tested; as a rule, zinc was used as metallic coating and various epoxy compositions were used as polymer coating.

As soon as we can't exclude practically the effect of ground currents with use of active protection methods, it is important to realize properly passive protection of pipes via applying the coatings or their combinations. Such approach allows excluding forming of galvanic pairs on the outer pipe surface and excluding possibility of electrochemical corrosion in the case when coating lamination from the pipe surface occurs. Thus, a rational combination of the components with don't conduct electric current, i.e. a composition excluding use of metallic components, is the best option of passive coatings. Thereby this research was devoted to study of different combinations of polymer coatings on the base of epoxy and polyurethane enamels, while determination of their optimal contents and development of their application technologies on the pipe outer surface (which is processed preliminarily by laser for creating the best coating adhesion) was the aim of this research.

The following goals were solved in this work in accordance with the formulated aim:

– conduction of comparative investigations on strength increase of adhesion of polymer coatings due to preliminary laser treatment of metal and intermediate surface phosphatizing before applying the main coating;

– studying different variants of combinations of polymer coatings on the base of epoxy and polyurethane enamels;

– determination of the optimal composition of the main polymer components for forming corrosion-resistance coating on the outer surface of a steel pipe in heat supply pipelines.

Materials and methods

Flat plates of St3 steel were used as the samples for coatings application, in addition to the samples for elasticity testing during bending; this steel id applied for manufacture of heat supply pipelines as the economically profitable material [21]. Size of these plates was set depending on the kind of testing.

Properties of the coatings were evaluated on the samples, which were fabricated using preliminary laser treatment for forming of developed metal surface structure and for increasing the coating adhesion strength [22–24]. Part of the samples was subjected to additional phosphatizing [25–27]. Influence of preliminary treatment on adhesion properties of a steel plate was established in the previous works of the authors and these results allow to emphasize several pros: creation of the developed and controlled relief, which increases useful square of metal surface without peaks and "pockets", allowing obtain of good adhesion parameters even without a primer layer. The process of treatment of a pipe outer surface by laser beam, to form its roughness, is presented in the **Fig. 1**. The surface micro-picture after treatment is shown in the **Fig. 2**.

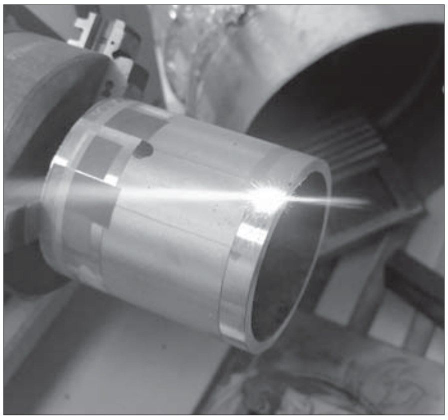

Fig. 1. Pipe surface processing by laser beam in the unit with rotating part

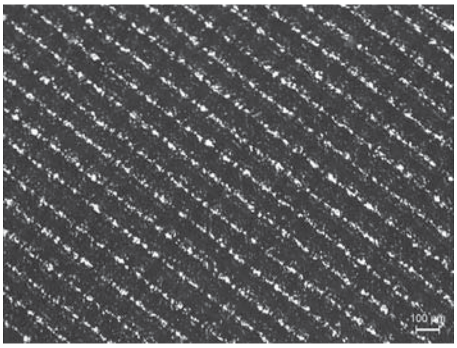

Fig. 2. Surface microstructure of the steel sample after laser treatment (magnification 50x)

Two kinds of polymers were chosen for examination of protective coatings: epoxy enamel and polyurethane enamel, their influence was considered as independent uniform coatings and as a combination of the layers of polymers [28–30]. Enamel application on the surface of the steel sample was carried out manually, using a brush. Thickness of the one enamel layer is varying within the ranges 30–60 μm for polyurethane and 20–30 μm for epoxy enamel; summarized thickness of all dual-layer coatings does not exceed 120 μm. Consequent treatment of the coating is not anticipated.

The following physical and mechanical properties – integrity, adhesion impact coating strength, bending elasticity – were evaluated in this research.

Several coatings were obtained, with shortened names of the particles for more suitable analysis: E – epoxy enamel, P – polyurethane enamel, P/E – dual-layer coatings with both enamels (in the order corresponding to the order of layers). To evaluate impact strength, the samples P1 and P2 with polyurethane enamel and the samples E1 and E2 with epoxy enamel, as well as the samples P/E1, P/E2, E/P1 and E/P2. To evaluate integrity strength, the samples E/P0.1, E/P0.2, P/E0.1 and P/E0.2 were examined. To evaluate bending elasticity of a film, the samples E1, E2, P1, P2 with

Table 1. The results with maximal measured parameters of adhesion strength of the samples using the tearing-off method

Coating type	Tearing-off force, MPa, depending on the coating preparation method (maximal values)		
	Laser treatment, phosphated composition 1	Laser treatment, phosphated composition 2	Laser treatment, without phosphatizing
Epoxy enamel	8.0	8.4	17.9
Polyurethane enamel	7.9	6.6	9.4

single-layer coating as well as E/P1.1, E/P1.2, P/E1.1 and P/E1.2 with dual- layer coating were used.

Preparation of the samples for testing of painting and lacquering materials corresponds to the requirements of the GOST 8832-76 "Methods of manufacturing painting and lacquering coating" [31]. Coating integrity was assessed in correspondence with the GOST 34395–2018 [32], using electrolytic and electric spark methods of non-destructive testing for coatings on metallic base. At the first stage, the samples were subjected to testing via electrolytic non-destructive testing unit Elcometer 270 with voltage values 9 V and 90 V, using water as a contact medium; integrity was evaluated afterwards, meeting the GOST requirements. Preliminary integrity control of coatings was directed on excluding of the influence of defects on the results of the following investigations; it ensured primary assessment of the quality of formed coatings.

Adhesion was determined via two variants: the cross-cut test method according to the GOST 31149-2014 (ISO 2409) [33] and the tearing-off method according to the GOST 32299–2013 [34] using a manual adhesion meter PosiTest AT. Two mushroom knobs were stuck on each of the six tested samples. Tearing-off with fixation of maximal load was carried out after 3 day holding. After observing the torn-off area of a mushroom knob and coating, the features of tearing-off were evaluated, among them mushroom knob / glue, glue / coating, coating delamination, coating / metal surface.

Impact strength of the coating was determined according to the GOST 4765-73 [35] via the sensor "Konstanta U-1A" (flat die 5.8 mm) and the sensor for measuring impact strength of coatings (flat die 20 mm). Each sample was subjected to minimum of three impacts, then the results were analyzed and compared, in order to determine the most efficient coating to withstand to impact load.

Bending testing of the samples was conducted via two methods: classic bending method around cylinder mandrel and Eriksen method, which concludes in a sample deformation by indenting a spherical matrix until the moment of appearance of coating destruction signs.

Results and discussion

The results of examination of adhesion properties for all variants of protective coatings displayed that all samples withstood the cross-cut testing. All six variants of coatings received the zero ball (according to the scale where 0 is the best mark and 6 is the worse mark) in accordance with the GOST 31149-2014: coating edges remained smooth and no one square in a lattice delaminated.

Adhesion tearing-off strength for polyurethane and epoxy enamels usually is not measured, but this testing allows to establish strength of the coating fixing on a substrate and to reveal which enamel displays better adhesion with metal surface. The experimental data are presented in the **Table 1**. Presence of a phosphated layer had no practical effect on adhesion strength of enamels. Analysis of the experimental results demonstrated that use of a phosphated layer in this case did not provide any influence on quality, what allows excluding this operation from the technological process.

It should be noted that interpretation of the data of the required coating tearing-off force needs taking into account the features of destruction mechanism in an adhesion compound.

When analyzing the tearing-off strength of coating, especial attention should be paid to the samples demonstrating cohesion tearing-off in the main volume of tested material or on the metal-coating boundary. The samples with adhesion tearing-off between glue and mushroom knob, which constitutes less than 20 % of a mushroom knob square, arise increased interest. It is caused by the fact that destruction in such cases occurs most often in the coating itself or in the metal-coating system, thus reflecting its true strength. The samples with wide adhesion tearing-off between glue and mushroom knob can distort the results, displaying weakness of a glue-coating compound, but not the actual strength of the coating itself. Thereby analysis of the data for the samples with minimal adhesion tearing-off allows obtaining more reliable and representing results about the coating tearing-off strength. The values of tearing-off force, obtained for the polyurethane sample with practically 100 % cohesion tearing-off in the upper layer of the coating is equal to 9.4 MPa, what provides more exact data on adhesion strength between metal and enamel. Presence of such rupture testifies on the fact that the strength of the substrate-coating compound is higher than the strength between enamel layers. It is confirmed once more the quality of obtained adhesion strength of the coating.

Most part of measurements with epoxy enamel is characterized by the surface area about 50 % with adhesion tearing-off between glue and mushroom knob. The remained areas have the following distribution: the samples with phosphated layer were torn off via cohesion mechanism (destruction inside this layer), while pure metal demonstrated complete enamel saving on the surface with rupture on the coating-glue boundary. It manifests on high strength between epoxy enamel and metal, which even exceeds that strength of the phosphated layer. The sample with maximal tearing-off values between epoxy enamel and pure metal is characterized by almost 100 % adhesion tearing-off between enamel and metal (see **Fig. 3**).

The experimental results allow to suggest that epoxy enamel is more suitable for the first layer of combined coating.

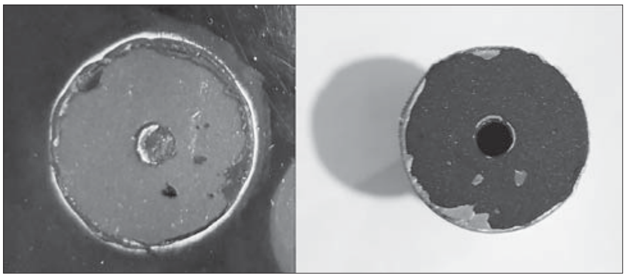

Fig. 3. Surfaces of the sample (left) and the mushroom knob (right) after tearing-off for epoxy enamel

Fig. 4. Delamination of the coating P/E during strike of a flat die from the height 40 cm; after opening the polymer film, it is seen that the detachment occurred between the metal surface and polyurethane

When determining the impact coating strength, the regulating document establishes the strength requirements ≥ 30 kgf·cm. The conducted testing displayed that all combinations except P/E (**Fig. 4**), containing the first polyurethane layer and the second epoxy layer, withstood the testing for 30 cm and higher, up to 50 cm (maximal value of flat die discharge), what confirms the previously suggested proposal.

Bending strength was measured with gradual decrease of a rod to its minimal diameter. All samples withstood the bending test for the smallest rod diameter 1 mm. The surface of coatings became dull in the bending area, it was caused by polymer extension. Fracture traces were not observed, what testify about successful testing.

Additional bending tests via Ericsen method allowed to establish deformation degree of metallic base, which is required for coating destruction during indentation of a round matrix. So, previously rejected sample withstood deformation 5.4 mm with cracks. The control samples with dual-layer epoxy-polyurethane coating E/P withstood deformation

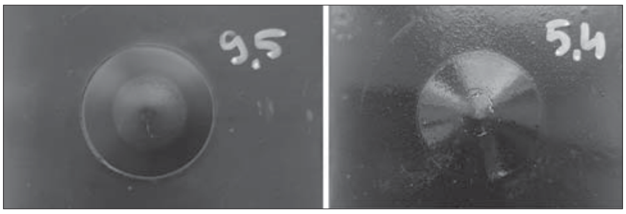

Fig. 5. The surface of the sample E/P (left) and P/E (right) after indentation of metallic plate of round matrix; the figures in the upper right angles mean depth of matrix indentation, mm

above 9.5 mm. The surfaces of metallic plates with dual-layer coatings E/P and P/E are presented in the **Fig. 5**. It can be seen that the coating damages (dulling and cracks) appeared in the center of the ledge during deformation.

The results of all conducted tests with various compositions of epoxy and polyurethane coatings are presented in the **Table 2**.

The following indicators are recognized as unsatisfactory strength parameters were determined: the samples which didn't withstand dropping of a flat die from the height 50 cm; the coatings bursting during evaluation of bending strength via bending with diameter > 3 mm; the variants of coatings having more than half of test plates with defects during integrity assessment.

Conclusion

1. The conducted analysis revealed permanent actuality of the problem of increasing corrosion resistance of the coatings, which are applied for protection of steel heat supply pipelines. Development of the methods and technological processes, providing improvement of adhesion strength of the system "coating – metal", is the key aspect for solving this problem. Development of the efficient technical solutions for improvement of adhesion strength of coatings is a multi-factor problem, including both choice of materials and optimization of technological parameters of application process.

2. Use of laser treatment allows to form a developed relief, characterizing by cellular structure and increased roughness, on the surface of a steel pipe. Such surface modification provides high adhesion properties of a coating even without intermediate binding layer.

3. The combined coating, excluding metallic electric conducting components and consisting of two polymer layers (epoxy enamel and polyurethane enamel), can be con-

Table 2. The testing results for epoxy and polyurethane enamels: comparison of the parameters

Comparison parameters	Epoxy enamel	Epoxy enamel on phosphated substrate	Polyurethane enamel	Polyurethane enamel on phosphated substrate	Epoxy enamel 1 layer, polyurethane enamel 2 layer	Polyurethane enamel 1 layer, epoxy enamel 2 layer
Surface adhesion, average parameter for all samples, MPa	8.2	8.0	9.4	7.9	8.3	7.7
Impact strength, flat die height 50 cm*	+	–	–	+	+	–
Bending strength, ø > 3mm*	+	–	+	–	+	–
Integrity*	–	+	+	+	+	+

* + and – mean respectively fulfillment or non-fulfillment of parameters noted in the left column by a sample

sidered as a prospective corrosion-resistant coating for steel pipelines used for heat supply routes; it is mainly located underground, in the conditions of active negative influence of ground currents on corrosion of outer surface of pipes. Dual-layers coating with the first epoxy layer and the second polyurethane layer demonstrated excellent results.

Based on the presented results of investigations, the idea of expedience of using the combined enamel system – epoxy and polyurethane – for corrosion-resistant protection was suggested by the authors. This combined enamel system allows uniting the strong features and neutralizing the disadvantages of each its component.

Input of the authors:

Pryakhin E. I. – scientific leadership, formulating of the main research directions, scientific editing of the article;

Pribytkova D. A. – writing the article, carrying out the experiments, data analysis.

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