Analysis of the effectiveness of sulphite liquor-based inhibitors in metal corrosion protection

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Abstract. The study addressed to protective properties of paint and varnish coatings, which include rust modifying primers based on sulfite liquors, applied to a rusty surface with an upper coating layer of PF-115 enamel. The effectiveness of the use of sulfite liquors as inhibitors of steel corrosion in rust converters based on orthophosphoric acid has been investigated. Polarization curves recorded in water extracts of rust modifying coatings based on sulfite liquors confirm their inhibitory effect. By using electrochemical methods we showed that the system P-2 rust converter + liquor + piperidine had the best protective properties. The inhibiting effect of the system P-2 rust converter + liquor + piperidine + maleic anhydride increased over time.

1. Introduction
One of the areas that ensure intensive industrial development is the rejection of ineffective technologies for anticorrosive protection of machines and structures, improving the quality of protective materials, and introducing resource-saving technologies. In the modern world, along with the global deterioration of the environment, corrosion destruction of metal products and structures has intensified due to an increase in the chemical activity of the environment [1]. The use of pulp and paper industry waste in anti-corrosion protection will make it possible to return material resources to the production cycle and will contribute to solving environmental problems.

Application of paint and varnish coatings is one of the most common methods of protecting metals from corrosion. It is known that such coatings reliably protect a metal surface only when applied to a thoroughly cleaned surface. In cases where the known cleaning methods do not produce the desired result, surface preparation without removing corrosion products is used. This method of surface preparation consists of application of special primers-converters or rust converters. When treating a surface with rust converters, over-etching of the treated surface can be observed, because corrosion products cover it unevenly. To reduce this negative effect, corrosion inhibitors are used [2, 3]. Prospects for the use of sulfite liquors are determined by the availability of raw materials and ability to obtain on their basis a product that is both a corrosion inhibitor and a film-forming agent in rust modifying primers.

The aim of this work is to investigate the effectiveness of steel corrosion inhibitors developed on the basis of sulfite liquors when they are introduced into a P-2 rust converter with a top coating layer of PF-115 enamel.
2. Methods and Materials

Previously, studies were carried out on the possibility of using waste from the pulp and paper industry as inhibitors of metal corrosion [4]. It was revealed that sulphite liquors are inhibitors of steel corrosion in an acidic environment. The following compositions of rust modifiers with a top coating layer of PF-115 enamel were tested: rust converter P-2; liquor + rust converter P-2; liquor + piperidine + rust converter P-2; liquor + piperidine + maleic anhydride + P-2 rust converter. To investigate the effectiveness of the proposed inhibitors based on sulfite liquors, the studies were continued.

Since a condensed sulfite liquor produces very fragile films, it was modified by condensation with piperidine.

Before condensation, the sulfite liquor was evaporated to a resinous state and dried at room temperature. A certain weighed portion of dry liquor (7 g) was dissolved in a small amount of water (13 ml) and mixed with a piperidine solution. The amount of piperidine was twice smaller than that of the liquor, that is, 3.5 g. To provide the crosslinking of macromolecules, 2 g of maleic anhydride was added to the second film-forming mixture. The mixture was boiled in a flask with a reflux water condenser in an air bath for 10 hours. To accelerate the reaction of piperidine with ligninsulfonic acids, a catalyst was used — tetrabutylammonium bromide in an amount of 0.004 mol. This catalyst dissolves in both organic and inorganic layers, i.e. it accelerates the reaction at the interface between the two phases. The introduction of the catalyst reduces the reaction time from 15 to 10 hours.

Rust converter P-2 had the following composition (wt. %): orthophosphoric acid - 50; ethyl alcohol - 20; distillate - 30.

Studies were conducted using samples of sheet steel of grade St.3, with the dimensions of 150x70 mm and a thickness of corrosion products of 100 microns. The samples were preliminarily cleaned from loose and layered rust. Acetone was used to remove grease stains. The studied system of coatings was applied to the surface with a brush. A 3% NaCl solution was used as a test medium.

The kinetics of anodic dissolution of metal under the paint film can be judged from anodic polarization curves. Polarization curves were recorded in a potentiostatic mode using a potentiostat. Polarization resistance (Δi/ΔE) was determined from the shape of polarization curves with an electric potential shift of 20 mV by 1 mV from the stationary value in the anode direction. Polarization curves were recorded after 10, 20 and 30 days.

To check and confirm the inhibitory effect of the modifier primer components, polarization curves were recorded in water extracts. The technique consisted in the following: a free dry film was prepared by applying a rust modifier (RM) primer to polyethylene. After drying for 20 days, the film of primer was removed and cut into pieces 5 x 20 mm in size. Then a suspension was prepared, consisting of 10 g of dry film pieces and 90 g of distilled water. The suspension, which consisted from the pieces of primer film and distilled water, was applied after seven days from the day of preparation.

3. Results and Discussion

The method of recording the polarization curves allows us to judge the speed with which electrochemical reactions causing the corrosion process take place in the environment of the intended operation of the metal and the coat that protects the metal [4].

Polarization curves were recorded after 10, 20 and 30 days on samples coated with the test systems. For instance, anodic polarization curves based on 10 days sample are presented on figure 1.

It can be seen that systems 3 and 4 are the most effective ones in terms of protection. The same pattern can be observed on the results based on longer period of the observation that are presented on figure 2.
Figure 1. Anodic polarization curves recorded on samples protected by various systems taken after 10 days.

Comparing all the estimates illustrated on figures 1, 2, and 3, we can notice the increasing inhibiting effect of systems 3 and 4, for which the strongest inhibition of the anodic process is observed.

Figure 2. Anodic polarization curves recorded on samples protected by various systems taken after 20 days.
Figure 3. Anodic polarization curves recorded on samples protected by various systems taken after 30 days

In a humid environment, water diffuses through the paint film to the metal-paint primer interface, dissolves its constituents and saturates them. In theory, it can be assumed that, ultimately, at this border there is a saturated solution of soluble constituents of the primer pigments, products of chemical interaction of pigments with a binder, together with low molecular weight, water-soluble organic substances, mainly arising from the air drying of the binder. Therefore, the processes occurring at the metal-primer interface can be simulated by leaching water-soluble primer components from pieces of dry film with distilled water and study the effect of the solution on a steel surface.

According to the anodic and cathodic polarization curves recorded in water extracts of the rust modifier primer (figures 4 and 5), it can be concluded that all systems are corrosion inhibitors for both anodic and cathodic processes. In figure 4, the shift of the curves to the region of more positive values indicates a slowdown of the anodic process, i.e. the process of destruction of metal under the coating.

Figure 4. Anodic polarization curves recorded in water extracts.
The difficulty of cathodic overvoltage is indicated by the displacement of the curves (figure 5) towards more negative values of the potential.

![Figure 5. Cathodic polarization curves recorded in water extracts.](image)

4. Conclusions
The study addressed the protective properties of paint and varnish coatings, which include rust modifying primers based on sulfite liquors and applied to a rusty surface with an upper coating layer of PF-115 enamel. It is shown that sulfite liquors can be used as corrosion inhibitors of steel in rust converters based on phosphoric acid. Using electrochemical methods, it has been shown that the P-2 rust converter + liquor + piperidine system had the best protective properties. The increasing over time inhibiting effect of the P-2 rust converter + liquor + piperidine + maleic anhydride system is detected.

Polarization curves recorded in aqueous extracts of rust modifying primers based on sulfite liquors confirm their inhibitory effect.

References
[1] Rakovskaya E G, Yagunova L K and Kudryashova O A 2017 The use of corrosion inhibitors to improve the protective properties of the rust converter P-2 Diagnostics of materials [Diagnostika materialov - in Russian] 9 pp 41–45
[2] Balybin D V, Kostyakova A A, Popova E D and Kudryavtseva N M 2014 The use of rust modifiers as a method of transforming corrosion products on the surface of metal products Bulletin of the Tambov University [Vestnik tambovskogo universiteta - in Russian] (Tambov: TSU Publishing House) 3 pp 903–907
[3] Rakovskaya E G and Zanko N G 2019 Modification of rust converters with N-containing organic compounds Corrosion: materials, protection [Korrozija: materialy, zaschita - in Russian] 5 pp 26–30
[4] Rakovskaya E G and Zanko N G 2020 Assessment of the possibility of using wastes from pulp and paper industry in mechanical engineering IOP Conf. Ser.: Earth Environ. Sci. 574 012068