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Anti-corrosion action of the extract of *the larix sibiric barrus* with different methods applying on the surface of metal

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Abstract. This article provides a method of the larch bark extract applying on a metal surface and also determining its anticorrosive protective action. It has been established that the protective effect of the larch bark extract was 37.5%, and when applying the extract after phosphoric acid, the protective effect increases to 65%, since the formed iron phosphates, having a porous structure, are a good primer and increase the adhesion of the rust converter. The sequence of the solutions application was determined: firstly, phosphoric acid and only after that the extract of larch bark. This sequence of components application leads to an improvement of the anticorrosion characteristics of the studied extract: at the same time, the protective effect of the extract Z and the inhibiting factor of corrosion γ increase 1.7-1.8 times.

1. Introduction

Spontaneous destruction of metals under the influence of chemical or physico-chemical influence of the environment causes enormous damage to the national economy of each country. Corrosion causes both direct and indirect damages. The indirect losses include losses due to equipment failure that has become unusable due to corrosion processes, its idle time, replacement or repair, damage to products of other industries due to contamination by its products of materials destruction, high tolerances for corrosion, the cost of additional electricity, water, materials, etc. To direct losses - the cost of pipelines spoiled by corrosion, equipment, machines, etc. The fight against corrosion of materials and structures is of great national economic importance. One way to protect metals from corrosion is inhibitors usage. Corrosion inhibitors - substances that, being in a corrosive environment in sufficient concentration or when adsorbed to a metal surface, slow down or even stop corrosive destruction of the metal altogether. A corrosion inhibitor can be either a single compound or a mixture of several. By chemical nature, inhibitors are divided into: volatile, organic, inorganic [1].

One of the natural corrosion inhibitors are tannins - organic compounds containing phenolic groups [2-24]. It is known that tannin is obtained from plant materials. Tannins are obtained from the bark of oak, willow, larch, etc. [16, 17, 22]. Basically, in Russia, tannins are obtained when disposing of wastes from woodworking enterprises and the paper industry. Inhibitors are used in conjunction with corrosion converters. Rust converters are mostly expensive and toxic. The search for new natural corrosion inhibitors, which will be much cheaper and safer, is relevant. Some common characteristics of effective inhibitors are known, such as the formation of durable compounds with the protected material, blocking the surface from the action of aggressive media.

The corrosion product, for example, $Fe(OH)_3$ rust, which contains Fe^{3+} iron cations, is an oxidizing agent. Tannins are used as a corrosion inhibitor, because their molecules having phenolic groups form a strong complex with the iron (III) cation, like iron (III) phenolate, black [15]. The scheme of interaction of tannins with iron cations Fe^{3+} is shown in Figure 1. The interaction with iron cations Fe^{2+} occurs in a similar way.

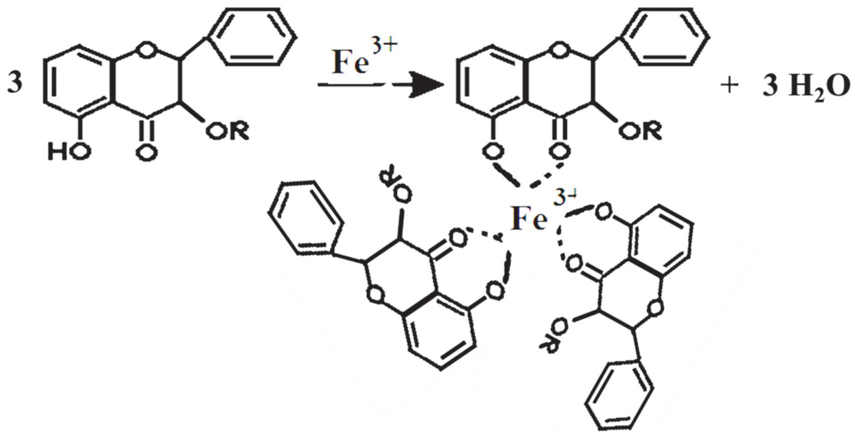


Figure 1. The interaction scheme of tannin with iron (III) cation.

From the literature it is known that phosphoric acid H_3PO_4 is added to rust converters to remove rust and form stable iron (II and III) phosphates [25]:

$$Fe(OH)_3 + H_3PO_4 = FePO_4 + 3H_2O,$$
$$3Fe(OH)_2 + 2H_3PO_4 = Fe_3(PO_4)_2 + 6H_2O$$

Iron phosphates do not protect the metal from further corrosion, because they have a porous structure, but are a good basis for paints, increasing the adhesion of varnish or inhibitor to the surface of the metal [1].

In this work, Siberian larch bark extract (*Larix sibirica*) was used as an inhibitor.

The purpose of this work is to determine the method of the larch bark extract applying to improve its adhesion with the metal surface and determine its effectiveness.

2. Models and Methods

For research, we used an aqueous extract of tannins, obtained at a temperature of 60 °C for 1 hour. Previously, we experimentally proved that this extract contains the highest amount of tannins compared to water extraction at a higher temperature and a duration of up to 2.5 hours [26].

In order to determine the anticorrosion protective effect of the extract with the two methods of deposition on the surface of iron, the following experiment was performed. To do this, four test samples of the metal (iron nails), treated with components: 1 - control nail (without coating); 2 - treated with the extract; 3 - treated with 30% phosphoric acid solution; 4 - phosphoric acid, and then the extract. After drying the components, the samples were immersed in a solution of sulfuric acid (pH 3) with potassium hexacyanoferrate (III) for 1 minute. The corrosion rate was determined by the intensity of the blue coloration of the complex compound of iron (II) cations - $Fe_3[Fe(CN)_6]_2$ on a photocolorimeter with a yellow light filter at a wavelength of 590 nm.

3. Results and Discussion

The average corrosion rate is calculated by the concentration of the resulting Fe^{2+} cations (within 1 minute) using the formula:

$$\vartheta_{corr} = \frac{C_2 - C_1}{t_2 - t_1} \quad (1)$$

where, C_2 and C_1 is the concentration of $Fe_3[Fe(CN)_6]_2$ at the final and initial time, respectively, t_2 and t_1 - the final and initial moment of time.

Using obtained results, it was calculated the average values of the iron corrosion rate, which are shown in Figure 2.

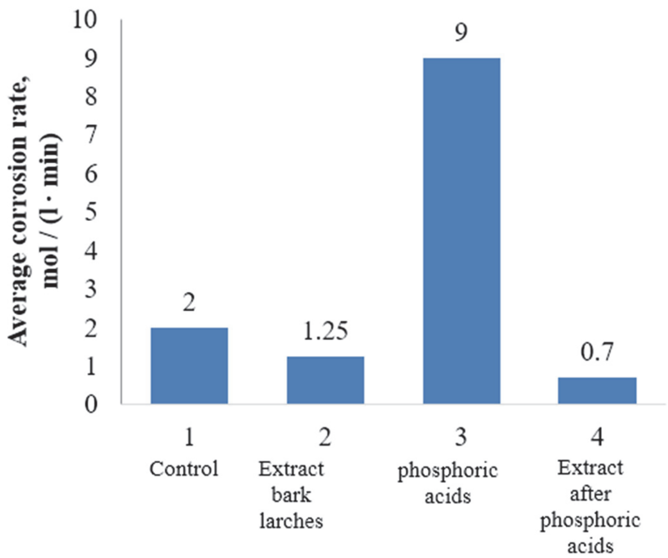


Figure 2. The corrosion rate of experimental samples in an acidic environment pH 3.

Based on the average corrosion rates, the protective effect of the extract (Z) and the braking coefficient (γ) were calculated using the formulas [23, 27]:

$$Z = \frac{\vartheta_0 - \vartheta_{inh}}{\vartheta_0} \cdot 100\%, \quad (2)$$

$$\gamma = \frac{\vartheta_0}{\vartheta_{corr}}, \quad (3)$$

where, υ_0 and υ_{corr} - corrosion rate in the absence and presence of inhibitor.

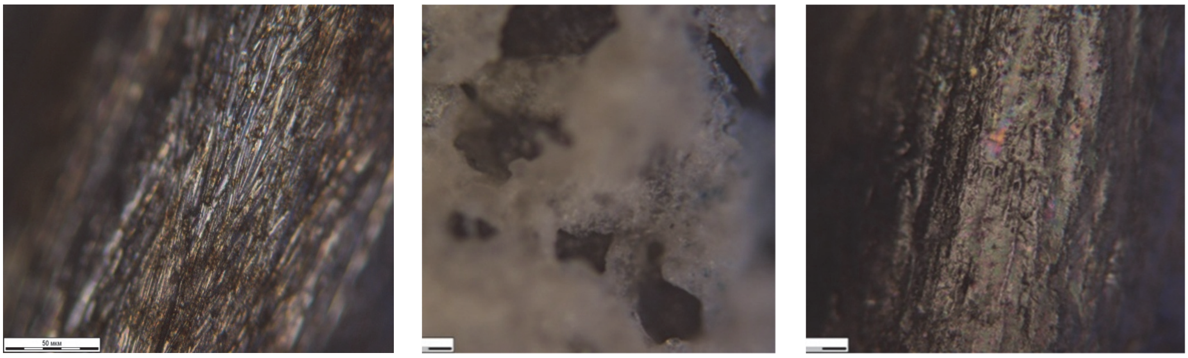
The obtained results are shown in the Table 1.

Table 1. The protective effect of the extract (Z) and the coefficient of corrosion inhibition (γ) without and with the preliminary application of phosphoric acid on the metal surface.

Samples	Protective action Z, %	Braking coefficient γ
Control	-	
Larch bark extract	37.5	1.6
Phosphoric acid	-	-
Phosphoric acid and then extract	65.0	2.9

It can be seen from the figure that direct coating of the iron surface with the aqueous extract of larch bark lowers the corrosion rate 1.6 times as compared to control due to the formation of stable complex compounds of iron tannates (II and III). In this case, the protective effect of the larch bark extract was 37.5% (Table). Treatment of iron with a 30% phosphoric acid solution, as expected, increases corrosion by 4.5 times compared with the control. As mentioned earlier, phosphoric acid with metal forms porous, stable crystalline iron phosphates, which have good adhesion to the metal surface. Therefore, phosphoric acid is used as a primer for paint, which increases the adhesion of the paint coating [28]. We applied this property of phosphoric acid to our corrosion inhibitor based on Siberian larch bark extract. Our experiment showed that when the larch bark extract is applied after phosphoric acid, the protective effect of the inhibitor increases to 65%, and the corrosion inhibition rate increases 1.8 times (Table 1).

In order to prove the porous structure of the formed iron phosphates on the metal surface, we carried out an additional study - we took micrographs of the samples surface with an Olympus BX 41 electron microscope with a scale of 50 μm, which are shown in Figure 3.



a) b) c)

Figure 3. The samples surface covered with a) extract;
b) 30% solution of H_3PO_4; c) larch bark extract after H_3PO_4.

It can be seen from photo (a) of Figure 3 that the tannins of the larch bark extract react unevenly with the metal surface, forming dark spots of iron tannates II and III. It can be seen from photo (b) that when the surface of iron samples is treated with a 30% solution of H_3PO_4, porous white metal phosphates are formed. Application of the extract after phosphoric acid leads to the uniform colored structure (c) of the iron surface. Thus, it was proved that the formed iron phosphates contribute to the binding and response of tannins to the metal surface over the entire area.

4. Conclusion

- It has been established that the protective effect of the larch bark extract, when directly applied to the surface of iron, is 37.5%. The contained tannins in the extract inhibit corrosion due to the formation of a protective film of stable complex compounds - iron tannates II and III (like an oxide film) and the transfer of an additional oxidizing agent (Fe^{3+}) into the complex.
- It was determined that the resulting phosphates of iron Fe^{2+} and Fe^{3+}, when treated with 30% H_3PO_4 solution, do not protect the metal from further corrosion, but serve only when cleaning from rust, and also as a primer to the metal surface for paints and varnishes and corrosion inhibitors.
- It was revealed that the protective effect of the extract when applied after phosphoric acid increases to 65%, since the formed iron phosphates, having a porous structure, are a good primer, increase the adhesion of the rust converter.
- The importance of the sequence of the solutions application of: phosphoric acid, and only after that the extract of larch bark is determined. It is this sequence of application of components that leads to an improvement in the anticorrosion characteristics of the studied extract: at the same time, the protective effect of the extract Z and the inhibiting factor of corrosion γ increase 1.7-1.8 times.

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