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

I E Kuzmina¹ and A I Fedorova¹

¹ Northeastern Federal University, Chemical Department, Yakutsk 677000, Russia

E-mail: fedorovaanaivanovna@mail.ru

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 Fe³⁺ 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](image-url)  
**Figure 1.** The interaction scheme of tannin with iron (III) cation.

From the literature it is known that phosphoric acid H$_3$PO$_4$ is added to rust converters to remove rust and form stable iron (II and III) phosphates [25]:

\[
\begin{align*}
\text{Fe(OH)}_3 + \text{H}_3\text{PO}_4 &= \text{FePO}_4 + 3\text{H}_2\text{O}, \\
3\text{Fe(OH)}_2 + 2\text{H}_3\text{PO}_4 &= \text{Fe}_3(\text{PO}_4)_2 + 6\text{H}_2\text{O}
\end{align*}
\]

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:
\[ \vartheta_{\text{corr}} = \frac{C_2 - C_1}{t_2 - t_1} \]  

(1)

where, \( C_2 \) and \( C_1 \) is the concentration of \( \text{Fe}_3[\text{Fe(CN)}_6]_2 \) 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.](image)

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

\[ Z = \left( \frac{\vartheta_0 - \vartheta_{\text{inh}}}{\vartheta_0} \right) \times 100\%, \]  

(2)

\[ \gamma = \frac{\vartheta_0}{\vartheta_{\text{corr}}} \]  

(3)

where, \( \vartheta_0 \) and \( \vartheta_{\text{corr}} \) - 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 (\( \gamma \)) without and with the preliminary application of phosphoric acid on the metal surface.

| Samples                        | Protective action \( Z, \% \) | Braking coefficient \( \gamma \) |
|--------------------------------|-------------------------------|---------------------------------|
| 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.

![Figure 3. The samples surface covered with a) extract; b) 30% solution of H₃PO₄; c) larch bark extract after H₃PO₄.](image)

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 H₃PO₄, 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 (Fe³⁺) into the complex.
- It was determined that the resulting phosphates of iron Fe²⁺ and Fe³⁺, when treated with 30% H₃PO₄ 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.
References

[1] Korovin N V 2011 General chemistry ed Kostyan T S (Moscow: Higher School publishing house) 496 p
[2] Dmitruk S E 2004 Medicinal plants, raw materials and phytopreparations (Tomsk: Tomsk University Press) 148 p
[3] Shirmohammadi Y, Efhamisisi D and Pizzi A 2018 Tannins as a sustainable raw material for green chemistry: A review Industrial Crops and Products 126 316-32
[4] Rahim A A, Kassim M J, Rocca E and Steinmetz J 2011 Corrosion Engineering Science and Technology 46 (4) 425-31
[5] Shah A M, Rahim A A, Yahya S, Raja P B and Hamid S A 2011 Pigment and Resin Technology 40 (2) 118-22
[6] Jain T, Chowdhary R and Mathur S P 2006 Electrochemical behavior of aluminium in acidic media Materials and Corrosion 57 (5) 422-6
[7] Abdul Rahim A, Rocca E, Steinmetz J, Adnan R and Kassim M J 2004 Mangrove tannins as corrosion inhibitors in acidic medium - Study of flavanoid monomers Proc. Of EUROCORR 2004 - European Corrosion Conference: Long Term Prediction and Modelling of Corrosion
[8] Haddadi S A 2019 Influence of organic corrosion inhibitor on corrosion behavior of St-37 carbon steel in NaCl medium Proc. Of AIP Conf. 2097 030008
[9] Qian B, Michaildis M, Hilton M, Zheng Z and Shchukin D 2019 Electrochimica Acta 297 1035-41
[10] Montoya L F, Contreras D, Jaramillo A F, Rojas D and Melendrez M F 2019 Progress in Organic Coatings 127 100-9
[11] Guedes L A L, Bacca K G, Lopes N F, da Costa E M 2019 Materials and Corrosion (New York: Wiley) 648 p
[12] Božović S, Martinez S and Grudic V 2019 Acta Chimica Slovenica 66 (1) 112-22
[13] Berrani A, Benassaoui H, Zouarhi M, Hajjaji N and Bengueddour R 2018 Analytical and Bioanalytical Electrochemistry 10 (10) 1299-316
[14] Tambun R, Christamore E, Pakpahan Y F and Haryanto B 2018 IOP Conf. Ser.: Mat. Sci. and Eng., 420 (1) 012059
[15] Saleh R M, Ismail A A and Hosary A A 1984 Corrosion prevention and control 31 (1) 21–3
[16] Afidah A R and Jain K 2008 Recent Patents on Materials Science 1 223-31
[17] Jaén J A, De Obaldía J and Rodriguez M V 2011 Hyperfine Interactions 202:1-3 25-38
[18] Winkelmann H, Badisch E, Roy M and Danninger H 2009 Materials and Corrosion 60:1 40-8
[19] Kuzmina I E, Platonov A S, Fedorov A I 2017 Tannins in larch bark extracts of Aykra LLC Proc. of Sci., ed., society: trends and development prospects: materials 1 40-41
[20] Kilimnik A B, Gladysheva I V 2008 Chemical resistance of materials and corrosion protection: study guide (Tambov: TSTU Publishing House) 80 p
[21] Nazarova N A 1960 Primer based on phosphoric acid, pigments, a binder and solvents Invention certificate No. 126972