Methods of electrochemical research of corrosion resistance of metal treated with corrosion inhibitors, created on the basis of plant-based raw materials

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Abstract. The use of corrosion inhibitors based on raw materials of plant origin has been a poorly studied method of metal processing so far. To show the degree of corrosion protection, it is necessary to examine it. It is possible to do this by means of electrochemical research, the method of which consists of several methods: the extrapolation method; the polarization resistance method; the related methods. As a result of this method, a significant advantage of samples treated with corrosion inhibitors based on raw materials of plant origin was revealed.

1. Introduction
There are many ways to determine the corrosion resistance of metal, used in different conditions for different types of treatment. One of the most promising treatment methods is metal coating with corrosion inhibitors based on vegetable raw materials [1]. The method of investigation of corrosion resistance of metal samples processed with these materials requires a detailed study. It is necessary to achieve the most accurate results in determining corrosion resistance, as all research in this area of science will depend on it.

2. Materials and methods
The electrochemical methods for determining corrosion rate are based on the results of polarization measurements, most often obtained with potentiostats or various types of corrosion meters. The advantage of these methods is manifested in the ability to evaluate the mechanism of processes [2]. Their disadvantage is the incomplete adequacy of the results obtained and the theoretical concepts used in their interpretation, which may not always take into account the complexity of phenomena occurring on the surface.

To date, most methods for evaluating corrosion process parameters have been based on the analysis of the kinetic equation:
\[ I = I_{\text{cor}} \left\{ \exp \left( \frac{2,3\Delta E}{b_a} \right) - \exp \left( \frac{-2,3\Delta E}{b_k} \right) \right\} \]

where \( b_a \) and \( b_k \) are respectively the anodic and cathodic Tafel constants; 
\( \Delta E = E - E_{\text{cor}} \) — electrode polarization, measured from corrosion potential (\( E_{\text{cor}} \)).

3. The extrapolation method
The classical method of polarization curve analysis is the extrapolation method [3]. Figure 1 schematically shows anode and cathode polarization curves in a medium with and without corrosion inhibitor. In semi-logarithmic coordinates, these curves turn into straight lines at a sufficient distance from the corrosion potential. Extrapolation of straight sections of anode or cathode polarization curve to the stationary potential allows determining the corrosion current density (\( i_{\text{cor}}, \text{A/m}^2 \)) and calculating its speed (\( K, \text{g/m}^2\text{h} \)):

\[ K = \frac{i_{\text{cor}}A}{nF}, \]

where \( A \) is the atomic weight of metal (55.85 for iron); 
\( n \) — metal ion valence (2 for iron); 
\( F \) — Faraday constant, A·h/g-equivalent.

Comparison of corrosion current values in the presence of the inhibitor (\( i_{\text{cor}}^i \)) and without it (\( i_{\text{cor}} \)) allows to calculate the protective effect (\( Z, \% \)) and the protection factor (\( \gamma \)):

\[ Z = 100 \frac{i_{\text{cor}} - i_{\text{cor}}^i}{i_{\text{cor}}} \]

\[ \gamma = 100 \frac{i_{\text{cor}}}{i_{\text{cor}}^i} \]

Figure 1. Anodic and cathodic polarization curves with and without corrosion inhibitor

The slope of rectilinear sections of polarization curves is related to the degree of polarizability of anode or cathode components of the corrosion process, respectively. It allows to calculate Tafel constants and to find out the nature of inhibitor action by type of control (cathode, anode, mixed) and to determine its degree.

The tests related to the polarization curves are carried out according to the instructions for the potentiostat used. Electrolyte (e.g. formation water or 3% solution of NaCl + 250 mg/l CH₃COOH) with aggressive gases dissolved in them or mixtures of electrolyte - liquid hydrocarbon (hydrocarbon condensate, kerosene) are used as the test medium.
Consistent testing of a sample in a solution with and without an inhibitor (after exposure in an inhibited solution) allows us to evaluate the effect of the inhibitor.

The disadvantage of the extrapolation method is the need for significant polarization of the electrode (~ ±0.5…1.5 V) so that the Tafel sections on the curves can be clearly detected. This also determines the limitations of the method, which are associated with possible irreversible changes in the electrode system, resulting in irreversibility and hysteresis of potential-current curves.

To evaluate the effect of the inhibitor separately on the cathode or anode process, you can use the polarization of the electrode in the appropriate direction by some constant value, for example, in the range of 5…30 mV. At the selected potential shift from the stationary value, the current value is determined. Such determinations are performed for pure and inhibited solutions either from both pairs of polarization curves, or (preferably due to less electrode exposure) directly by measuring the current value at a corresponding potential displacement.

As a result of such definitions, two pairs of current values will be found (see Figure 6.2): $i^k$, $i^{au}_k$ and $i^a$, $i^{au}_a$ mainly related to the rate of cathode and anode processes in the initial and inhibited environment. The comparison of values $i^a$ and $i^{au}_a$ characterizes the inhibitor effect on the anodic component of the process, while $i^k$ and $i^{au}_k$ refer to the cathodic one.

4. The polarization resistance method
This method is often associated with the names of Stern and Giri, who contributed most to its development. It is based on the assumption that the relationship between potential and superimposed current at a potential close to corrosion potential does not correspond to equation (6.5), but is linear. This assumption leads to a simple ratio between the corrosion current and polarization resistance ($R_p$):

$$I_{cor} = \frac{b_a \cdot b_k}{2.3(b_a + b_k)} \cdot \frac{1}{R_p} = \frac{B}{R_p},$$

where $-R_p = \frac{dE}{dl}$

$$B = \frac{b_a b_k}{2.3(b_a + b_k)}.$$  

- constant depending on the Tafel constants

The polarization resistance method eliminates most of the problems associated with intense electrode polarization. In practical measurements, the polarization of the electrode rarely exceeds ±20 mV and is most often limited to ±10 mV. The method involves the use of conventional laboratory equipment for polarization measurements. In addition, the simplicity of the method stimulated the development of corrosion meters based on polarization resistance measurements by many companies [4]. When working with them, one should follow the instructions attached to them, taking into account the disadvantages of the method.

One of the disadvantages of the method is the assumption of the linearity of the basic kinetic equation leading to systematic errors [5]. The greater the polarization value, the more these errors become, they can reach several tens of percent. Another disadvantage of the method is related to the uncertainty of the $B$ constant, the value of which cannot be obtained directly by measuring $R_p$ and is set a priori or determined in a separate experiment, the use of one or another of its quantitative value must be reasoned in each particular case. Theoretically, the $B$ value can vary from 6.5 to 51.11. Additional difficulties in the interpretation of the results obtained occur in low conductive media, as well as in the deposition of corrosion products on corrosive surfaces, such as hydrogen sulfide corrosion.
The use of corrosion meters based on polarization resistance measurements, taking into account the reservations made, can be recommended when it is necessary to obtain a large number of measurements in a short period of time, for example, when selecting an inhibitor from a large series of samples to obtain the dependence of the change in corrosion rate over time, to control the effectiveness of the inhibition with a constant nature of the corrosion process, etc.

5. Related methods
The related methods of polarization curve analysis largely combine the advantages of both previous methods, with almost no disadvantages [6]. Like the polarization resistance method, they provide for relatively small polarization, but, in contrast to this method, being based on the nonlinearity of equation (6.5), they allow all three parameters of the corrosion process to be determined in one experiment \((b_a, b_k, I_{cor})\). This only requires the determination of several current values with negligible polarization of the electrode near the corrosion potential. The distinctive feature of these methods, developed by various authors, is the nature of the necessary polarization and its direction. It can be defined as cathodic, anodic, or cathodic-anodic. The most convenient are the adjacent Belevsky-Kudelin methods, which allow, depending on the choice of the experimenter, to choose either cathode or anode measurements, or to use the polarization of both signs, depending on the expedient need [7]. In particular, cathode measurements are preferred for systems where anode currents cause surface etching. Anodic polarization has an advantage when cathode shift of potential leads to deposition of corrosion products on the electrode or to restoration of the oxide formed during corrosion, as well as when another electrode process is applied (cathode emission of hydrogen in the study of corrosion with oxygen depolarization).

For the analysis of experimental data corresponding to the ratio (6.5), two variants can be used, based on the precise analytical solution of the system of initial equations at a certain choice of variables \(I_1\) and \(\Delta E\).

In particular, for points of any branch of the polarization curve selected with equal pitch \((\Delta E, 2\Delta E, 3\Delta E)\) or \((-\Delta E, -2\Delta E, -3\Delta E)\) the required values are determined by the following formulas:

\[
I_{cor} = \frac{|I_1|}{\sqrt{\Delta I_3 - 3(I_2/I_1)^2}} \quad (7)
\]

\[
b_a = \pm \Delta E / \log 0,5 \left[ I_2 / I_1 \pm \sqrt{4I_3 / I_1 - 3(I_2 / I_1)^2} \right] \quad (8)
\]

\[
b_k = \pm \Delta E / \log 0,5 \left[ I_2 / I_1 \pm \sqrt{4I_3 / I_1 - 3(I_2 / I_1)^2} \right] \quad (9)
\]

At other choice of variables, namely at \(\Delta E\), divisible by two: \((\Delta E, 2\Delta E, 4\Delta E)\) and \((-\Delta E, -2\Delta E, -4\Delta E)\) corrosion current and Tafel constants are found from:

\[
I_{cor} = \frac{|I_1|}{\sqrt{4I_4 - (I_2/I_1)^2}} \quad (10)
\]

\[
b_a = \pm \Delta E / \log 0,5 \left[ I_2 / I_1 \pm \sqrt{2I_4 / I_2 - (I_2 / I_1)^2} \right] \quad (11)
\]

\[
b_k = \pm \Delta E / \log 0,5 \left[ I_2 / I_1 \pm \sqrt{2I_4 / I_2 - (I_2 / I_1)^2} \right] \quad (12)
\]

where the signs \(\leftrightarrow\) and \(\leftrightarrow\) in (3.11), (3.12), (3.14), (3.15) refer to anodic currents, while \(\leftrightarrow\) and \(\leftrightarrow\) – to the cathodic ones;

\(I_1, I_2, I_3, I_4\) – currents respectively at polarization \(\Delta E, 2\Delta E, 3\Delta E, 4\Delta E\).
Under the conditions of the applicability of equation (6.16), which is a special case of general equation (6.5), provided that \( b_k \to \infty \) (diffusion control of cathode reaction in case of corrosion with oxygen depolarization) or \( b_a \to \infty \) (metal passivity):

\[
I = I_{\text{cor}} \left\{ \exp \left( \frac{2,3 \Delta E}{b_a} \right) - 1 \right\}
\]

or

\[
I = I_{\text{cor}} \left\{ 1 - \exp \left( \frac{-2,3 \Delta E}{b_k} \right) \right\}
\]

The calculation of \( b_a, b_k, I_{\text{cor}} \) is possible by (6.10)...(6.15). It is reasonable to determine the parameters of such electrode systems by two values of currents \( I_1 \) and \( I_2 \), corresponding to anode (cathode) polarization of the electrode \( \Delta E \) and \( 2\Delta E \) (i.e. polarization of one sign). In this case:

\[
I_{\text{cor}} = \frac{I_1}{I_2 / 2 - 1}
\]

\[
b = \Delta E / \log(I_2 / I_1 - 1)
\]

The research was conducted in a three-electrode electrochemical cell made of Pirex glass with anode and cathode spaces separated by grinding. The electrochemical measuring complex by Solartron (UK) was used, consisting of an SI 1255 impedance analyzer and a potentiostat SI 1287 (Figure 2).

**Figure 2.** Electrochemical measuring complex by Solartron (UK)

Working electrode - carbon steel St.3 (composition, %: Fe – 98,36; C – 0,2; Mn – 0,5; Si – 0,15; P – 0,04; S – 0,05; Cr – 0,3; Ni – 0,2; Cu – 0,2) \((S_{el} = 0,14 \text{ cm}^2)\), reinforced into a mandrel made of epoxy resin ED-5 with polyethylene polyamine hardener. Auxiliary electrode - smooth platinum. Silver chloride electrode was used as a comparison electrode. After immersion the electrodes were kept in the solution to establish quasi-stationary potential (10...15 min). The samples were polished up to purity class 6 and degreased with acetone and alcohol in series.
6. Results and discussion
In the course of the research, three methods were analyzed to study the corrosion resistance of metal treated with corrosion inhibitors based on plant origin raw materials. As a result of the research carried out with these methods, a significant advantage of metals subject to processing has been revealed.

7. Conclusion
Anticorrosive properties of metals are the main assessment indicator in studies of corrosion inhibitors based on raw materials of plant origin. The received method of electrochemical research of anticorrosive firmness of the metal processed by the corrosion inhibitors created on the basis of raw materials of a plant origin, allows to define an indicator of anticorrosive firmness with high accuracy that makes it advantageous in researches of this direction.

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