Assessment of the possibility of using wastes from pulp and paper industry in mechanical engineering

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Abstract. The aim of this study was to assess the possibility of using wastes from pulp and paper industry as metal corrosion inhibitors. We studied protective properties of various systems, including the primers with rust modifiers developed on the basis of sulfite spent liquors and an upper coating layer of PF-115 enamel applied to a rusty surface. Using the gravimetric method and the method of polarization curves, we found that sulfite spent liquors inhibit steel corrosion in an acidic environment. We found that the P-2 rust modifier with an addition of lye + piperidine is the most effective inhibitor of steel rusting.

1. Introduction

Recently, a new approach to the problem of industrial and household waste has been proclaimed globally. This principle is called "Zero Waste", that is, the absence of waste. A quote from a book by R. Murray [1] became the starting point of our work: “From the point of view of environmental pollution, the problem boils down to the question of what is waste. From the point of view of the rational use of resources, this is a question of what waste can be turned into.”

Pulp and paper industry is one of the most polluting. In Russia, most pulp and paper enterprises currently produce cellulose mainly by the sulfite process. It consists in heat treatment of wood with a pulping liquor, due to which cellulose is separated from lignin. The latter passes into the solution in the form of lignosulfonates. The main waste products are sulfite spent liquor and purge condensates. A significant proportion of the organic substances of the sulfite spent liquor are known as lignosulfonates, which do not degrade and thus pollute the hydrosphere.

Steel and cast iron are the main engineering materials. They make up to 95% of all alloys used. Until now, the fight against corrosion has been an important problem in improving the efficiency of the use of metals and alloys. Corrosion causes significant material damage. According to estimates, each year a quarter of the total global output of steel is lost due corrosion. Currently, various methods are used to protect metals from corrosion; one of the most common is the application of paints and varnishes. However, this method has a lot of drawbacks; it does not always eliminate corrosion, but serves only as a protection against it and only slows down the rate of its spread. Therefore, a different approach has been proposed; namely, the use of special compounds with modifiers of corrosion products (rust) which improve the protective properties. It is noteworthy that to increase the efficiency of their application, it is necessary to make such compounds from cheap raw materials and simplify the technology of their use. Thus, these problems are relevant and have to be solved.

Research objective was to evaluate the possibility of using pulp and paper industry waste (sulfite spent liquor) as a corrosion inhibitor.
2. Methods and materials
The use of sulfite liquors as the basis of a rust modifier is justified by the fact that lignosulfonates present in them have high surface activity. Table 1 shows the group composition of organic substances of liquors which varies depending on the cooking mode and the raw materials used [2]. Based on sulfite liquor, film-forming compounds were prepared.

Table 1. Group composition of organic substances of sulfite liquors, %.

| Components                      | Treatment options | Sulfite | Bisulfite | Neutral sulfite |
|---------------------------------|-------------------|---------|-----------|-----------------|
|                                 | Wood species      | Coniferous | Deciduous | Coniferous | Deciduous | Deciduous |
| Lignosulphonates                |                   | 55-60    | 30-37     | 65-66         | 55-56     | 45-49     |
| Carbohydrates by RV (reducing substances) |                   | 23-26    | 38-42     | 16-17         | 17-19     | 12-14     |
| Organic acids                   |                   | 11-12    | 23-26     | 16-18         | 24-25     | 36-38     |
| Extractives and other components |                   | 1        | 2         | 1             | 2         | 3         |

Since evaporated sulfite spent liquor produces unstable films, it was modified by condensation with piperidine. Thus, the following compositions of primers with rust modifiers with the top coating layer of PF-115 enamel were tested:

1) rust modifier P-2;
2) lye + rust modifier P-2;
3) lye + piperidine, rust modifier P-2;
4) lye + piperidine + maleic anhydride, rust modifier P-2.

Studies were conducted using samples of steel sheets of grade St.3, and corrosion products were formed in an artificial climate chamber. Sample preparation included following procedures: the surface was cleaned of loose rust, and fatty contaminants were removed with acetone. The coating system was applied to the prepared surface with a brush. The test medium was a 3% NaCl solution.

A generalized assessment of the state of the coating was carried out on the basis of the results of inspection of the samples according to the formula:

\[ A = 0.05 (aB + aC) + 0.10 aP + 0.20 (aS + aSC + aK + aLr) \]  

where, \( aB, aC \) are relative estimations of the state of coatings according the changes in gloss and color; \( aP, aS, aSC, aK, \) and \( Lr \) are relative of the state of coatings as a result of the appearance of bubbles, peeling, wrinkling, corrosion centres, based on linear sizes of damages [3].

The gravimetric method was used to measure the corrosion rate. The test samples were cleaned, degreased, washed with distilled water, dried with filter paper and weighed on an analytical balance. Then the samples were placed in a cell with a test medium for 36 hours. Then they were cleaned from corrosion products and weighed. The corrosion rate (\( i_{cor} \)) was calculated as:

\[ i_{cor} = \frac{\Delta m}{S \cdot \tau} \text{ (g/m}^2\text{h)} \],

where, \( \Delta m \) is the change in mass of the sample, g; \( S \) is the surface area of the sample, \( S = 3.96 \times 10^{-4} \text{ m}^2; \tau \) is the duration of the experiment, hours.
The protective effect was calculated according to the following formula:

\[ Z = \left( \frac{\Delta m_1 - \Delta m_2}{\Delta m_1} \right) \times 100 \% \quad (3) \]

where, \( \Delta m_1 \) is the change in the mass of the sample in the electrolyte without additives; and \( \Delta m_2 \) is the change in the mass of the sample in the electrolyte with an inhibitor.

In order to evaluate the effectiveness of the protective coating, the change in an electric potential over time was monitored. Polarization curves were recorded in a potentiostatic mode using a potentiostat. The polarization resistance \( \frac{\Delta i}{\Delta E} \) was determined from the shape of the polarization curves with an electric potential shift of 20 mV from the stationary value in the anode direction assuming \( \Delta E \) equal to 1 mV.

The corrosion rate was determined by the formula:

\[ I_{\text{corr}} = \frac{\beta_a \cdot \Delta i}{2.3 \cdot \Delta E} \text{ (mA/cm}^2\text{)}, \quad (4) \]

where, \( \beta_a \) is the Tafel coefficient determined from the slope of the straight sections of the anode polarization curves:

\[ \beta_a = \frac{\Delta E}{\Delta \log i_a} \approx \frac{\Delta E}{\Delta \log i_a} \quad (5) \]

The method of recording polarization curves allows us to measure the speed of the electrochemical reactions which cause the corrosion process in the environment of the intended operation of the metal and give a specific coating that protects the metal [4].

The protective effect of the paint system, which included one of the obtained condensation products, was calculated by the formula:

\[ Z = \left( \frac{i_{\text{corr}} - i_{\text{corr}}^0}{i_{\text{corr}}^0} \right) \times 100 \% \quad (6) \]

where, \( i_{\text{corr}} \) is the corrosion rate in an electrolyte with an inhibitor; \( i_{\text{corr}}^0 \) is the corrosion rate of the metal in the electrolyte without an inhibitor.

The value of the anode current density was calculated by the formula:

\[ i_a = \frac{I}{S} \quad (7) \]

where, \( S \) is the area of the sample, cm\(^2\); and \( I \) is the electric current strength, A.

3. Results and Discussion

Based on data on the corrosion rate of steel samples without rust (table 2) obtained by the gravimetric method, it can be argued that synthesized compounds are corrosion inhibitors, since in their presence the corrosion rate reduces significantly.
As it could be seen from table 2, the corrosion rate decreases from 13.67 to 5.01 g/m²*h when adding system 3 to P-2, and to 6.52 g/m²*h when adding system 4. The corrosion current decreases from 1.74 to 0.52 mA/cm² and to 0.66 mA/cm² when systems 3 and 4 are added, respectively. The inhibitory properties of the obtained compounds can be explained by the presence in the condensation products of various functional groups that have adsorption properties due to the high electron density on the S, N, and O heteroatoms. The mechanism of action of organic compounds is the formation of adsorption layers on the metal surface. Organic compounds containing S, N, and O form donor-acceptor bonds between the iron surface and the inhibitor. The higher the electron density at the heteroatom, the more reliable the protection.

The protective properties of the prepared compounds are confirmed by the anode polarization curves (figure 1). The curves recorded in the P-2 solution with additives 2, 3, and 4 are in the region of more positive electric potentials; therefore, in their presence, the anode process slows down. Moreover, the best protective properties are observed when composition 3 (P-2 + lye + piperidine) is used.

As it can be seen from figure 2, the electric potential of the metal surface coated with a layer of PF-115 enamel with systems 3 and 4 is reached maximum on the second day; it remains stable and has more positive values compared to the electric potentials of systems 1 and 2. The stable potential
suggests that the studied systems have an inhibitory effect. The shift of the curves towards more positive values of the electric potential suggests the anode mechanism of action of the systems.

![Figure 2](image_url)

**Figure 2.** Electric potential change versus time for samples with top coat of enamel PF-115: 1 - no additives; 2 - lye; 3 - lye + piperidine; 4 - lye + piperidine + maleic anhydride.

4. Conclusions
We demonstrate that the main waste of pulp and paper industry, sulfite spent liquor, can be used as a corrosion inhibitor. Using the gravimetric method and the method of polarization curves, we found that sulfite liquors inhibit steel corrosion in an acidic media. It was found that the addition of lye + piperidine to the P-2 rust modifier has the most effective inhibitor effect.

References

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