INHIBITING PROPERTIES OF LIGNIN

Yu. N. Forostyan and Miamufiti Prosper

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Inhibitory efficacy has been determined by the method of the weight losses of steel in acid with native lignin, hydrolysis lignin, ammoniated native lignin, chlorinated hydrolysis lignin, and ammoniated hydrolysis lignin, and without these additives. It has been established that the efficacy of lignin and its modifications as inhibitors of acid corrosion increases with a rise in the number of carboxy groups in the macromolecule, and therefore the ammoniated hydrolysis lignin is the most effective.

Hydrolysis lignin and, particularly, some of its derivatives are effective surface-active agents [1] and possess sorption properties [2]. For this reason a number of compositions of hydrolysis lignin [3] and of its graft copolymers [4] are recommended as inhibitors for the acid corrosion of steels. The ammoniated hydrolysis lignin used in the preparation of lignin rust converters (LRCs), is an active anion-exchanger with amphoteric properties which is capable of forming chelate compounds with Fe^{3+} cations [5].

In our opinion, the high anticorrosion efficacy of LRCs must be considered not only from the point of view of the ion-exchange capacity of the ammoniated lignin but in combination with its other properties and, in particular, its inhibiting properties. This is the reason for our interest in some derivatives of hydrolysis lignin as inhibitors of the acid corrosion of steels.

Attention is attracted by the fact that with an increase in the number of functional groups (OH, COOH, NH_2, Cl) in the lignin macromolecule its properties as ion-exchanger and sorbent are considerably improved [6, 5]. In view of this, to determine the inhibitory effect of lignin against the corrosion of metals we selected a number of its modifications containing different numbers and types of functional groups, these being given in Table 1.

A comparison of the results obtained in a solution of an acid with the addition of native lignin (NL), hydrolysis lignin (HL), ammoniated native lignin (ANL), chlorinated hydrolysis lignin (CHL), and ammoniated hydrolysis lignin (AHL) and without these additives showed that some modifications of HL are fairly effective inhibitors of the acid corrosion of steel. Table 1 shows the increase in the amount of carboxy groups in the lignin modifications.

On analyzing the results represented in the integral scheme, it can be stated that a direct relationship exists between the number of carboxy groups (COOH) in the macromolecule of lignin or its modifications and the protective effect (γ), the rate of corrosion (v, $g/cm^2 \cdot h$), and also the protective action (z, %).

For example, the NL, containing the smallest amount of COOH groups (0.04%) also had the lowest values of γ, 1.8, and of z, 0.45, and the largest value of v, 9.9, while the AHL, which contained 12.36% in COOH, was characterized by the values $\gamma = 7.20$, $z = 86$, and $v = 2.40$.

TABLE 1

Lignin	Amount, %				
	OCH_3	OH_{tot}	COOH	NH_2	Cl
Native	14,06	2.38	0.40	—	—
Hydrolysis	10,28	8.63	1,56	—	—
Ammoniated native	10,75	7.50	4,18	1,60	—
Chlorinated hydrolysis	4.35	0.54	5,67	—	16,40
Ammoniated hydrolysis	5,73	18.41	12,36	2,73	—

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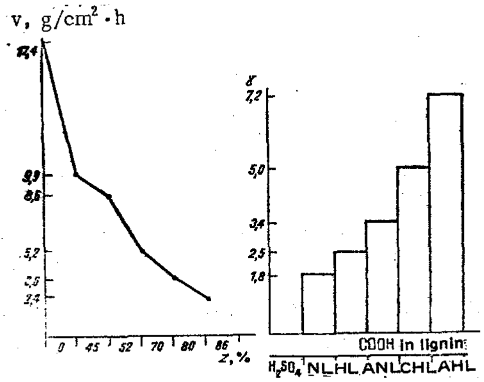

Fig. 1. Integral scheme of the dependence of v, z, and γ on the amount of COOH groups in the lignin.

In the presence of nitrogen the lignin modifications did not have such a great effect on the efficacy of their protective properties as has been assumed. The native lignin, containing 1.60% of NH_2 groups, was a distinctly less effective corrosion inhibitor ($\gamma = 3.4$; $z = 70$; $v = 5.2$) than the CHL, containing no nitrogen but 5.6% of COOH groups ($\gamma = 5.0$; $z = 80$; $v = 3.6$).

It must be assumed that the second functional group participating in the conferment of inhibitory properties on various lignins is the OH group, which is clearly seen from the results given above and the integral scheme.

EXPERIMENTAL

We used native lignin obtained from sunflower husks and fir sawdust under the conditions described by Lazur'evskii et al. [7], its ammonolysis being carried out in an aqueous ammoniacal medium in the presence of atmospheric oxygen [8]; hydrolysis lignin from sunflower husks carefully washed free from sulfuric acid; and ammoniated hydrolysis lignins used for the industrial preparation of lignin rust converters (both from the Zaporozh'e hydrolysis yeast factory). The chlorinated hydrolysis lignin was obtained by chlorinating hydrolysis lignin with elementary chlorine in carbon tetrachloride solution [9].

Samples of steel St.3 (2.60 × 23 and 80 × 39.80 mm) were placed in 100 ml of a 5% aqueous solution of H_2SO_4 containing 5 g of lignin (NL, HL, ANL, CHL, AHL) with a dispersity of 10–30 μ, and they were kept there for 24 h at 22°C with constant stirring.

The inhibitory effect was determined by comparing the weight losses of the steel in the acid with the inhibitor and without it [10].

SUMMARY

The efficacy of lignin and its modifications as inhibitors of acid corrosion increases with a rise in the number of COOH groups in the macromolecule, and ammoniated lignin therefore has the greatest efficacy.

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