



(Brief Communication)

Hydrolytic Lignin Inhibiting Effect in Corrosion Products Converters

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ABSTRACT

This article is devoted to the research of lignin influence on structural and mechanical properties of paint and varnish coverings in a complex with the lignin corrosion modifier, mostly defining their adhesive stability on metals Fe_2O_3 and Fe_3O_4 . In the result of research it was proved that molecules of the lignin containing surface-active substances not only shield separate sections of metal, but also create the power barrier existing even at a partial covering of a surface, interfering penetration of aggressive components of the environment through the adsorptive layer of surfactant molecules. The result of the research allows reviewing more accurately the mechanism of anticorrosive activity of lignin modifiers of corrosion products.


Key words: Lignin, Corrosion, Solvent, Wood, Renewable raw material, Environmental pollution, Hydrolytic structure.

INTRODUCTION

Hydrolytic lignin is an amorphous substance, from light brown to dark brown color. In the hydrolysis of wood or other vegetable raw materials which represents processing by the diluted sulfuric acid under the temperature of 185-190 °C and pressure of 1,2-1,25 MPas, disintegration (destruction) of a natural lignin happens which is followed by change of a chemical composition, dispersion, humidity and other characteristics and formation of final stable "product" - a hydrolytic lignin. Its outcome is about

30% of the primary wood mass¹. It is a complex, irregularly constructed, resistant to decomposition, high-molecular polymer, with branched macromolecules, insoluble in water and organic solvents. It is a conglomerate of different chemicals - a natural lignin, polysaccharides, resins, fats, waxes, mineral and organic additives. The molecular weight as well as a chemical structure is not definitely defined. Density of HL is equal 1,25-1,45 g/cm³. The index of refraction is equal to 1.6. The damp HL has low calorific ability which for absolutely dry lignin is 5500-6500 kcal/kg, for a product with 18-25% humidity is 4400-4800 kcal/kg and with 65%



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humidity is 1500-1650 kcal/kg². The hydrolytic lignin processed at plants is usually highly contaminated by various impurities and is not identical by the chemical structure which considerably complicates its processing and usage.

The hydrolytic lignin has no regular structure therefore its element structure fluctuates over a wide range. The content of carbon is from 52% to 64%, hydrogen from 5% to 7%, sulfur from 0% to 3%, the rest is oxygen and other chemical elements.

According to the physical and chemical characteristic the hydrolytic lignin represents polydisperse system with sizes of particles from several millimeters to microns and less. Researches of samples from different plants showed that their average composition has the following fractions: more than 250 microns in size - 54-80%, less than 250 microns - 17-46%, less than 1 micron - 0,2-4,3%.

According to its structure - hydrolytic lignin is not a dense body, it represents the developed system of micro pore and a macro pore with the size depending from its humidity (for a damp lignin it makes 760-790 m/g, and for dry only 6 m/g).

According to analytical data, researches of functional groups and studying of deep oxidation products it is possible to conditionally present the scheme of a structure of a fragment of a hydrolytic lignin on the basis of a known scheme of a natural lignin of K. Freudenberg. Such scheme of a fragment of a hydrolytic lignin can be used for predicting its processing directions, explanation of secondary structures formation and accumulation of interfaced communication systems causing qualities of radicals³.

The hydrolytic lignin and especially some of its derivatives are effective surfactants and possess sorption properties.

The hydrolytic lignin used in preparation of lignin contained corrosion solvents - an active ionite with amphoteric properties capable to form chelate connections with Fe⁺³ cations. High anticorrosive efficiency of the developed lignin corrosion modifiers should be considered not from the point of view of ion-exchange ability of a hydrolytic lignin, but in a complex with other its qualities, in particular, with the inhibiting properties. Chemical activity of lignin is caused by existence of etherous bonds and functional groups. Phenolic hydroxyls are donors, and carbonyl and hinoid hydroxyls are acceptors that afford ground to consider a lignin macromolecule as a complex with charge transfer. Therefore, formation of intracomplex salts is possible that allows using lignin as a passivator of a metal surface.

MATERIAL AND METHOD

The object of the research was hydrolytic lignin (HL), which is a complex mixture of substances of wood hydrolytic disintegration. Lignin is a part of the difficultly hydrolyzed polysaccharides, reducing substances (monosaccharides, furfural), resins, cindery elements, sulfuric and organic acid residuals. Physical chemical characteristics of the lignin and its composition is given in the Table 1.

Table 1: Characteristic of a lignin

No	Component	Contents (for absolutely solid material)
1	Ash-content	0,5-10,9
2	Reducing agents	0,1-9,6
3	Acidity in conversion to sulfuric H ₂ SO ₄	0,6-1,3
4	The substances extracted by alcohol-benzol mixture	5,4-8,3
5	Polysaccharides	3,1-54,2
6	Metaksinol	18,7
7	General hydroxyls	9,5
8	Carboxyl groups	4,0
9	Lignin	38,9-87,5

Technical properties of the lignin modifier of corrosion products have been defined according to standard researches techniques⁴.

RESULTS AND DISCUSSION

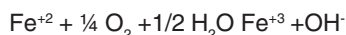
As affinity of metal ions to donor atom of nitrogen is higher, than to oxygen, strength of complex salts increases with the introduction of nitrogen into lignin molecule. That can be reached in various ways⁵. Ability of lignin strongly bond oxidic and hydrooxidic forms of metal, particularly iron, is explained by this. With the increase in number of functional groups (alcohol, hydroxyl carboxyl, phenolic) the properties of lignin macromolecule as an ion exchanger of m sorbent considerably increase. And by that process of ion exchange and a complex formation with oxides and hydroxides of iron proceeds more actively that, in turn, leads to modification of corrosion in stable water insoluble products, this means that the more COOH- and OH - groups in a molecule, the more effective is corrosion solvent.

Sorption of Fe⁺³ ions from water solutions on a hydrolytic lignin showed that process of sorption goes in 2 stages: in the beginning there is a Langmuir adsorption of ions, then goes the linear law adsorption in lignin pores. Sorption of ions of iron on hydrolytic lignin, is generally connected with an ion - dipolar interaction between polar functional groups and ions of Fe⁺³ and dimentioonal structure of a sorbent. For this reason a number of

compositions of a hydrolytic lignin and its imparted copolymers are recommended as inhibitors of steel acid corrosion⁶.

This principle is applied in use of a hydrolytic lignin in powder corrosion modifiers. At interaction of a lignin with urea, apparently, semi-complexes form, in which a ligand, that is a neutral molecule forming the internal coordination sphere, is a molecule of amines. Further, at reaction with products of metals corrosion such complexes form the chelate connections of a high strength, as the central atom in them is as "blocked" by a cyclic ligand. The thin layer of corrosion is covered by an inert porous superficial film which slightly influences anode dissolution of metal and slows down processes of diffusion at cathodic restoration of oxygen.

Thus, electrode reaction of restoration of oxygen proceeds only on a surface of metal iron. Actually at sufficient electronic conductivity of iron oxides it is necessary to take into account that this reaction can happen also on a corrosion surface or on walls of pores of thick corrosion layers. There will be the simultaneous oxidation of Fe^{+2} to Fe^{+3} according to reaction:



Later in quite thick corrosion layers on iron surface there can form a Fe_3O_4 magnetite which is in thermodynamic equilibrium with metal iron. In this regard for defining inhibiting effect of lignin against corrosion of metals some of its modifications has been chosen. They contain various numbers of functional groups which are described in Table 2.

Comparison of the results received in acid solution with an additive of the native lignin (LN), hydrolytic lignin (HL), hydrolytic chlorinated lignin (HCL) and without these additives allowed to find out that some modifications of hydrolytic lignin are effective inhibitors of acid metal corrosion.

Analyzing the presented results (Table 3) it is possible to confirm that there is a direct dependence between number of COOH-groups in a macromolecule of a lignin or its modifications and protective effect (Y), speed of corrosion (V), and also protective capability (Z). It is possible to consider that the second functional group contributing to inhibiting properties of lignin is OH-group. This is clearly observed from the above data.

The lignin is a complex of substances, which vary by their chemical nature. It contains a significant amount of the plant cell modified lignin, part of polysaccharides, group of substances of a lignohumic complex, monosaccharide, mineral and organic acids, cindery elements and other substances¹⁻².

Table 2: Modifications of lignin, which contain different quantities of functional groups

Functional groups	OCH ₃	HO _{com}	COOH	Cl
Native	15,3	2,26	0,43	-
Hydrolytic	11,02	9,8	5,32	-
Hydrolytic chlorinated	4,27	0,45	4,97	16,40

Table 3: Data on protective effect (Y), speed of corrosion (V), and protective capability (Z) of various types of lignin

Lignin	Y	V, kg/m ² sec	Z, %
Native	2,1	9,6	0,40
Hydrolytic	5,0	2,6	0,80
Hydrolytic chlorinated	3,4	5,4	0,62

In hydrolytic lignin there is a significant amount of reactive and etherified phenolic and aliphatic hydroxyls and unreplaced positions of an aromatic core of phenelprapane lignin units. In this regard the lignin easily interact with electrophilic reagents which create actual conditions for modification of its polymolecule with adding a number of ionogenic groups, and also oxidizing and hydrolytic splitting in sour and alkaline environment.

Theoretical base of creation of the lignin converter of corrosion products on the basis of a hydrolytic lignin is its ability to form complex combinations with metals and, in particular, with iron oxides and its combinations.

Soap stock is the penetrating additive in a lignin modifier of corrosion products. Once getting into corrosion, it increases its mechanical durability and adhesion to metal.

Lignin converter of corrosion products contains orthophosphoric acid which dissolve corrosion, and lignin interacts with salts and oxides of iron, then transform them into insoluble complexes of chelate type. On a surface of metal the dense layer reaction products of lignin with iron ions forms serving as soil for the following painting.

As a filling agent a Kulantau expanded vermiculite⁹⁻¹⁰ is used. For giving of elastic properties to protective film of the modifier a drying oil is introduced into corrosion modifier. Introduction into the structure of corrosion modifier of a complexing compound (a hydrolytic lignin) of emulsifier (monoethanol amine), and surfactant allows to reduce porosity to a minimum, to increase adhesion, hardness and durability of a protective layer.

For reduction of volume of pilot studies while solving the problem of optimization of structure

of composition of a lignin modifier of corrosion products the orthogonal plan of the second order (two-factorial experiment) was used.

This method allows receiving the communication equation of property and structure of the studied compositions. And the possibility of graphic interpretation of results remains. It was found experimentally that the ratio of hydrolytic lignin in liquid corrosion solvents fluctuates from 10,3 up to 16,1 mass. h. on 100 mass. h. of product.

Table 4 : Technical properties of the lignin modifier of corrosion products (LMCP)

No	Indicator	Norm	
		LMCP	PRL
1	Color	Oily liquid of dark brown color	Oily liquid of dark brown color
2	Appearance	After drying the film has to be uniform, from light till dark brown color.	
3	Apparent viscosity at (20 [±] 0,5) 0 C on the VZ-4 viscometer, not less	12	25
4	Mass fraction of nonvolatile substances, not less	18-25	20-25
5	Density at (20 [±])° C, g/cm ³	No	-
6	Mass fraction of orthophosphoric acid, no more	7-14	3-14
7	Rate of milling, micron, no more	30	30
8	Drying time to degree 3 at (20 [±] 2) °C, no more	50-60	-
9	Reformativity ability (thickness of transformed layer), micron, in limits	80-120	80-10

CONCLUSION

Thus, structural change of lignin has an effect on structural and mechanical properties of paint and varnish coverings in a complex with the lignin corrosion modifier, mostly defining their adhesive stability on metals Fe₂O₃ and Fe₃O₄. Molecules of the lignin containing surface-active substances not only shield separate sections of metal, but also create the power barrier existing even at a partial covering of a surface, interfering penetration of aggressive components of the

Proceeding from analyses of studied data^{1,7} limits of a variation of concentration of orthophosphoric acid in the modifier are chosen from 11,0 up to 27,1 masses. h. on 100 masses. h. of product. By the analogy with known lignin corrosion modifier technical water was used. The lignin modifier of corrosion products represents the single-component oily mass of dark brown color. Technical properties of lignin m of corrosion products in comparison with PRL are given in Table 4.

environment through the adsorptive layer of surfactant molecules. It allows reviewing more accurately the mechanism of anticorrosive activity of lignin modifiers of corrosion products.

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