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## INHIBITION OF CORROSION OF IRON IN ACIDS

John Corning Ball, Jr., Summerville, S. C., assignor to West Virginia Pulp and Paper Company, New York, N. Y., a corporation of Delaware

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This invention relates to the inhibition of the corrosion of iron by acids. More particularly, the invention has to do with the use of lignin amines as corrosion inhibitors for iron in acid solutions.

As is well known, acid solutions attack metallic iron in the form of free metal, steel, cast iron, etc. very rapidly. Each year millions of dollars are lost by acid attack on irons. This loss occurs in many different places, e. g., chemical production involving acid solutions, industrial cleaning, metal pickling, and oil well acidizing. In an effort to reduce this loss the use of inhibited acids has increased considerably in recent years.

Over the past twenty-five years many corrosion inhibitors for metals in acids have been developed and some of them are very effective. In general these inhibitors are expensive, however, and corrosion control is therefore expensive.

Many of the aliphatic and aromatic amines have been used as corrosion inhibitors for metals in acids. These are generally expensive chemicals. I know of no instance in which the use of lignin amines has been practiced or proposed.

I have found that the comparatively inexpensive lignin amines are effective corrosion inhibitors for iron in acid solutions. Our tests, while not exhaustive, have been sufficiently extensive to indicate that lignin amines are, as a general class, effective as corrosion inhibitors in acid solution. The more available lignin amines for this purpose are, of course, those which can be most economically produced, either because of the low cost of source ingredients, or because they can be prepared by a simple and inexpensive procedure. These amines are prepared most advantageously by the Mannich reaction, according to the procedure disclosed and claimed in a pending application for Letters Patent of the United States of Frank J. Ball and William G. Vardell, Jr., Serial No. 643,511, filed March 4, 1957, for Lignin Amines and the Preparation Thereof, preferably by reacting lignin with a primary or secondary amine and formaldehyde. Other aldehydes and equivalent ketones may be used in place of formaldehyde to make these products. The reaction involved in their production may be of the type shown:



where L is lignin or a sulfonated lignin less one atom of displaceable hydrogen, and R is an atom of displaceable hydrogen or is a substitute element or radical such as an alkali metal.

The lignin used to prepare the lignin amines which are to be used as corrosion inhibitors may be derived from any of the known sources, e. g., wood, corn cobs, bagasse, bark, straw, and it may be extracted from these sources by any of the known methods, e. g., sulfate or soda, pulping liquors, acid hydrolysis, and solvent extraction.

I have found that very small amounts of the lignin amine are effective in inhibiting corrosion of iron in acid solutions. Quantities as low as 0.05 percent of the lignin

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amine based upon the amount of acid used give good inhibition. The amount of lignin amine to be used would, of course, vary with the concentration and amount of acid and with the area of the metal exposed.

5 The corrosion inhibition of the lignin amines is effective in hot or cold acid solutions and is also effective standing in the acid solutions for some time with the result that these compounds may be employed against corrosion of iron in storage tanks, drums, and cans.

10 The inhibitors may be employed either singly or in combination, or may be employed together with other agents.

For the purpose of illustration the following examples are furnished.

15 *Example 1.*—To 50 ml. of 15% aqueous hydrochloric acid was added 0.025 g. of a lignin amine prepared by a Mannich reaction of Indulin A (a purified wood lignin derived from the pulping of pine wood by the sulfate method and produced by the West Virginia Pulp and Paper Company), formaldehyde and dimethylamine. The lignin amine contained about 2.2 chemically combined amine groups for each lignin unit weight of 840 g. The acid mixture was placed in an eight-inch test tube and this was placed in a water bath. In a second test tube was 25 placed 50 ml. of the 15% acid only and this too was placed in the water bath. The bath was heated until temperatures of the acid mixtures were 165° F. and the temperatures were maintained at this point throughout the tests. In each of the hot acid solutions was placed 30 a tared coupon of #430 stainless steel of 0.005 in. x 0.5 in. x 2 in. size (the coupon was totally immersed in the acid). The metal was left in the hot acid solutions for 15 minutes, then removed and washed free of acid in a stream of distilled water. The coupons were wiped as 35 dry as possible with a cloth and then dried to constant weight in an oven at 105° C. The metal in the acid solution alone (control) lost 0.403 g. while that in the acid solution containing the lignin amine lost only 0.033 g.

40 *Example 2.*—This example was conducted in a manner similar to Example 1, except that the lignin amines used contained about 1.5 rather than 2.2 chemically combined amine groups for each lignin unit weight of 840 g. The metal in the acid solution alone (control) lost 0.403 g. while that in the acid solution containing the lignin amine 45 lost only 0.063 g.

*Example 3.*—This example was conducted in a manner similar to Example 1, except that the lignin amine used was prepared from Meadol (an alkali lignin derived from the pulping of hardwoods by the soda method and produced by the Mead Corporation) rather than Indulin A. The metal in the acid solution alone (control) lost 0.1524 g. while that in the acid solution containing the lignin amine lost only 0.021 g.

55 *Example 4.*—This example was conducted in a manner similar to Example 1, except that the lignin amine used was prepared from Polyfon O (a sulfonated lignin produced by the West Virginia Pulp and Paper Company) rather than Indulin A. The metal in the acid solution alone (control) lost 0.425 g. while that in the acid solution containing the lignin amine lost only 0.068 g.

60 *Example 5.*—This example was conducted in a manner similar to Example 1, except that the acid solutions tested were 5% aqueous sulfuric acid rather than the 15% hydrochloric acid. The metal in the acid solution alone (control) lost 0.520 g. while that in the acid solution containing the lignin amine lost only 0.114 g.

65 *Example 6.*—This example was conducted in a manner similar to Example 1, except that the acid solution tested was 56% phosphoric acid rather than the 15% hydrochloric acid, the steel tested was #1010 mild steel of 0.064 in. x 0.5 in. x 2 in. in size, and the time of exposure 70



was 60 minutes. The metal in the acid solution alone (control) lost 0.393 g. while that in the acid solution containing the lignin amine lost only 0.118 g.

*Example 7.*—This example was conducted in a manner similar to Example 1, except that the steel tested was #1010 mild steel of 0.064 in. x 0.5 in. x 2 in. in size, rather than the #430 stainless steel. The metal in the acid solution alone (control) lost 0.197 g. while that in the acid solution containing the lignin amine lost only 0.031 g.

*Example 8.*—This example was conducted in a manner similar to Example 1, except that the lignin amine used was prepared with morpholine rather than dimethylamine and the lignin amine was added in the aqueous reaction media in which it was prepared rather than as a dry solid. The metal in the acid solution alone (control) lost 0.322 g. while that in the acid solution containing the lignin amine lost only 0.029 g.

*Example 9.*—This example was conducted in a manner similar to Example 1, except that the lignin amine used was prepared with butylamine rather than dimethylamine and the lignin amine was added in the aqueous reaction media in which it was prepared rather than as a dry solid. The metal in acid solution alone (control) lost 0.417 g. while that in the acid solution containing the lignin amine lost only 0.015 g.

*Example 10.*—This example was conducted in a manner similar to Example 1, except that the lignin amine used was prepared with acrolein rather than formaldehyde and the lignin amine was added in the aqueous reaction media in which it was prepared rather than as a dry solid. The metal in solution alone (control) lost 0.174 g. while that in the acid containing the lignin amine lost only 0.057 g.

*Example 11.*—This example was conducted in a manner similar to Example 1, except that the lignin amine used was prepared with benzaldehyde rather than formaldehyde, and the lignin amine was added in the aqueous reaction media in which it was prepared rather than as a dry solid. The metal in solution alone (control) lost 0.388 g. while that in the acid containing the lignin amine lost only 0.268 g.

As previously noted, advantageous procedures for preparing lignin amines suitable for use in practicing the invention are disclosed in a pending application of Frank J. Ball and William G. Vardell, Jr., Serial No. 643,511, filed herewith, for Lignin Amines and the Preparation Thereof. Lignin amines produced by other operative procedures are not, however, excluded from use in the present invention.

While there have been shown and described certain procedures typifying the invention, and compositions constituting embodiments of the invention, it is to be understood that the invention is susceptible of many modi-

fications. Changes, therefore, may be made without departing from the spirit and scope of the invention as described in the appended claims, in which it is the invention to claim all novelty inherent in the invention as broadly as possible, in view of the prior art.

I claim:

1. A process for inhibiting the corrosion of iron in acid solutions, which consists essentially in the addition to the acid solution of a small amount of a lignin amine, sufficient in quantity to effect a substantial measure of corrosion inhibition, and maintaining the so modified acid solution in contact with iron.

2. A process for inhibiting the corrosion of iron in acid solutions, which consists essentially in the addition to the acid solution of .05 to 1.0 percent of a lignin amine prepared by the Mannich reaction, and maintaining the so modified acid solution in contact with iron.

3. A process for inhibiting the corrosion of iron in acid solutions, which consists essentially in the addition to the acid solution of a small amount of a lignin amine sufficient to effect a substantial measure of corrosion inhibition, said lignin amine being prepared by the reaction of the following ingredients: (a) an ingredient chosen from the group consisting of lignin, sulfonated lignin and alkali metal salts of lignin and sulfonated lignin, (b) an aldehyde, and (c) an amine chosen from the group consisting of the primary and secondary amines, and maintaining the so modified acid solution in contact with iron.

4. A process as set forth in claim 3, in which the (b) ingredient is formaldehyde.

5. A process as set forth in claim 3, in which the (c) ingredient is dimethylamine.

6. A process as set forth in claim 3, in which the (b) ingredient is formaldehyde and the (c) ingredient is dimethylamine.

7. A process for inhibiting the corrosion of iron in acid solutions as set forth in claim 3, which consists essentially in the addition to an acid solution of .05 to 1.0 percent of the lignin amine.

8. A process as set forth in claim 7, in which the (c) ingredient is dimethylamine.

9. A process as set forth in claim 7, in which the (b) ingredient is formaldehyde.

10. A process as set forth in claim 7, in which the (b) ingredient is formaldehyde and the (c) ingredient is dimethylamine.

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