

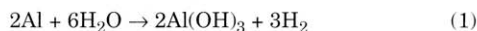
Corrosion Inhibitors for Aluminum

Student Experiments

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The inhibition of the electrochemical corrosion of metals in aqueous media is of great economic and scientific interest (1, 2). A special application of corrosion inhibitors is the stabilization of aluminum pigments in waterborne paints, e.g., metallic basecoats for the automotive industry (3). A general overview regarding aluminum pigments is given in reference (4). These waterborne metallic basecoats reduce significantly the emission of organic solvents to the atmosphere during the paint application (3). One of the problems of waterborne metallic basecoats is the corrosion of the aluminum pigments in alkaline (pH about 8) aqueous paint medium, which causes the formation of hydrogen (5):



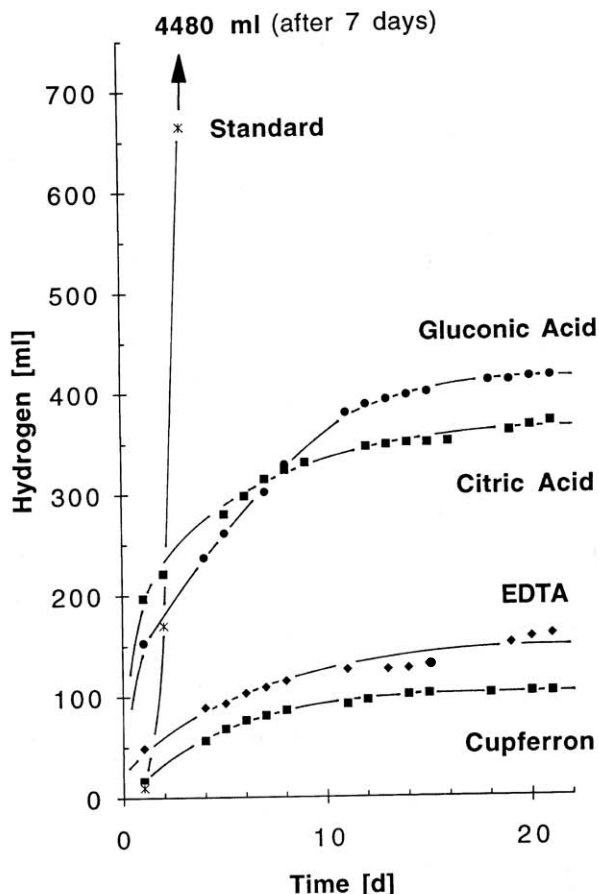
A disadvantageous consequence of this corrosion reaction is that the color of the paint changes from silver to grey (5). A review about different stabilization methods for aluminum pigments is presented in reference (5). An additional possibility for the inhibition of corrosion of aluminum pigments is the application of chelating agents (6). Therefore, a simple and reliable test method is applied in the present study to investigate the corrosion inhibiting effects of various chelating agents on aluminum pigments in aqueous alkaline media. This test is recommended to

demonstrate to students the effect of corrosion inhibitors in general because the corrosion reaction of the aluminum pigments, compared with bulk materials, is accelerated by their larger surface area of about 5 m²/g. Spherical aluminum powder already was used in a similar way to investigate corrosion inhibitors (7). The disadvantage of spherical particles is that they have a smaller surface area compared with flake-like pigments, and they often settle as a hard cake, which may be difficult to redisperse. Aluminum flakes are easily redispersible and better suited for this kind of test.

Experimental

Standard non-leafing aluminum pigment pastes¹ for solvent-borne basecoats, which contain 65 weight percent aluminum and 35 weight percent hydrocarbon solvent, were used. 5.0 g of such a paste is dispersed for five minutes by a magnetic stirrer in a glass beaker in 100 mL of a mixture of water and butyl glycol in the ratio 1:1. Butyl glycol is the most common organic cosolvent in waterborne

¹Appropriate aluminum pigments are, e.g.: OBP 8507 from Obron Atlantic Corp., 72 Corwin Drive, P. O. Box 747, Painesville, OH 44077-0747. Sparkle Silver 5000 AR from Silberline Manufacturing Co. Inc., P. O. Box B, Tamaqua, PA 18252-0420.



Time dependency [days] of the hydrogen formation in water/butyl glycol = 1:1 at pH = 10 of the standard aluminum dispersion (only DMEA) and with addition of 2.0 mmol/100 mL of different chelating agents.

paints and wets the hydrophobic aluminum paste. The pH of the solvent is raised to 10 to accelerate the corrosion reaction with dimethylethanolamine (DMEA), a commonly used amine for waterborne baking enamels. This unstabilized dispersion reacts in about one week at room temperature to a colorless precipitate (presumably aluminum hydroxide). The hydrogen formation can be seen as small gas bubbles. If an appropriate corrosion inhibitor is dissolved in the solvent mixture before dispersing the pigment, the aluminum pigment keeps its silver sparkle for more than 10 weeks at room temperature. With our students we run this qualitative experiment over a period of about three weeks. The corrosion inhibiting effect of the chelating agents is obvious because the standard is corroded after about one week. For this purpose, a large variety of common chelating agents can be used, e.g., ethylenediaminetetraacetic acid (EDTA), citric acid, gluconic acid, nitrilotriacetic acid, salicylic acid, oxalic acid, salicylaldehyde, 8-quinolinol, or cupferron. The concentration of the inhibitors should be 2 mmol/100 mL.

Per mole of arising aluminum(III) ions, 1.5 moles of hydrogen molecules are evolved (eq 1). Therefore, it is possible to examine the corrosion reaction in a more advanced way by volumetric measurement of the hydrogen. This hydrogen evolution method can be used for estimating corrosion rates (8). The hydrogen volume by total consumption of the aluminum pigment is calculated to 4.3 L.

• Use caution and good ventilation.

Volumetric measurement of the hydrogen is performed simply with a glass flask connected by a glass tube to an inverted graduated cylinder filled with water.

Results and Discussion

By the use of the described simple qualitative test procedure, structure-efficiency relations of corrosion inhibitors can be shown.

- The first results concern dicarboxylic acids: If oxalic, malonic, succinic and maleic acid are tested, oxalic and malonic acid prove to be good corrosion inhibitors, the others not.
- The explanation for this phenomenon is the ring size of the formed aluminum chelates because oxalic acid form five membered, malonic acid six-membered chelate rings.
- On the other hand, succinic and maleic acid lead to seven-membered rings, which are not formed readily.
- If salicylic acid, salicylamide, 2-aminobenzoic acid and 2-aminobenzamide are tested, only salicylic acid acts as a corrosion inhibitor.
- In this series the importance of the combination of carboxyl and phenolic hydroxyl group becomes apparent.
- Both experiments demonstrate the high specificity of the corrosion inhibiting action. A small change in the chemical constitution may cause a big change in efficiency.
- Heterocyclic corrosion inhibitors (9, 10) like 1 *H*-benzotriazole, the sodium salt of 2-mercapto-benzothiazole or 2-(5-aminopentyl)-benzimidazole are well-known corrosion inhibitors for copper.
- They are not inhibiting the corrosion of aluminum. This points out the strong interdependence of corrosion inhibitor and metal.

The demonstrated experimental procedure can be extended easily to investigate the minimum concentration for corrosion inhibitors by lowering their concentration.

Volumetric measurement of the hydrogen reveals more impressive results. The figure shows the time dependency of the hydrogen formation of the standard aluminum dispersion (only DMEA) and those with addition of 2.0 mmol/100 mL of different chelating agents. The corrosion-inhibiting effect of the chelating agents is obvious. (See the figure.) The corrosion rate during the first day of the samples with EDTA and especially with gluconic and citric acid is higher than that of the standard. This behavior is normally observed after the application of chelating agents containing carboxylic groups. In a first reaction, an aluminum chelate is formed that is believed to act as the corrosion inhibitor (6). This method allows the comparison of the inhibiting effects of different chelating agents in a quantitative way. The examples shown in the figure indicate that cupferron is a very effective corrosion inhibitor. A simple calculation leads directly from the hydrogen volume to the amount of corroded aluminum. For cupferron the turnover of aluminum is 2.4%, for gluconic acid it is 9.7% (after 21 days).

Unlike the experiments performed in many studies on electrochemical corrosion, the experiments described here do not require any complicated and expensive electronic equipment and can be carried out easily by students.

Acknowledgment

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