Investigations of Vapor Phase Corrosion Inhibitors in Coatings

Cheryl A. Smith, Vapor Phase Products, Tempe, AZ

Corrosion is the change from a metallic to nonmetallic form, resulting from chemical reaction caused by the environment in which the metal is placed. Metals are chemically unstable, because it is energetically favorable for them to revert to a chemical compound, such as oxide, the type found in nature. Corrosion usually is undesirable because it starts at the surface and is detrimental to appearance and movement, and ultimately causes destruction of the metal. The corrosion phenomena depends on the surrounding environment of the metal. Diclohexlamine nitrate through diethanolamine benzoate account for 90 percent of the vapor phase inhibitor market. These materials are highly metal-specific and must be used only where the target metal is used. Toxicity is also an issue, as some can be considered carcinogenic. This paper documents the testing of a non-toxic, non-metal-specific vapor phase corrosion inhibitor added to two coatings.

For more information, contact:
Cheryl Smith
Vapor Phase Products
6340 South Rural Road
Suite 118-173
Tempe, AZ 85283
Phone: 602/820-8722
FAX: 602/820-1715

BACKGROUND

Corrosion is the destruction of metal by chemical or electrochemical reaction with its environment. Most environments are corrosive to some degree. Environments that advance corrosion are air and moisture, fresh, distilled or salt water, rural, urban and industrial atmospheres, steam and other gases, mineral acids, organic acids, alkalis, soils, solvents and oils.

Selection of metals and/or the means of protecting them is a dynamic problem in the metals industry. There are many other factors adding to the complexity of the problem of estimating corrosion rates and selecting materials that will provide acceptable performance. Almost without exception, whether the environment is mild or aggressive, corrosion rate for an otherwise constant set of conditions will increase as temperature increases.

Corrosion can be classified as wet or dry, direct or electrochemical, by corrosive media, liquid, and solid. Wet corrosion occurs when liquids are present and at temperatures below the dew point. Dry corrosion occurs in the absence of liquids or above the dew point. Direct corrosion involves a reaction between a metal and nonmetallic elements or compounds. Electrochemical corrosion occurs in liquids or electrolytes.

Where a corrosion failure has occurred, economical and practicable measures for prevention of future failures of the same type are required. The major types of corrective and preventative measures are change in alloy, heat treatment or product form, use of resinous and inorganic base coatings, use of inert lubricants, use of electrolytic and chemical coatings and surface treatments, use of metallic coatings, use of galvanic protection, design changes for corrosion control, use of inhibitors, changes in pH and applied potential, and continuous monitoring of variables.

Where the environment cannot be changed to solve a corrosion problem, a change in alloy, heat treatment or product may be required. Selection of the proper alloy and product form requires a complete knowledge of the operating conditions, including chemical environment, and operating temperatures and stresses. Acrylics, epoxies, phenolics, furanes and urethanes are used extensively for corrosion protection in the form of paints, potting compounds, adhesives, coatings and linings. Their chemical resistance makes them suitable for many applications. Organic and inorganic vehicles are effective in healing small, narrow breaks in the film and in preventing underfilm corrosion.

Chemically inert resins can serve both as effective lubricants and as corrosion resistant coatings and linings. Electrolytic and chemical coatings and surface treatments include anodizing, chemical conversion coatings and passivation treatments. These processes vary widely in their effectiveness in protecting treated metals against corrosion. Electrodeposition of zinc or cadmium is widely used to protect steel from corrosion. These coatings offer sacrificial protection to the steel substrate and will minimize dissimilar-metal effects when the coated part is joined to aluminum or magnesium.

Galvanic protection can be either cathodic protection or anodic protection. Anodic and cathodic protection tend to complement one another. Each method has its advantages and disadvantages.

A simple change in design is sometimes the most appropriate way to eliminate a corrosion problem. Changes in design may necessitate a change in materials.

The successful application of inhibitors requires knowledge and understanding of their chemical behavior and of the corrosion processes in the system under consideration. The concentration of inhibitor will be greater the higher the concentration of aggressive corrodents that interfere with the formation and maintenance of a passivating film on the metal. In choosing an inhibitor, the engineer must consider the difference in behavior of "safe" and "dangerous" inhibitors. Safe inhibitors reduce the total amount of corrosion without increasing the intensity on unprotected areas. Dangerous inhibitors produce increased rates of attack on unprotected areas. The amount of inhibitor required depends on the velocity of movement of atmosphere and the relative ratio of volume of atmosphere to area of metal surface. The higher the velocity of movement, the thinner the diffusion boundary layer, and the greater the amount of inhibitor reaching the surface.

A coating is applied for one of two reasons. The reasons are decoration and protection. An entire range of corrosion inhibitors are known to prevent rusting in coated products. They can be divided into four groups. They are oxidizing substances such as chromates, dichromates, metaborates, sodium carbonate, sodium molybdate, sodium nitrite, and sodium or potassium nitrate. The next group is organic substances such as polar substances with active groups including amines, carboxyl groups and sulfur groups. The third group is metallic cations and lastly non-oxidizing inorganic and organic salts such as benzoates, naphthenates, and octoates. When considering inhibitors not only their effectiveness but environmental compatibility must be considered. Heavy metal salts are excluded because of this consideration. With respect to the amount of addition, it must be noted that corrosion inhibitors, being salts and water soluble compounds, can themselves injure the function of corrosion-protecting coatings by increasing water swelling. We engaged in the testing of two coatings with a non-toxic, non-metal specific vapor phase corrosion inhibitor. Included in the test were salt spray and humidity exposure testing to determine that the correct quantity of inhibitor was used. The theory of the mode of action of corrosion inhibitors has not been completely developed, since the relationships are relatively complicated. The key statement about the mechanism is that in the presence of salts of weak acids, the pH of the metal surface is set so that the iron is pacified by formation of oxidative layers. Similar effects are achieved by addition of nitrites, which also passivate the iron by reduction of dissolved oxygen to hydroxyl ions. In this connection, it has been described that complex formers such as tannins, acetylacetonates, salicyclic acid, and certain emulsifiers can also have a favorable effect. They stabilize the oxidative pacifying layers of the iron while not impacting the water swelling of the coatings. Emulsifiers must not be added to the total formulation but must be present in the binder.

Another concern is "early rusting". This phenomenon occurs while the coating is drying if the substrate is cold or at high humidity. Since the drying process occurs from top to bottom, the inner areas of the coating remain wetter than the top. Corrosion may occur in the fresh state. Corrosion inhibitors are suited for prevention of this phenomenon.

TEST PARAMETERS

The ideal test is one that exactly replicates some aspect of the coating function. Unfortunately, most tests are hurry-up approximations and may not directly measure actual performance. The ideal test would measure exactly some parameter that directly relates to the end use. A physical test applies a complex stress to the coating. The coating may fail owing to only one or another of the actual pure stresses.

The performance on the test of a coating film is likely to depend on the physical form of the film. Film thickness is an important factor in physical and appearance measurements. Appearance is related to how smooth the film surface is. The protective or decorative aspects of the coating depend on its survivability. The two coatings were polyurethane and an epoxy amine with the addition of an active vapor phase corrosion inhibition system.

Unlike conventional coatings, such as epoxies, where there is only a very narrow range of raw materials to select from, polyurethanes come in an extremely wide variety of shapes and forms. The term `polyurethane coating' is actually very generic because it covers everything from wood sealers to floor paint to underground tank coatings. The most common polyurethanes (such as aliphatic top coats, moisture cures and automotive paint) are solvent based systems. The inclusion of the terminology, `100% solids' only narrows the field slightly. There are literally hundreds of different isocyanates and thousands of polyols available for a polyurethane formulator to choose from resulting in millions of permutations and combinations.

One further distinction of the 100% solids polyurethanes is the type of isocyanate used. The most common isos are known as `aromatic'. These systems are economical and good performers but tend to chalk and darken when exposed to ultra violet radiation (sunlight). The corrosion resistance and other physical properties are not affected by the sunlight but the aromatic systems need to be topcoated if they are to be used in an aesthetic application where color is important. Aliphatic isocyanates, are used in the formulation of polyurethanes to give them excellent color and gloss retention. The primary drawback of aliphatic iso is its high cost. It is typically three to four times that of an aromatic.

The properties of 100% solids polyurethanes vary from rubbery elastomers to hard coat systems. The chemical bonds in the more rigid systems are highly cross-linked to each other to create hard, dense systems that have very good chemical and moisture resistance. The systems usually have very good adhesion and are the best choice for the corrosion protection of metals.

A more resilient chemically resistant paint film is the primary advantage of a two component epoxy amine. One component coatings dry by oxidation or solvent evaporation. Two components coatings require a crosslinking reaction between two chemical groups for curing to occur.

Two component catalyzed epoxy coatings are known for their toughness and excellent adhesion. Once mixed two component coatings must be used within a specified time. The pot life of two component coatings commonly range from 2-8 hours. The epoxy amine we tested is a high solid, low VOC conductive coating. Polymer development for this coating was especially challenging because of the low molecular weight of the resin system.

The samples were 2024 and 7075 aluminum panels, and 4340 steel panels. They were vapor degreased with TCE for 3-5 minutes and then aqueous cleaned for 10 minutes with a proprietary cleaner.

The testing included accelerated corrosion resistance. These test included:

- Marine atmosphere (in a salt spray test chamber) in accordance with ASTM B117.
- Industrial-marine atmosphere (in an acid salt spray test chamber) in accordance with ASTM B 368.
- Industrial atmosphere (in a sulfur dioxide test chamber) in accordance with ASTM G 85.
- Atmospheres with different relative humidity and temperatures of tropical climates (in a climatic test chamber) in accordance with ASTM D 2247.

TEST RESULTS

The salt fog test is the most commonly used corrosion test. Parts are exposed to a constant environment of 35°C and 100% relative humidity, with 5% sodium chloride solution atomized for 2000 hours. The coatings protected by the vapor phase corrosion inhibited polyurethane and conductive epoxy amine panels showed no signs of corrosion, delamination, blistering or lifting. The uncoated panels showed 100% corrosion. The panels coated with an uninhibited coating indicated 50-70% corrosion.

The CASS test is widely used. It consists of a 5% salt solution with the addition of .25g/l of copper chloride. The test is performed at 49°C for 120 hours. The coatings protected by the vapor phase corrosion inhibited polyurethane and conductive epoxy amine panels showed no signs of corrosion, delamination, blistering or lifting. The uncoated panels showed 100% corrosion. The panels coated with an *uninhibited coating indicated* 30-50% corrosion.

The humidity test was performed at 38°C and 95% to 100% relative humidity for 120 hours.

The coatings protected by the vapor phase corrosion inhibited polyurethane and conductive epoxy amine panels showed no signs of corrosion, delamination, blistering or lifting. The uncoated panels showed 100% corrosion. The panels coated with an uninhibited coating indicated 60-100% corrosion.

Moist sulfur dioxide tests have been used for many years as a means of simulating corrosion found in industrial atmospheres. The test was performed at

100% relative humidity and 100°F with the introduction of 2 L of sulfur dioxide in a 300 L chamber for 24 hours.

The coatings protected by the vapor phase corrosion inhibited polyurethane and conductive epoxy amine panels showed no signs of corrosion, delamination, blistering or lifting. The uncoated panels showed 100% corrosion. The panels coated with an uninhibited coating indicated 80-100% corrosion.

CONCLUSION

With the various test methods available, one should select the test method that most appropriately suits the material being tested, either through near simulation of the actual exposure conditions or by previously established confirmations of the ability of the test method to rank materials according to their suitability for the environment.

The paint coatings, due to several technical and economical reasons, are the most utilized method for protecting metallic materials against corrosion. The service life for a paint coating and its effectiveness as a corrosion preventive method will depend, to a very great extent, on an adequate selection and/or design of the protective system, adequate surface preparation and coating application, supervision and on site inspection and quality control of paints and protected systems.

The coatings incorporate the advantages of the vapor phase corrosion inhibition system with the benefits of the coatings. This enables the coating to actively prevent corrosion on the substrate surface and provides non-chromated, non-toxic, self healing for any breaks in the coating. Overall, the addition of vapor phase corrosion inhibitors, increase the life and corrosion resistance of the coatings by 50% minimum.

ACKNOWLEDGEMENTS

We would like to thank Coutaulds Aerospace Coatings, AlliedSignal Materials Laboratory, METL Testing Laboratory for testing and materials, Ronald J. Smith and Joseph E. Benjamin for their editorial assistance.

REFERENCES

Klaus Doren/Werner Freitag/Dieter Stoye, *Water-Borne Coatings*, Hanser Publishers, New York 1994

R. Craft, *Modern Paint and Coatings*, No. 3, 1991