The Chemist

Number 81, Volume 2 Spring 2004

Official Publication of
The American Institute of Chemists

Subscription: $35 per year to members. $75 per year to non-members. Single copy, $15

The Chemist (ISSN: 0009-3025) is published quarterly by the American Institute of Chemists.

The Chemist

American Institute of Chemists
315 Chestnut Street
Philadelphia, PA 19106-2702
Phone: (215) 873-8224 • Fax: (215) 925-1954
E-mail: AICOffice@TheAIC.org
www.TheAIC.org
ISSN: 0009-3025

Volume 81, Issue 1
Spring 2004

ENVIRONMENTAL AGING OF METALS USING A ROTATING WHEEL AND DIP TANK

Paul McGrath, Dana M. Barry, Hideyuki Kanematsu, and Takeo Oki

Abstract:
This international effort was initiated to address the challenges that our ever-changing environment places on various protected steel structures due to acid corrosion. A unique experimental setup was designed to determine how hot-dip galvanized steels behave in a dilute acid environment. A variety of hot-dip galvanized steel samples were fabricated in Japan and tested in natural acid rain conditions using a rotating wheel and dip tank in the environmental aging laboratory at Clarkson University. The experimental results provide useful information about the effect of natural environmental conditions on the service life of structural materials being used throughout the world.

Introduction

Today a major problem is acid rain damage from environmental pollution (1,3). Of particular concern is the corrosion of galvanized steels used to make bridges and buildings. The service life of these structural materials is of great importance to the economy and safety of our global community (1).

The main goals of this investigation were to determine how a variety of hot-dip galvanized steels react in acid rain conditions and to assess the service life of these materials. A unique experimental setup, which includes a rotating wheel and dip tank, was designed to test metal samples in a simulated acid rain environment (2). In this project three types of galvanized steels (pure zinc, 5% Al-Zn, and 55% Al-Zn film specimens), with and without silicone sealer, were tested under natural acid rain conditions. The experimental setup and results are provided.

Experiment

1. Experimental Setup

An experimental setup has been designed and successfully tested to environmentally age metals under simulated acid rain conditions. Equipment used in this project includes a rotating wheel and dip tank, which holds approximately 92 liters of acid rain solution (Figure 1). The rotating wheel is operated at a constant speed of three revolutions per minute (RPM). These items and all components of the setup are made of stainless steel. Samples to be tested were attached to the periphery of the 1 m diameter wheel by placing a stainless steel bolt through a mounting hole in the corner of each specimen (Figure 2). The samples were tested for 168 consecutive hours. During testing each sample was submerged in the dip tank for half of the wheel cycle and then exposed to air for the other half of the cycle. The samples were mounted such that their surfaces were perpendicular to the direction of motion in the test solution contained in the dip tank.

For this investigation, the acid rain solution used in the dip tank had an average pH of 5.08, an average conductivity of 29.6μS/cm, and an average temperature of 20°C. The solution was checked and adjusted daily to maintain the pH and conductivity. The pH was selected to represent that of average natural acid rain for the US (4,5). The solution was prepared with sulfuric and hydrochloric acid, together with the following salts: potassium sulfate, ammonium sulfate, magnesium chloride, sodium chloride, sodium nitrate, and calcium nitrate.

2. Samples

Description: A total of 9 samples were tested simultaneously: a substrate, three different hot-dip galvanized steel samples, and five different test panels from Rhombic Corporation in Japan. In all cases the substrate was carbon steel (JIS SS 400). The hot-dip samples included films of 5% Al - 95% Zn, 55% Al - 45% Zn and 100% Zn. For simplicity these samples are referred to as 5, 55, 100, and in addition, sub (substrate). The samples from Rhombic Corporation include the following: Test Panel 1: plated metal with pure zinc film plus sealer, Test Panel 2: plated metal with 5% Al - Zn film plus sealer, Test Panel 3: plated metal with 55% Al - Zn film plus sealer, Test Panel 4: metal spray sample plus sealer, and Test Panel 7: metal spray sample without sealer. For simplicity these specimens are referred to as 100P (pure Zn), 5P (5% Al), 55P (55% Al), MSS (metal spray with sealer), and MS (metal spray).

Preparation: Each hot-dip sample was fabricated with a corner mounting hole prior to the galvanizing process. Holes of a similar size and location were drilled in the metal spray samples and the substrate. The dimensions of the samples were measured to the nearest millimeter. Each sample was cleaned with a standard industrial degreaser, 1,1,2 - Trichlorotrifluoroethane 99%. Then the samples were labeled with permanent ink (sub, 5, 55, 100, 5P, 55P, 100P, MS, and MSS). The dry samples were weighed to the nearest hundredth gram before and after aging, using a 5300 D Fisher Scientific digital balance. Details of these weights are shown in the Mass Chart (Table 1). Hydrophobicity tests were performed on each sample before and after acid rain exposure. Hydrophobicity was quantified using static contact angle measurements, where the angle between the metal surface and water drop was measured. A sessile drop of distilled water was placed on the sample surface and dimensions of the drop were determined with the aid of a video camera. The results of the contact angle calculations can be seen in the Contact Angle Chart (Table 2). To aid in discerning changes in physical appearance, each dry sample was placed on a table and photographed before the experiment started and again after its completion.

Results

For the purpose of quantifying the progress of aging, a qualitative estimate of the dynamic surface wetting of each sample was performed. In each case the percentage of the surface covered with the aging solution was noted when the sample was at the end of the drying portion of the wheel rotation. This was performed throughout the lifetime of the experiment and was done with the naked eye. It was found that after only 1 hour of testing, the samples referred to as sub, MS, and 5 were all completely wet.

Sample observations: After 1 hour of testing the substrate had a uniform light gray color, which shifted to a yellow-gray after 1.8 hours. It took on a light orange-yellow color after 4.3 hours. The substrate, which rapidly assumed a rust covered surface, was removed from the experiment after 24 hours to avoid contamination of the other samples. After 24 hours of testing, the upper part of sample 55 had a slight grey-brown color. This developed into a slight grey-brown cast (over 80% of its front and over 90% of its back) after 48.67 hours. At 96.12 hours this sample acquired a solid brown cast, which remained unchanged throughout the rest of the experiment. At 48.67 hours of testing, sample 5 had a grey surface. At 96.12 hours a slight yellow cast was seen on its front surface and at 168 hours, it also had a similar color change on its back surface. At 148.52 hours, sample 100 had a slight yellow cast on its front surface, and at 168 hours it assumed a light yellow cast on both its front and back surfaces. At 4.3 hours of testing, sample MS had a very slight yellow cast, which turned to a slight orange color after 24 hours. After 96.12 hours this sample exhibited a slight brown cast, which by the end of the experiment was more pronounced on the front surface. After the full 168 hours of testing, sample 100P had only a few small grey spots on its back surface. At 48.67 hours of testing, sample 5P had a dull grey surface. After 96.12 hours, this sample had a mixed grayish pattern on the back surface and a texture change on the front surface. After 148.52 hours this sample had a few small black spots on its back surface. At the end of testing, sample 5P had a few small black spots and gray streaks on the back surface and small spots with a yellow cast on both its front and back surfaces. It should be noted that samples 55P and MSS did not change in appearance throughout the experiment.

Discussion & Conclusions

All samples were tested simultaneously for 168 hours. The average testing conditions throughout the experiment were a pH of 5.08 and a conductance of 29.6μS/cm. With the exception of the substrate and sample 100, most samples appeared to exhibit very small changes in mass during this investigation (Table 1). The substrate gained 0.06 grams after 24 hours of testing. This increase may be due to the formation of significant rust (Fe_2O_3) on its surface. Sample 100 lost 0.08 grams, which was the most mass loss of all the tested galvanized steel samples. This weight change is suggestive of some loss of the 100% zinc film used for its protective coating having dissolved in the acid solution.

The hydrophobicity tests provided some interesting contact angle information. After only 24 hours of testing, the substrate had a contact angle of 0 degrees. At the completion of this experiment, samples 100, 5, 55, and MS also had contact angles of 0 degrees. During the aging experiment all of these samples were seen to be the first to become completely wet, and were seen to exhibit a tendency to corrode and rust at a faster rate than those samples with final contact angles greater than 0 degrees. It should be noted that samples 55P and MSS had only small changes in contact angle from start to finish, and that it was these samples that did not change in appearance during the 168 hours of testing.

Overall all samples other than the substrate showed good corrosion resistance to natural acid rain conditions. Corrosion properties depend on the thickness and chemical makeup of the protective coating of films and sealers. Our results indicate that the use of alloy films, especially 55% Al – Zn, and the use of sealers improves the resistance of a metal to corrosion, and extends its service life.

Acknowledgment: Special thanks to Japan's Galvanizers Association and to the Rhombic Corporation of Japan for providing the samples used in this investigation.

References

1. Dana M. Barry, Paul McGrath, Hideyuki Kanematsu, and Takeo Oki, "Corrosion Resistance for Some Galvanized Steels Under an Extreme Acid Rain Environment," *Proceedings for the Asian-Pacific Corrosion Control Conference*, Osaka, Japan (November 2003).
2. N.E. Frost, G. Xu, and P.B. McGrath, "An Examination of the Environments for Aging of Polymers," *Proceedings for the Conference on Electrical Insulation and Dielectric Phenomena,* Minneapolis (October 1997).
3. http://www.epa.gov/airmarkets/acidrain/
4. http://nadp.sws.uiuc.edu/insopleths/maps2002/
5. http://nadp.sws.uiuc.edu

***Dr. Paul McGrath** is a Professor in the Deparrtment of Electrical and Computer Engineering at Clarkson University (P.O. Box 5720 CAMP, Clarkson University in Potsdam, New York 13699, USA).*

Dr. Dana M. Barry is President of Ansted University's Scientific Board and Technical Writer / Editor of Clarkson University's Center for Advanced Materials Processing (P.O. Box 5665 CAMP, Clarkson University in Potsdam, New York 13699, USA).

Dr. Hideyuki Kanematsu is Associate Professor in the Department of Materials Science and Engineering at Suzuka National College of Technology in Shiroko-cho, Suzuka, Mie 510-0294, Japan.

Dr. Takeo Oki is Professor Emeritus at Nagoya University at 3-39, Tennodori, Tsuhima, Aichi 496-0807, Japan.

Table 1

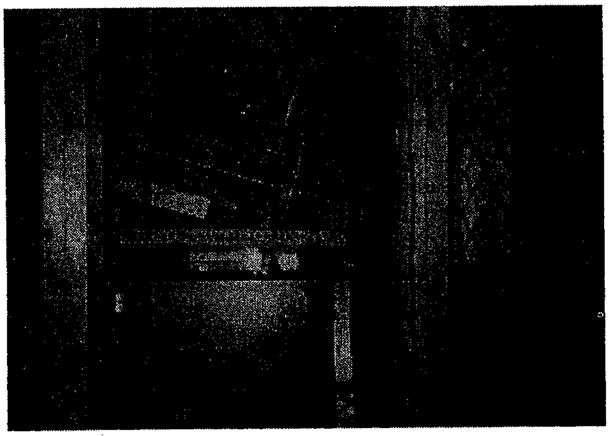
Mass Chart (to nearest hundredth gram)

pH = 5.08				
Sample	Mass before testing in grams	Mass after testing in grams	% (% mass change, nearest hundred th %)	Change in mass in grams
substrate (only tested for 24 hrs.)	65.06	65.12	0.09	0.06 gain
55	86.59	86.56	0.03	0.03 loss
100	92.40	92.32	0.09	0.08 loss
5	89.10	89.06	0.04	0.04 loss
5P	89.68	89.66	0.02	0.02 loss
55P	87.25	87.23	0.02	0.02 loss
100P	92.25	92.22	0.03	0.03 loss
MS	121.75	121.75	0	0.00
MSS	121.28	121.24	0.03	0.04 loss

Table 2

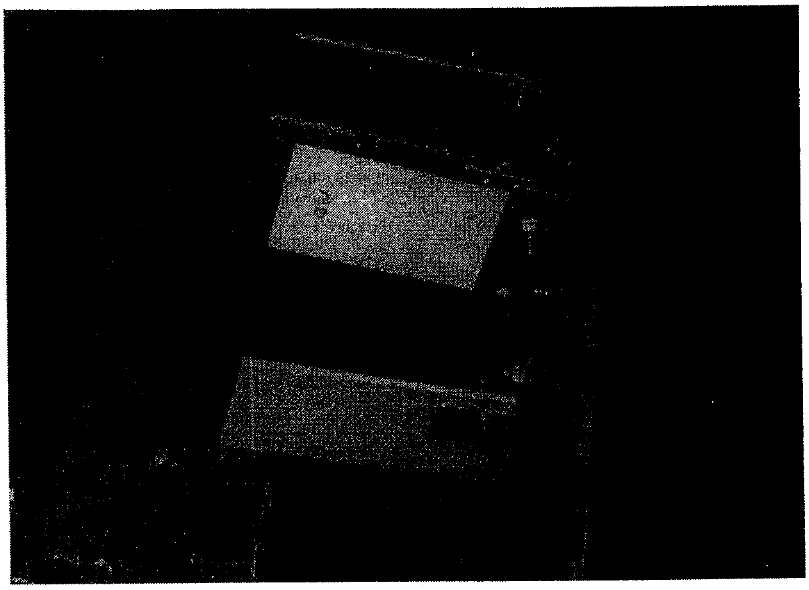
Contact Angles from Hydrophobicity Tests			
		average angles in degrees	
Sample	Before testing with pH = 5.08	After testing with pH = 5.08	Change in degrees
substrate (only tested for 24 hrs.)	68.4	0	68.4
100	68.7	0	68.7
5	70.5	0	70.5
55	70.7	0	70.7
MS	101.2	0	101.2
100P	74.2	52.2	22.0
5P	71.2	54.0	17.2
55P	64.0	57.6	6.4
MSS	71.3	59.6	11.7

Figure 1



Rotating Wheel and Dip Tank

Figure 2



Samples mounted on rotating wheel

Heritage Day 2004

Date: 17 June 2004

Location: Chemical Heritage Foundation

Join our colleagues for Heritage Day 2004 as we celebrate and honor excellence and achievement in the chemical and molecular sciences. Highlights will include the presentation of the following awards to distinguished individuals in the field:

The Othmer Gold Medal - *Jon M. Huntsman, chairman, Huntsman Corporation*

The Commercial Development and Marketing Association Award for Executive Excellence –

Madeleine Jacobs, Executive Director, American Chemical Society

The American Institute of Chemists Gold Medal Award

Carl Djerassi, Ph.D., Professor of Chemistry, Stanford University

The Chemists' Club's Winthrop-Sears Medal –

George Rosenkranz, Ph.D. Former CEO and founding chairman of Sytex Corporation

Alejandro Zaffaroni, Ph.D. Founder, ALZA Corporation

Contact Information:

Nancy Vonada, Manager of Events
(215) 873-8226, nvonada@chemheritage.org