The Development and Application of Corrosion/Weathering Cyclic Testing

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SUMMARY

In 1988, Skerry was the first to report on how the significance of a coating's UV resistance could affect its ability to protect against corrosion. Since then his research has been corroborated and expanded by a number of researchers. This paper will show how current research on the "Corrosion/Weathering Cycle" has shown it to be effective for testing the usefulness of industrial maintenance coatings.

KEYWORDS

CYCLIC CORROSION TESTING (CCT), CORROSION, SALT FOG, PROHESION, QUV, WEATHERING, CORROSION/WEATHERING, ASTM G53, ASTM G85, ASTM B117, ASTM D5894, ASTM D6675-01

BACKGROUND

Salt spray was first used for corrosion testing around 1914. In 1939, the neutral salt spray test was incorporated as ASTM B117.[1] This traditional salt spray specifies a continuous exposure to a 5% salt fog at 35^{o}C. During the course of 80 years of use, there have been many modifications and refinements to B117. In spite of all these refinements, there has long been general agreement that "salt spray" test results do not correlate well with the corrosion seen in actual atmospheric exposures. Nevertheless, B117 has been generally accepted as *the* standard corrosion test method and is still widely specified for testing painted and plated finishes, military components and electrical components.

As the demand for improved corrosion protection increased, engineers and scientists attempted to develop test procedures to more accurately predict the corrosion of materials. In England, during the 1960's and 1970's Harrison and Timmons[2, 3] developed the cyclic Prohesion™ test, which has been found especially useful for industrial maintenance coatings. More recently, the Society of Automotive Engineers (SAE) and The American Iron and Steel Institute (AISI) have been studying cyclic testing for automotive applications. Their progress has been encouraging and is well documented.[4, 5, 6, 7, 8, 9, 10] Japanese researchers have also developed a number of cyclic corrosion test methods. The result of this explosion of research has been something of a mass movement away from static salt spray toward cyclic corrosion tests (CCT).[11]

Of the plethora of cyclic corrosion test procedures under study, one in particular is of special interest for industrial maintenance coatings. This is the Combined Corrosion/Weathering Cycle developed by Skerry and his associates at the Sherwin Williams Company in the USA. Skerry's work was based on combining the British Prohesion test with QUV accelerated weathering.

WHAT IS CYCLIC CORROSION TESTING?

Cyclic corrosion testing is intended to be a more realistic way to perform salt spray tests than traditional, steady state exposures. Because actual atmospheric exposures usually include both wet and dry conditions, it makes sense to pattern accelerated laboratory tests after these natural cyclic conditions. Research indicates that, with cyclic corrosion tests, the relative corrosion rates, structure and morphology are more similar to those seen outdoors. Consequently, cyclic tests usually give better correlation to outdoors than conventional salt spray tests. They are effective for evaluating a variety of corrosion mechanisms, including general, galvanic and crevice corrosion.

Cyclic corrosion testing is intended to produce failures representative of the type found in outdoor corrosive environments. CCT tests expose specimens to a series of different environments in a repetitive cycle. Simple exposures like Prohesion may consist of cycling between salt fog and dry conditions. More sophisticated automotive methods call for multi-step cycles that may incorporate immersion, humidity, condensation, along with salt fog and dry-off. Originally, these automotive test procedures were designed to be performed by hand. Laboratory personnel manually moved samples from salt spray chambers to humidity chambers to drying racks. More recently, microprocessor controlled chambers have been used to automate these exposures and reduce variability.

Any or all of the following environments may be used for cyclic corrosion testing:

Ambient Environment

As used in CCT procedures this term means laboratory ambient conditions. Ambient environments are usually used as a way to very slowly change the test sample's condition. For example, the sample is sprayed with salt solution and allowed to dwell at "ambient" for two hours. The sample is actually going through a very slow dry-off cycle while subject to a particular temperature and humidity.

Typically, "ambient environments" are free of corrosive vapors and fumes. There is little or no air movement. Temperature is usually 25 ± 5 °C. Relative Humidity is 50% or less. The ambient conditions should be monitored and recorded for each test.

Fog (Spray) Environment

Salt fog application can take place in a B117 type test chamber or be done by hand in a laboratory ambient environment. The fog nozzle should be such that the solution is atomised into a fog or mist. Commonly, in addition to sodium chloride, the electrolyte solution contains other chemicals to simulate acid rain or other industrial corrosives.

Humid Environment

CCT procedures often call for high humidity environments. Typically they specify 95 to 100% RH. These may be achieved either by using ASTM D 2247[13] or as an alternative a B 117 chamber may be used to apply a pure water fog.

Dry-Off Environment

A dry-off environment may be achieved in an open laboratory or inside a chamber. The area should be maintained with enough air circulation to avoid stratification and to allow drying of the material. The definition of "dry-off" can be problematic. There is disagreement on whether a specimen should be considered dry when the surface is dry, or when the specimen has dried throughout. As corrosion products build up, the time necessary to achieve full dry-off may increase.

Corrosive Immersion Environment

This environment would normally consist of an aqueous solution with an electrolyte at a specified concentration, typically up to 5%. Typical pH is 4 to 8 and temperature is usually specified. The solution will become contaminated with use, so it should be changed on a regular basis.

Water Immersion Environment

Distilled or de-ionized water should be used. ASTM D 1193[14] provides useful guidance on water purity. The immersion container should be made of plastic of other inert material. Acidity of the bath should be within a pH range of 6 to 8. Temperature should be 24 °C ±3°C. Conductivity should be < 50 mho/cm at 25 °C.

WHAT IS PROHESION?

In the 1960's, Harrison and Tickle observed that zinc phosphate primers performed well outdoors in an industrial environment but poorly in a salt spray. To improve correlation with actual field results, Harrison decided to use a mixture of commonly occurring atmospheric salts. The mixture included ammonium sulphate and sodium chloride. Elaborating further on Harrison's work in the 1970's, Timmins decided to dilute the solution to 0.40% ammonium sulphate and 0.05% sodium chloride (by weight). He also determined that one hour of spray at ambient temperature followed by one hour of a dry environment at

35°C would provide results more consistent with actual service environments.[2] This came to be known as the “Prohesion” test. Mebon Paints trademarked the Prohesion name, which comes from combining the words ***Pro***tection and Ad***hesion***. The Prohesion test was standardized by the ASTM in 1994 in document G85, Annex A5 (Dilute Electrolyte Cyclic Fog/Dry Test).[12]

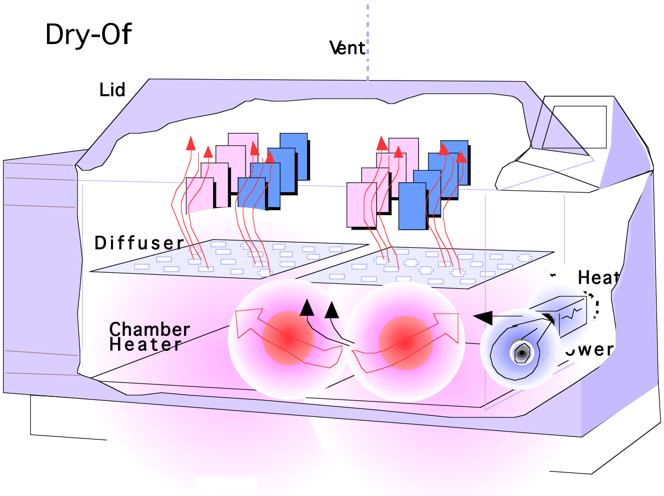


Figure 1, Q-Fog showing dry-off environment

RECENT CORROSION WEATHERING RESEARCH

Skerry of the Sherwin Williams Company picked up this work in the 1980’s and added the use of the QUV accelerated weathering tester to incorporate the degradation from UV light exposure. The theory was that UV might degrade coatings to the point that they would become susceptible to corrosion attack. The theory proved to be correct and for the coatings investigated, the results were a large improvement over conventional salt spray results. The gross corrosion rates and the morphology of the products of corrosion were more like outdoors. As a result of the Prohesion electrolyte the products of corrosion were chemically more similar to those specimens exposed to an industrial environment.

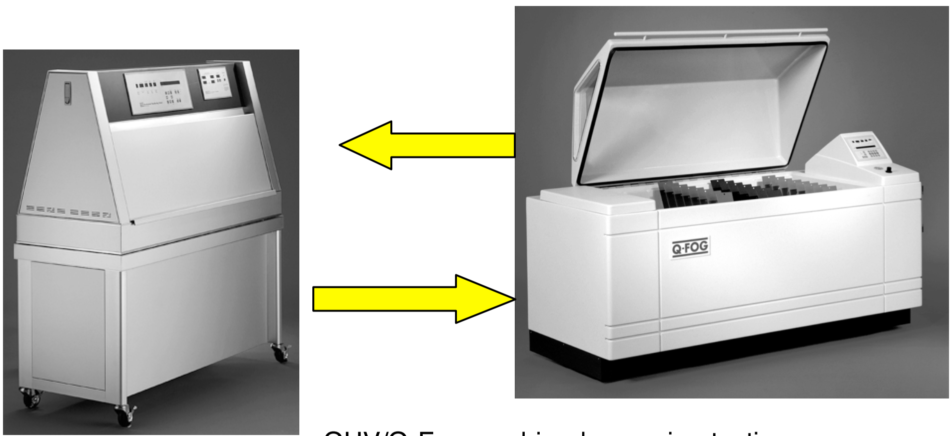


Figure 2, QUV/Q-Fog combined corrosion testing

Continuing his work into the 1990’s Skerry employed Scanning Electron Microscopy (SEM) and X-ray Photoelectron Microscopy (XPS) to more accurately evaluate the corrosion products created on the specimens. He also changed the QUV lamp type to the UVA-340 in order to improve correlation. The UVA-340 spectrum is a better match with the UV portion of sunlight than the UVB-313 and allows better correlation.

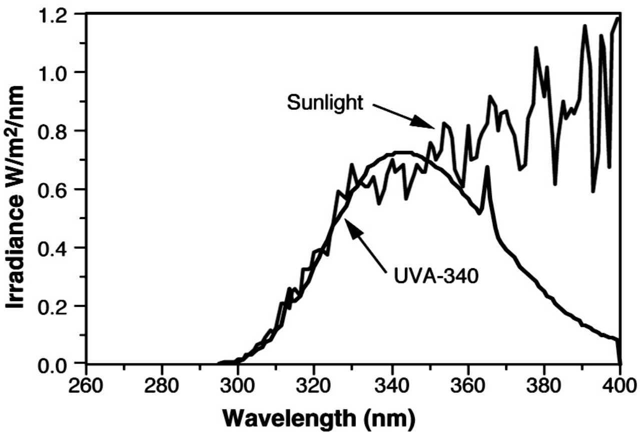


Figure 3, The spectrum of the QUV's UVA-340 Lamp compared to Noon Summer Sunlight.

The UVA-340 allows an excellent simulation of the short wave UV region of sunlight

Combined Corrosion/Weathering Cycle

The Corrosion/Weathering Cycle consists of one week of QUV exposure alternating with one week of Prohesion.

Typical Duration 2,000 hours

The Corrosion/Weathering exposure cycle is:

1 Week QUV Weathering

8 hours	UV exposure, UVA-340 lamps, 60 °C
4 hours	Condensation (pure water), 50 °C

Manually move the samples to a CCT tester:

1 Week Prohesion (ASTM G85-A5)

1 hour	Salt fog application at 25 °C (or ambient)
1 hour	Dry Off at 35 °C (The dry-off is achieved by purging the chamber with fresh air, such that within 3/4-hour all visible droplets are dried off of the specimens.)
Electrolyte Solution	0.05% sodium chloride & 0.35% ammonium sulfate
Solution Acidity	pH between 5.0 and 5.4.

Repeat for one week, then manually move the samples back to the QUV Accelerated Weathering Tester and repeat cycle.

The Combined Corrosion/Weathering Cycle, sometimes referred to as the "Skerry Cycle" has gained significant popularity in the USA. When compared to B117, it has proven to do a superior job of ranking the performance of waterborne coatings.[15, 16] With greater emphasis on compliance, the US coatings industry is turning to this type of testing on a large scale.

Skerry's Rank Correlations of Outdoor vs Lab Exposures

Exposure Condition	Ranking (best to worst)
Exterior – Marine Environment	Latex>Alkyd>Epoxy
Exterior – Industrial Environment	Latex≈Alkyd>Epoxy
Conventional Salt Spray	Epoxy>Alkyd>Latex
Prohesion	Latex≈Alkyd≈Epoxy
Combined Corrosion/Weathering Cycle	Latex>Alkyd>Epoxy

ASTM RESEARCH

ASTM Committee D01 on Paint and Related Coatings has standardized the Combined Weathering/Corrosion Cycle in a new document. It is titled *"ASTM D5894[17], Cyclic Corrosion/UV Exposure of Painted Metal (Alternating Exposures in a Fog/Dry cabinet and a UV/condensation Cabinet)"* and was developed by the Subcommittee D01.27 on accelerated Testing.

Subcommittee D01.27 is doing two parallel studies – one on Coil Coatings and one on Industrial Maintenance Coatings. All samples are being exposed outdoors at seven different locations. The outdoor results will be compared to various laboratory exposures including the Combined/Weathering Cycle, a variant on the Combined/Weathering Cycle with a different electrolyte to simulate acid rain and conventional salt spray. Due to the length of the outdoor exposures results will not be forthcoming for a number of years.

Subcommittee D01.27.30 has also proposed a new document "*Standard Guide for the Laboratory Cyclic Corrosion Testing of Automotive Painted Steel Parts. This practice is designed to assist in determining the corrosion resistance of paint and related coatings on automotive steel surfaces. It should produce failures representative of the type found in outdoor corrosive environments*"

The method prescribes that any or all of the following environments may be used for cyclic corrosion testing:

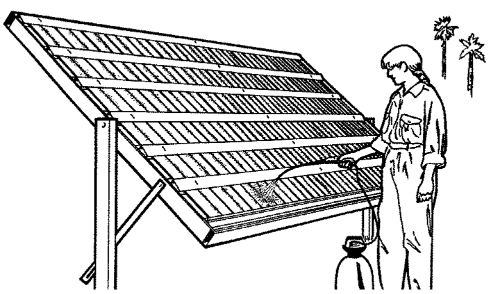
a. Cabinet conditions
    - Dry off Conditions
    - High Humidity
b. Water Immersion
c. Salt Solution Application
d. Surface Contamination
e. Ambient Conditions

Salt solutions may be applied as a spray or mist in a test chamber, manually or by dipping. A range of salt solutions and cycles are permitted. The method provides and alternative to General Motors Standard GM 9540P.

According to the research done by the Society of Automotive Engineers Automotive Corrosion and Prevention Committee (SAE ACAP) and the American Iron and Steel Institute (AISI), this is currently considered one of the preferred CCT methods for automotive cosmetic corrosion (painted or pre-coated metals). GM9540P/B requires a 16 hour work day or an automatic cycling test chamber. If performed manually, a sprayer is used to mist the samples until all areas are thoroughly wet. Parts should be visibly dry before each mist application. If performed manually, the samples should be left at the ambient conditions over the weekend. There are a number of automated testers available that will perform this exposure in a single chamber.

ASTM has recently published "*ASTM D 6675-01[18] Standard Practice for Salt-Accelerated Outdoor Cosmetic Corrosion Testing of Organic Coatings on Automotive Sheet Steel*"

This method applies to outdoor exposures and includes the periodic (twice weekly or every 3 to 4 days) wetting of the test specimens with a 5% aqueous salt solution in compliance with B117. The test specimens to be mounted on a rack at and angle or 45° facing the equator and the salt solution should be applied with a hand pump atomizer or spray.



CLEVELAND SOCIETY FOR COATINGS TECHNOLOGY STUDIES

The Technical Committee of the Cleveland Society for Coatings Technology (CSCT) working under the leadership of Mr. Ben Carlosso of Mameco International is currently researching the correlation of a number of accelerated laboratory corrosion tests compared to several outdoor service environments. The accelerated tests investigated include salt spray (B117), wet-dry cyclic 5% salt spray, Prohesion and Combined Corrosion Weathering Cycle. The outdoor test sites are located in New Jersey, North Carolina coastal, Florida, California inland, California coastal, Ohio, Missouri and Oregon. The test specimens are nine coatings on cold rolled steel substrates. All of the coatings are compliant under existing California Law. The coatings were chosen to represent a wide range of performance criteria:

1. Self priming acrylic latex – top coated with a DTM acrylic latex
2. Acrylic latex primer – top coated with an acrylic latex semi-gloss
3. 2-component high solids urethane basecoat - 2-component high solids urethane basecoat
4. High solids solvent epoxy aluminium mastic – elastomeric styrene-acrylic latex topcoat
5. Waterborne acrylic-cross-linked epoxy basecoat - waterborne acrylic-cross linked epoxy topcoat
6. Water reducible alkyd self priming - water reducible alkyd self priming
7. Styrene acrylic maintenance coating, self primed - styrene acrylic maintenance coating, self primed
8. Water reducible epoxy ester primer – semi gloss acrylic latex topcoat
9. Specification alkyd primer, TTE-266 – specification alkyd, TTE-266

The method of evaluation included commonly used ASTM evaluation methods for rust creepage, rusting, blistering, filiform corrosion and specular gloss. Spearman rank correlation was used to compare the outdoor results to the laboratory tests.

Two year outdoor data is now available. When comparing the degree of blistering and surface rusting, the CSCT found that ASTM B117 salt spray does not correlate well with outdoor environments. The wet-dry testing using the 5% sodium chloride solution provided slightly better correlation than B117 salt spray. The Prohesion, Combined Corrosion Weathering Cycle and the cyclic immersion/UV test provided better rank order correlation with most of the outdoor exposure sites.[19]

STEEL STRUCTURES PAINT COUNCIL PROGRAMME

Since the mid1990's the Steel Structures Painting Council (SSPC) has embarked on a comprehensive test programme called APEC or "Advances in Performance Evaluation of Coatings". The programme is designed to improve coating testing in a number of areas. They are developing a large pool of control coatings and are expanding the use of statistical methods to improve the precision of correlation between natural and laboratory exposures.

The SSPC tested 15 different systems including alkyds, acrylics, epoxies and urethanes. The SSPC research compared outdoor results (31 months) with results from the Combined Corrosion/Weathering Cycle, conventional salt spray, a cyclic salt spray employing a 5% sodium chloride solution, Prohesion and two types of cyclic immersion test. The SSPC research has confirmed that the Combined Corrosion/Weathering Cycle provided the best agreement with severe outdoor marine exposure.[20,21]

Steel Structures Painting Council Correlation Results

Laboratory Test Method	Correlation with Severe Marine Exposure
Conventional Salt Spray	- 0.11
Prohesion	0.07
Cyclic Immersion Procedures	0.48
Cyclic Immersion with UV Procedure	0.61
Combined Corrosion/Weathering Cycle	

OTHER RESEARCH PROVIDES CONFIRMATION

Arabian Gulf States

Experience has shown that under conditions like those in Kuwait industrial areas coatings degradation has tended to be faster than in Western countries for which most coatings are developed. Consequently a study was performed to investigate the durability of 11 industrial coating systems for two and a half years at five weathering sites in the industrial belt of Kuwait. Coating performances was related to prevailing industrial atmospheric conditions and compared with their behaviour in laboratory accelerated tests.

The laboratory tests used in this research included modifications to earlier corrosion/weathering test programmes. Different cycles and solutions were used to better simulate the Kuwaiti industrial environment. The laboratory tests combined 100 hour salt spray employing 5% sodium chloride and 3000 ppm sulfate solution followed by 16 hours of ambient drying and then exposure in a QUV using a 12 hour UV at 60°C and 12 hours condensation at 40°C. The investigators found that this test programme provided good correlation with the Kuwaiti industrial environment.

The Institute of International Container Leesors (IICL)

The IILC has adopted a modified version of the Combined Corrosion/Weathering Cycle for testing container coatings. Due to the ocean going nature of containers the corrosion wet time was increased, the test specifies 4 hours spray at 30°C and 2 hours of dry at 40°C.

US Air Force

The US Air Force is currently performing trial tests on coated aluminium specimens to investigate the viability of the Combined Corrosion/Weathering Cycle, Prohesion alone and GM 9540P Method B and CCT-4 as possible replacement tests for coatings on aluminium. This work is of particular interest because there has been limited research on the viability of different cyclic corrosion tests for aluminium.

SUMMARY

The best summary may be to simply quote Skerry " Rankings predicted by the Combined Corrosion/Weathering tests were most consistent with rankings in the field." However, as could be expected, the relative advantages of various exposure temperatures, durations and sequences remain application specific. Researchers will no doubt continue to modify cycles and adjust solutions to better address their application. Some may prefer specialized electrolytes to simulate acid rain, others may prefer fluorescent UVB lamps to increase acceleration or to use xenon arcs.

However, there is a strong consensus that for coatings susceptible to degradation from sunlight the Combined Corrosion/Weathering Cycle gives the most realistic results.

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Note: Prohesion is a trademark of Mebon Paints Ltd. QUV and Q-Fog are trademarks of the Q-Panel Company.