

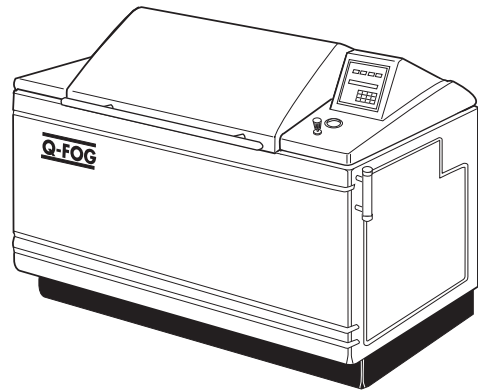
Introduction to Cyclic Corrosion Testing

This paper is intended to be a general introduction to cyclic corrosion testing (CCT). It outlines the rationale for cyclic testing, includes some guidelines for using cyclic tests and explains some common CCT cycles and applications. This discussion is not intended to be a complete, exhaustive tutorial on cyclic corrosion testing. Consult the referenced technical papers for more detailed information.

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°C. In the course of 80 years of use, there have been many modifications to B117. Despite all these modifications, 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 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 1960s and 1970s, Harrison and Timmons^{2,3} developed the cyclic Prohesion™ test, which was found to be 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.



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.

1. ASTM B117, Method of Salt Spray (Fog) Testing.
2. Cremer, N.D., "Prohesion Compared to Salt Spray and Outdoors: Cyclic Methods of Accelerated Corrosion Testing," Federation of Societies for Coatings Technology, 1989 Paint Show.
3. Timmins, F.D., "Avoiding Paint Failures by Prohesion," Journal Oil & Colour Chemists Assoc., Vol. 62, No. 4, p. 131 (1979).
4. M. L. Stephens, "SAE ACAP Division 3 Project: Evaluation of Corrosion Test Method," Paper No. 892571, Automotive Corrosion and Prevention Conference Proceedings, P-228, Society of Automotive Engineers, Warrendale, PA (1989), pp. 157-164.
5. H. E. Townsend, "Status of a Cooperative Effort by the Automotive and Steel Industries to Develop a Standard Accelerated Corrosion Test," Paper No. 892569, *ibid.*, pp. 133-145.
6. F. Blekkenhorst, "Hoogovens' Contribution to AISI Program, Accelerated Corrosion Testing: A Cooperative Effort by the Automotive and Steel Industries," Paper No. 892570, *ibid.*, p. 147-156.
7. M. Petschel, Jr., "SAE ACAP Division 3 Project: Evaluation of Corrosion Test Results and Correlation with Two-Year, On-Vehicle Field Results," Paper No. 912283, Automotive Corrosion and Prevention Conference Proceedings, P-250, Society of Automotive Engineers, Warrendale, PA (1989), pp. 179-203.
8. R. J. Neville, W.A. Schumacher, D.C. McCune, R.D. Granata and H. E. Townsend, "Progress by the Automotive and Steel Industries Toward an Improved Laboratory Cosmetic Corrosion Test," Paper No. 912275, *ibid.*, pp. 73-98.
9. F. Blekkenhorst, "Further Developments Toward a Standard Accelerated Corrosion Test for Automotive Materials," Paper No. 912277, *ibid.*, pp. 99-114.
10. D. D. Davidson and W. A. Schumacher, "An Evaluation and Analysis of Commonly Used Accelerated Cosmetic Corrosion Tests Using Direct Comparisons with Actual Field Exposure," Paper No. 912284, *ibid.*, pp. 205-220.

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 and 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, etc. More recently, microprocessor controlled chambers have been used to automate these exposures and reduce variability.

Exposure Environments

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

Ambient Environment 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 $25 \pm 5^\circ\text{C}$. Relative humidity is 50% or less. The ambient conditions should be monitored and recorded for each test.

Chamber Environments Non-ambient environments are usually chamber exposures. Cycling between different non-ambient environments can be performed by physically moving the test specimens from one chamber to another or, in automated chambers, by cycling from one condition to another.

The temperature and relative humidity should be monitored. Whenever possible, automatic control systems should be used. Temperature tolerances should be $\pm 3^\circ\text{C}$ or better.

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 atomized into a fog or mist. Commonly, in addition to NaCl, the electrolyte solution contains other chemicals to simulate acid rain or other industrial corrosives. Figure 1 shows a chamber in the fog mode.

Humid Environment CCT procedures often call for high humidity environments. Typically they specify 95 to 100% RH. These may be achieved by using ASTM D 2247.¹¹ As an alternative, a B117 chamber may sometimes be used to apply a pure water fog. Figure 2 shows a Q-Fog operating in the humidity mode.

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. Figure 3 shows Q-Fog dry-off.

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 deionized (DI) water should be used. ASTM D1193¹² provides useful guidance on water purity. The immersion container should be made of plastic or other inert material. Acidity of the bath should be within a pH range of 6 to 8. Temperature should be $24 \pm 3^\circ\text{C}$. Conductivity should be < 50 mmho/cm at 25°C .

11. D2247, Practice for Testing Water Resistance of Coatings in 100% Relative Humidity.

Figure 1

Q-Fog Performing the Fog Function

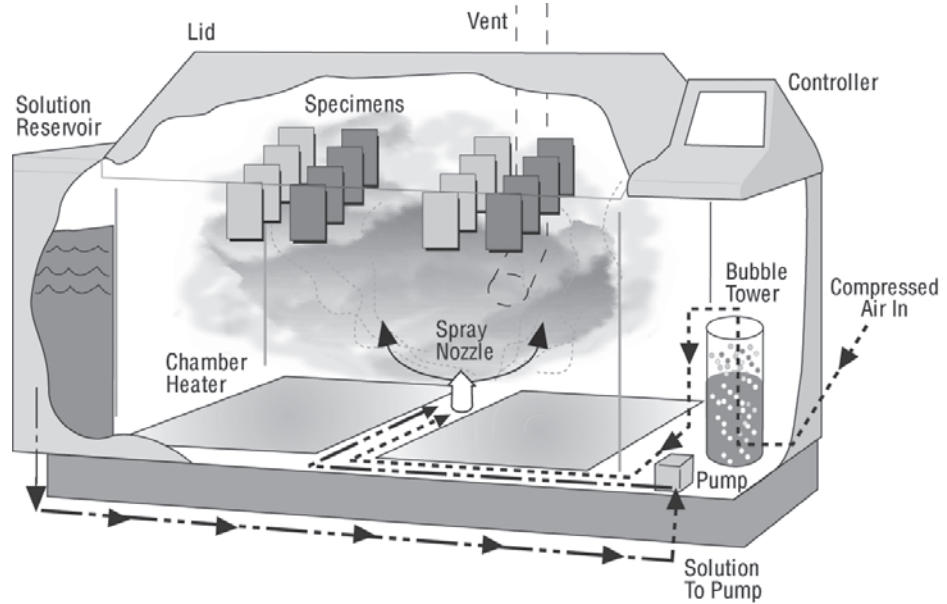


Figure 2

Q-Fog Operating the Humidity Function

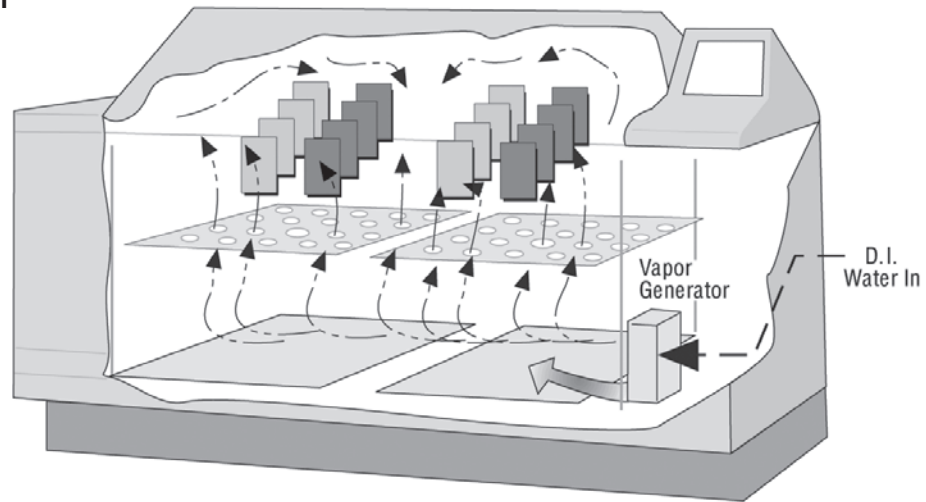
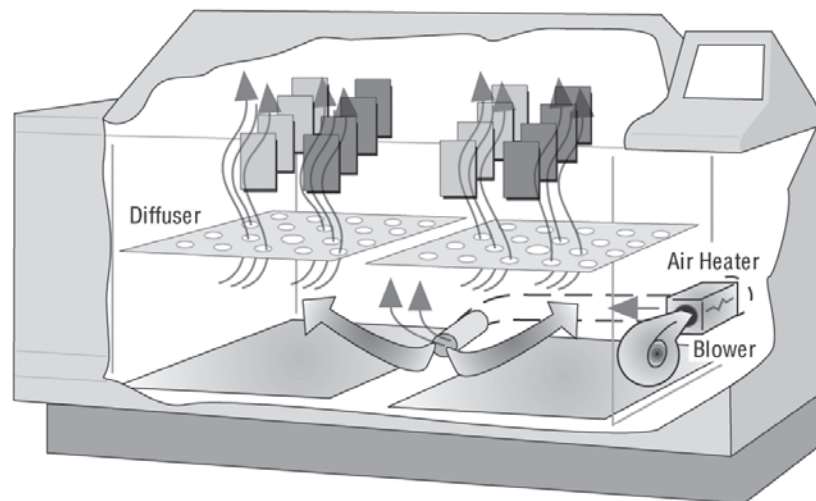


Figure 3

Q-Fog Showing the Dry-Off Environment



Guidelines for CCT Testing

Because CCT tests are often complicated, multi-step exposures, the procedures themselves can often confound the researcher. The following guidelines are intended to aid the user in understanding the possible sources of variability in CCT exposures. The guidelines are also intended to assist in obtaining good inter-laboratory agreement of results.

Use of Reference Specimens

Whenever possible, reference specimens (specimens of known performance in the test conducted) should be tested concurrently with the actual specimens under test. Preferably, more than one reference specimen will be used and the references chosen will bracket the test specimen's expected performance. The references will allow the normalization of test conditions during repeated running of the test and will also guide comparisons of test results from different repeats of the test.

Preparation of Test Specimens

It is common practice to scribe or chip coated test samples before exposure to the CCT. This provides a break in the coating which accelerates corrosion. When a gravelometer is used, the procedure shown in D3170¹³ is recommended.

There is a growing body of evidence indicating that differences in scribe depth can significantly affect the CCT test results. This is particularly important for galvanized substrates. In most cases, the scribe should penetrate into the base metal. It is especially important that the specific scribe tool be reported, since scribe geometry can also affect results. A microscope may be useful for characterizing the scribe damage. A scribing method is described in ASTM D1654.¹⁴

Exposure Precautions

In addition to the precautions specified in B117, the multi-functional nature of CCT exposures adds to the potential problems in the area of repeatability and reproducibility of results.

Chamber Loading Level Chambers that are loaded to capacity will normally take longer to make transitions between temperatures than will lightly loaded chambers. Chambers should be loaded evenly to maintain good air flow during the test.

Transition (Ramp) Time Transition time can be a factor affecting results in both manual and automated exposures. In manual exposures, transition time is the time that it takes to move the test specimens from one environment or exposure condition to another. In automated chambers, transition time refers to the time it takes the machine to change the exposure conditions inside the chamber. Automated chambers can be expected to give more predictable and reproducible transitions than manual exposures. The effect of transition times on test results still needs to be studied further. Therefore, transition times should be monitored and reported as often as is practical. Transition time can be expected to vary, depending upon:

- Variability in ambient conditions
- Variability in manual operational procedures
- Type of equipment used
- Cabinet loading

Fog Deposition and Uniformity In conventional salt spray tests, the uniformity of fog dispersion is typically determined by collecting the fog fall-out at various positions around the chamber. Unlike B117, monitoring of CCT fog deposition rates cannot be accomplished while the test is operating. This is because most CCT exposures specify relatively short fog cycles. Consequently, to determine the fog dispersion uniformity in a CCT tester, it is necessary to collect the fog fall-out between tests in a special continuous spray run of at least 16 hours. See section Method B117 for detailed instructions on fog collection.

Test Interruptions Whenever a test must be interrupted, the test panels should be stored under the least corrosive conditions available. All interruptions and handling of panels should be reported.

12. D1193, Specification for Reagent Water.

13. D3170, Standard Test Method for Chip Resistance of Coatings.

14. D1654, Method for Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments.

Corrosion/Weathering Cycle

For industrial maintenance coatings, the addition of UV has been found useful for improving correlation on some formulations.^{16, 17} This is because UV damage to a coating can make it more vulnerable to corrosion. The Corrosion/Weathering Cycle consists of one week of Prohesion alternating with one week of QUV exposure.

Electrolyte Solution	0.05% sodium chloride & 0.35% ammonium sulfate
Solution Acidity	pH between 5.0 and 5.4
Typical Duration	2,000 hours

The Corrosion/Weathering exposure cycle is:

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 45 minutes all visible droplets are dried off of the specimens.)

Repeat for one week, then manually move the samples to a QUV Accelerated Weathering Tester and expose at the following cycle:

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

Repeat for one week

Manually move the samples to a CCT tester and repeat the whole procedure.

Automotive CCT Exposures

The automotive industry has taken the lead in researching cyclic corrosion tests. Consequently, most of the CCT procedures are geared toward automotive applications.

GM 9540P/B According to the research done by the SAE ACAP Committee and the AISI, this is currently considered one of the preferred CCT methods for automotive cosmetic corrosion (painted or precoated 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 automated testers available that will perform this exposure in a single chamber.

The GM9540P/B exposure conditions include:

Electrolyte Solution	0.9% NaCl, 0.1% CaCl ₂ & 0.25 NaHCO ₃
Solution Acidity	pH between 6.0 and 8.0
Typical Duration	80 cycles (1,920 hours)

The GM9540P/B exposure cycle is:

–	Thorough Salt Mist Application
90 minutes	Ambient Conditions (25°C, 30 - 50% RH)
–	Thorough Salt Mist Application
90 minutes	Ambient Conditions (25°C, 30 - 50% RH)
–	Thorough Salt Mist Application
90 minutes	Ambient Conditions (25°C, 30 - 50% RH)
–	Thorough Salt Mist Application
210 minutes	Ambient Conditions (25°C, 30 - 50% RH)
8 hours	Humidity (95 - 100% RH)
8 hours	Dry-off (60°C, <30% RH)
Repeat	

16. Simpson, C.H., Ray, C.J., and Skerry, B.S., "Accelerated Corrosion Testing of Industrial Maintenance Paints Using a Cyclic Corrosion Weathering Method," *Journal of Protective Coatings and Linings*, May 1991, Volume 8, No. 5, pp. 28-36.

17. Skerry, B.S., Alavi, A., and Lindren, K.I., "Environmental and Electrochemical Test Methods for the Evaluation of Protective Organic Coatings," *Journal of Coatings Technology*, October 1998, Volume 60, No. 765, pp. 97-106.

Japanese Automotive Cyclic Corrosion Tests

The Japanese have developed a number of cyclic corrosion tests. Most are primarily for automotive applications.

CCT-1 CCT-1 is specified by some Japanese automotive manufacturers. It is also known as CCT-A.

The CCT-1 exposure conditions include:

Electrolyte Solution	5% sodium chloride
Solution Acidity	Not specified
Typical Duration	200 cycles (1,600 hours)

The CCT-1 exposure cycle is:

4 hours	Salt fog application at 35°C
2 hours	Dry-off at 60°C, <35% RH
2 hours	Humidity at 50°C, >95% RH
Repeat	

CCT-4 CCT-4 is specified by some Japanese automotive manufacturers. In the SAE and AISI research projects, CCT-4 was shown to be one of the exposures that best correlated with actual vehicle corrosion results. There are no special provisions for testing over the weekend. CCT-4 exposure conditions include:

Electrolyte Solution	5% sodium chloride
Solution Acidity	Not specified
Typical Duration	50 cycles (1,200 hours)

The CCT-4 exposure cycle is:

10 minutes	Salt fog application at 35°C
155 minutes	Dry-off at 60°C
75 minutes	Humidity at 60°C, 95% RH
160 minutes	Dry-off at 60°C
80 minutes	Humidity at 60°C, 95% RH
160 minutes	Dry-off at 60°C
80 minutes	Humidity at 60°C, 95% RH
160 minutes	Dry-off at 60°C
80 minutes	Humidity at 60°C, 95% RH
160 minutes	Dry-off at 60°C
80 minutes	Humidity at 60°C, 95% RH
160 minutes	Dry-off at 60°C
80 minutes	Humidity at 60°C, 95% RH
Repeat	

Acid Rain CCT

This procedure, intended to simulate an acid rain exposure, is a modification of the Japanese Automobile Standards Organization (JASO) test method M609 for automotive corrosion. Acid Rain CCT exposure conditions include:

Electrolyte Solution	5% (wt) NaCl, 0.12% (vol) HNO ₃ , 0.173% (vol) H ₂ SO ₄ , 0.228% (wt) NaOH
Solution Acidity	pH of 3.5

The Acid Rain CCT exposure cycle is:

2 hours	Fog at 35°C
4 hours	Dry-off at 60°C, less than 30% RH
2 hours	Wet/humid at 50°C, over 95% RH

Acid Rain CCT specifies transition times between environments as follows:

Fog to Dry	within 30 minutes
Dry to Wet	within 15 minutes
Wet to Fog	within 30 minutes

Summary

There are a large number of cyclic corrosion procedures to choose from. Each has advantages and limitations. Some researchers prefer fog environments to immersion. Some prefer specialized electrolyte solutions to simulate acid rain. Many prefer the advantages of automated chambers. The relative advantages of various exposure temperatures, durations and sequences remain somewhat controversial, and researchers will, no doubt, continue to modify cycle times and adjust corrosive solutions. However, there is a strong consensus that for most materials, cyclic corrosion testing gives more realistic results than traditional salt spray.



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