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Short-Term Evaluation Procedures for Coatings on Structural Steel

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NBS technical note

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ABSTRACT

This report presents the findings of the first of a two-phased study to aid the Federal Highway Administration in evaluating and selecting protective coatings for steel. The objectives of the study are to review existing short-term test procedures for selecting coatings, and to discuss analytical measurement techniques for characterizing coating systems and for monitoring coating degradation.

In assessing current accelerated aging testing procedures, several deficiencies became apparent. These included the reported lack of reproducibility in the rankings for different iterations of the same short-term test and the lack of correlatability between the rankings of short-term laboratory and long-term outdoor exposure tests.

It was concluded that, at the present time, coating manufacturers and users do not depend heavily on accelerated test results for making durability assessments. Instead, durability assessments are based on outdoor exposure performance. Recommendations are made to design future short-term test procedures using reliability theory.

Key words: accelerated aging tests; coatings; corrosion; time to failure; predictability; reproducibility.

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1. INTRODUCTION

1.1 BACKGROUND

The high frequency of failures of protective coatings on State and local highway bridges, signs, barriers, etc., contributes to the large economic losses from corrosion experienced in the United States. A recent report, proposing a model for predicting corrosion costs on highway structural steel [1], estimated that the total expenditure for corrosion protection of steel bridges amounts to $130 - 160 million per year; and according to the author's model, this expenditure should be doubled to obtain maximum bridge service life.

An essential first step in maximizing service life is selecting the best available coating for the expected environmental and operating conditions. In making this selection, quantitative estimates of the service lives of candidate systems should be available for the wide range of environmental conditions experienced in the United States. Traditional sources for obtaining estimates are short-term laboratory tests and outdoor exposure tests. Currently, outdoor exposure results are heavily relied upon for service life predictions.

Over the last few years, however, changes have occurred jeopardizing the reliance on outdoor exposure tests for durability assessments. These changes have resulted from legislation aimed at 1) reducing solvent emissions (Federal Clean Air Acts of 1970 and 1977) and 2) lessening worker exposure to hazardous materials (Occupational Safety and Health Act, and Hazardous Material Acts). The effect of this legislation, along with oil import restrictions, has been to supplant many traditional coating systems with systems having little or no history of outdoor exposure. These new coatings systems often require improved surface preparations and new application techniques. The quality and protection resulting from these changes must be determined, increasing the need for quick, reliable, durability assessment procedures. Long-term, outdoor exposure tests cannot meet this need due to the length of time required for obtaining results. The need can be met through the development of reliable short-term evaluation procedures.

1.2 OBJECTIVES

The purpose of the overall study is to aid the Federal Highway Administration in evaluating and selecting protective coatings for use on steel by identifying or developing improved short-term test procedures.

The study was divided into two phases having the following generalized objectives:

1. To evaluate the validity and reproducibility of existing short-term tests for predicting the service life of coatings on steel;

2. To develop, where needed, improved short-term tests; and

3. To develop, based upon the improved test methods, a guide for evaluating and selecting protective coatings for steel.

Phase I of the study, which is summarized in this report, addresses the following:

1. Development and justification of a set of criteria for evaluating the adequacy of accelerated aging tests for coating systems;

2. Review of currently used accelerated aging procedures;

3. Assessment of these procedures relative to the proposed criteria; and

4. Propose research needed for developing improved accelerated aging test procedures capable of satisfying the proposed criteria.

2. ASSESSMENT CRITERIA FOR SHORT-TERM ACCELERATED AGING TESTS

Accelerated aging tests serve two functions. For a particular end-use application, users of coatings employ them in making decisions between different coating systems. Manufacturers of coatings, on the other hand, use them in making decisions aimed at developing more durable coating formulations. The extent to which accelerated aging test results are useful in making these decisions depends, to a large degree, on the criteria used in setting up the experiment. Prior to large scale testing, therefore, it is important to state the set of criteria used in developing an accelerated aging test and in assessing the results.

In the process of reviewing these criteria, two sets were identified. The first is termed the proposed set. It is the set of criteria that the authors feel best insure that the maximum benefit is derived from the accelerated aging program. These criteria are currently used or are being considered as the basis for accelerated aging tests in many industries [4,5,6,7,8,9]. The second set of criteria more closely reflects the ones currently used in the coating industry. This is the set against which the short-term tests in section 3 are assessed. In the recommendations section of this paper, it is proposed that future accelerated aging tests be developed on the basis of the first set of criteria.

2.1 PROPOSED CRITERIA FOR ASSESSING COATING SHORT-TERM ACCELERATED AGING TESTS

Short-term tests should 1) provide results which aid in making quantitative service life predictions under service conditions; 2) be capable of distinguishing between the durability performances of two or more coating systems under all environments, and 3) provide a means for monitoring modifications in a coating system performance because of changes in formulation, surface preparation, etc. In order to meet these expectations, the following criteria are proposed:

- PREDICTABILITY - Accelerated aging procedures should provide quantitative service life predictions for the coating at its expected environmental operating conditions (see Appendix A).

- REPRODUCIBILITY - Once an accelerated aging procedure is specified, it should be reproducible and provide methods for testing for reproducibility.

- DISTINGUISHABILITY - The procedure should provide a methodology for making quantitative comparisons between the performance of different coatings. This would be useful in determining the superiority of one coating system over another and in ascertaining if improvements in the performance of a coating have occurred e.g., due to changes in formulation, surface preparation, application, etc.

- EXTENDABILITY - The analysis procedure should allow for more than one stress type. This should provide more realistic service life predictions, permit sensitivity analyses to be made on the effect of each stress type, and provide an opportunity for examining stress interactions.

One theoretical approach capable of satisfying these criteria is presented in Appendix A.

2.2 CRITERIA FOR ASSESSING CURRENTLY AVAILABLE SHORT-TERM ACCELERATED AGING TESTS

After reviewing the literature and after talking with personnel at many different coating laboratories, it became apparent that the criteria stated in section 2.1 are not applicable for assessing currently available accelerated aging tests. Current accelerated aging tests were developed using the concept of a "comparison" test as opposed to "predictability" tests (section 2.1). In comparison tests, specimens from multiple different coating systems are subjected to the same accelerated and outdoor test environments. The coating systems in both the accelerated and outdoor tests are then ranked. A good accelerated aging test is one in which the ranking is similar in both the accelerated and outdoor exposures. For a new coating system, the expected life is measured against control coatings exposed to the same environment. Control coatings are coatings having a known track record.

Comparison tests differ from predictability tests, therefore, in several key ways. First, predictability should be replaced with the term correlatability, since the measure of agreement is one of association. Reproducibility has the same meaning in both contexts; but distinguishability has a more qualitative meaning since coating systems are ranked relative to each other. In comparison testing, the term extendability has little meaning, since the objective is to develop an accelerated test good for all outdoor environments.

3. REVIEW OF ACCELERATED AGING TESTS

A successful durability procedure has two essential components: 1) an accelerated aging test procedure, and 2) a measurement procedure for monitoring material degradation. This chapter focuses upon currently used accelerated aging procedures. Degradation measurement techniques are reviewed in chapter 4.

3.1 SALT SPRAY

3.1.1 Description

The salt spray test [19] was originally designed to test the durability of metallic coatings exposed to ocean spray. Over time, it has evolved as the most popular accelerated aging test for organic coatings covering metallic surfaces. Basically this test entails spraying coatings housed in a special cabinet with a 5 percent sodium chloride solution at 35°C. The procedure is popular because coating failures usually occur in a short time.

Many variations of this salt spray test exist. Sodium chloride is reported to be more corrosive than seawater and to produce corrosion products different from those formed from either seawater or calcium salts [20, 21]. Example of some variations follow. The British continuous salt spray test (BS 3900 Part F4-1968) [22] uses a synthetic seawater solution ($NaCl$, 26.5 g; $MgCl_2$, 2.4 g; $MgSO_4$, 3.3 g; KCl, 0.73 g; $NaHCO_3$, 0.20 g; $NaBr$, 0.28 g; $CaCl_2$, 1.1 g; water to 1000 ml). Other salts are also used to simulate other service environments. The acetic acid/salt spray test, (ASTM B287-74) [23] specifies a solution of NaCl and acetic acid (pH 3.1-3.3). The copper-accelerated-acetic-acid-salt spray test, (CASS test, ASTM B368-68) [24] designates a 5 percent NaCl solution containing copper (II) chloride acidified with acetic acid.

Harrison [26] utilized 3.25 percent $(NH_4)_2SO_4$ and 0.25 percent NaCl solution in the salt spray test for simulating an industrial environment. He reports that his results correlate better with 14 years outdoor exposure than salt spray data resulting from a 3.5 percent NaCl solution. The ARE salt droplet test [27] (BS 1391:1952) requires a daily spray of a synthetic sea salt solution ($NaCl$, 23 g; $Na_2SO_4 \cdot 10\,H_2O$, 8.9 g; $MgCl \cdot 6H_2O$, 9.8 g; $CaCl_2$, 12 g; in 1 liter of solution) on coated panels. After spraying, the specimens are covered to prevent evaporation. In the above tests, temperature is controlled.

3.1.2 Extent of Usage

Salt spray testing is widely used to test coatings for corrosion protection. A salt spray test is included in nearly all steel coating specifications. Most industrial laboratories utilize the salt spray testing in evaluating new formulations.

3.1.3 Time to Failure

Time to failure in the salt spray test depends on many factors: type of steel (hot or cold rolled), surface preparation, coating (resin and pigment), thickness of coating, and inclusion or exclusion of a top coat. Testing times for alkyds are typically up to 1000 hours, longer for epoxies, and up to 7 months for inorganic zincs. Comparative performance of different binders in the salt spray test is discussed by Appleman and Campbell [29].

3.1.4 Surface Preparation

Surface preparation is an important factor in obtaining meaningful experimental results. Representatives from industrial laboratories commented that the ranking of coatings after salt spray testing would agree quite well with the ranking of exterior exposures if proper attention were given to surface preparation. The thickness of the coating is also an important factor in establishing reliable results in the salt fog test. A critical film thickness of 2.0 mils (50 μm) is indicated in the PACE study [31] and in work reported by Desea [39]. ASTM D609-73 [29] covers procedures to be followed in the preparation of steel panels. ASTM D1014-66 [30] describes methods to minimize the influence of variations in steel surfaces on any series of tests.

Surface preparation depends on the type of substrate to be coated. Both cold and hot rolled steel panels are used [31, 32, 33, 34]. Solvent cleaned cold rolled steel is justified when cold rolled steel is the substrate to be coated. Cold rolled steel panels are readily available and quite uniform. Hot rolled steel should be used, however, when coatings are to be applied to structural steel, since structured steel is hot rolled. Hot rolled steel panels typically have non-uniform surfaces. Both blast and hand cleaned hot rolled steel panels were used in the PACE study [31]. Hospadaruk [38], et al., suggested a large variation in salt spray performance of coated steel was due to carbonaceous residues. Their report shows that failure in a 240 hour salt spray test correlates strongly with high surface carbon concentration, substantiating the need for controlling steel surface cleanliness.

Surface preparation is similar for all the accelerated tests discussed in this chapter. Any requirements particular to an accelerated test will be discussed in connection with that accelerated test.

3.1.5 Modes of Failure

A scribe mark (ASTM D1654-79a) [40] is frequently made through the cured coating prior to testing.

Failures appear as undercutting at the scribe, rusting, and to some extent blistering. Excess amounts of chloride can act to depassivate the surface interfering with inhibitive pigment performance. The availability of an electrolyte permits sacrificial coatings (e.g., zinc rich coatings) to effectively protect the substrate, but at the same time a less protective film may be formed by the reaction products. A difference in zinc reaction products between salt spray testing and exterior exposure has been observed microscopically [41].

3.1.6 Properties Measured

Following salt spray exposure, panels are visually inspected for corrosion, blistering, and undercutting. ASTM standards (D610-68, rusting and ASTM D714, blistering [28]) are available for these properties. The NACE Technical Practice Committee T-6 reports that the above ASTM methods are sufficiently standardized to provide meaningful results. Besides visual ratings, other evaluative procedures are sometimes used after salt spray testing. These include adhesion testing, identification of corrosion products under the film by energy dispersive X-ray, microscopic inspection, and weight change of the panel.

3.1.7 Assessment

Results of salt spray testing are very sensitive to operating conditions. Variables that must be carefully controlled include uniformity of the environment throughout the cabinet, angle of the panels with respect to the vertical, nozzle design, atomization pressure, humidity of the air used for atomization, pH, purity of salt solution, and specimen collection rate [42]. Variations in these operating conditions among cabinets can account for poor reproducibility. Stone [43] reported a coefficient of variation (standard deviation/mean) between 0.1 to 0.3 for three primers. More definite information will soon be available from a committee of the National Association of Corrosion Engineers, which recently conducted an interlaboratory test.

Reports vary as to whether salt spray coating performance results correlate with exterior exposures. Variations in the rankings of coatings exposed to both salt spray environment and exterior environment often occur. Statistical studies aimed at elucidating these variations were not found. Most users look for qualitative agreement between the two exposures or for dramatic reversals. Examples of reversals are cadmium and zinc coatings [44], inorganic and organic zinc primers [45], and several coatings tested in the PACE study [31].

Comments from the authors of the PACE report [31] express the feelings of both users and producers in relation to the salt spray. They concluded that on the whole, "good" paints will usually do well in the salt fog and "poor" paints will usually do poorly, but the exceptions are far too numerous to justify basing decisions solely on salt spray testing methods.

3.2 CYCLIC WEATHERING TESTS

3.2.1 Description

Weathering tests, i.e., carbon or xenon arc or fluorescent lights with humidity, temperature and wetness control, are commonly used to characterize chalking, change in gloss, and change in color for coating systems. Typical cycles [46] are described in ASTM standards D822, D3361-74, G53-77, and G26-77. The development and use of weathering tests was reviewed recently by Ellinger [47].

3.2.2 Extent of Usage

Weathering tests are commonly used for gloss and chalking determinations. Few reports have been made on the use of weathering cycles for the evaluation of coatings for corrosion control; some doubt exists as to whether these tests are good indicators of primer corrosion control [48].

3.2.3 Time to Failure

Exposure times in most weathering cycles, excepting the Dew cycle and fluorescent UV-condensation type (ASTM G53-77) exposure, are from 1000-2000 hours. Dew cycle exposures are often between 50-150 hours. UV-condensation type exposure times depend on the cycle used; typical exposure times fall between 250 to 1000 hours.

In table 1, representative failure times for coatings in several weathering cycles are listed. Failure is designated as a 50 percent loss of gloss. While chalking also occurs during cyclic weathering exposure, quantitative failure times based on extent of chalking were not found in the literature.

3.2.4 Modes of Failure

Little evidence of rusting or blistering is reported after cyclic weathering. Failure is usually reported in terms of the amount of loss of gloss and degree of chalking. Degradation usually results from a combination of ultraviolet light, temperature, and humidity [56]. Chalking occurs if a binder is degraded, thereby, releasing pigment.

3.2.5 Properties Measured

Panels are examined for loss of gloss, color change, and chalking (ASTM 659-74 for chalking, ASTM 523-78 for gloss, and ASTM D1729-69 (1974) for color change) [57]. Chalking is sometimes determined by weighing panels before and after removal of the chalk. Color change can be measured spectrophotometrically.

Lindberg [54] examined the surfaces of several systems (including epoxy, acrylic, polyurethane, and fluoropolymer) using scanning electron microscopy after several hundred hours cyclic weathering exposure and several months outdoor Florida exposure. He also made gloss (ASTM D522) and loss of weight measurements. He concluded gloss measurement is not a good indicator of resin degradation and that gloss measurements should be supplemented with weight loss measurements.

3.2.6 Assessment

The reproducibility of these tests could not be ascertained. Papenroth [58] has shown that variations in UV irradiance in a weathering machine cause differences in chalking and change of gloss. The ranking of panels exposed in accelerated weathering cycles and outdoor environments often differ [49, 53, 54]. However, some researchers have reported good correlation [49-54].

Table 1. Observed Times to Failure[a] in Weathering Machines

Resin	Twin Carbon Arc	Dew Cycle	Xenon Arc 40-45% RH	UV cond.
alkyd	300-2000 hrs[c,d,f,g]	75[d,g]	200-500[f]	240[b]
epoxy	400-2000 hrs[c,d]	50-200[d,g]	400-600[d]	
polyurethane	1000- > 2000 hrs[c]	50-90[c,d]	> 1200[c]	
acrylic (thermosetting)	600- > 1000 hrs[c,f,g]	35-200[g]	400-1000[c]	740[b]
vinyl, chlorinated rubber	> 700 hrs[f]	200[d]	200-300[d,f]	

[a] failure defined as 50 percent loss in gloss

[b] Ellinger, N., J. Oil Col. Chem. Assoc., 62, 136 (1979) [49].

[c] Hoey, et al., J. Oil Col. Chem. Assoc., 57, 151 (1974) [50].

[d] Lindberg, J. J. Oil Col. Chem. Assoc., 58, 399 (1975) [54].

[e] Oakley, E., et al., J. Oil Col. Chem. Assoc., 57, 221 (1974) [52].

[f] Nowacki, L. J., Official Digest, 34, 1191 (1962) [53].

[g] Stanton, J. M., J. of Paint Technology, 39, No. 514, (1967) [55].

3.3 CYCLIC OR SEQUENTIAL TESTS WHICH INCLUDE SALT SPRAY

3.3.1 Description

Specialized tests have been designed which include exposure to salt spray as part of the cycle. The prohesion test described by Timmins [59] includes six periods of alternating salt spray and ambient air drying. The salt spray is Harrison's $(NH_4)_2SO_4$-NaCl [26] mixture. One major paint company designed its own exposure cabinet in which the samples are exposed to one hour 5 percent salt spray, one hour UV, and a one hour darkness cycle. The Texas Highway Department uses a cycle of 24 hour-heat lamp exposure (60°C black panel temperature) and 48 hour salt spray (20 percent NaCl). The Louisiana Highway Department utilizes an 18 percent salt spray at 67°C for 4 weeks to evaluate coating systems on steel. The Michigan Highway Department has developed a weathering cycle of 200 hours UV-condensation exposure, 50 hours salt spray, and 5 freeze-thaw cycles. Hospadaruk's cycle [38], which accelerates degradation compared to salt spray testing, consists of 0.25 hour immersion in 5 percent NaCl (air saturated), 1.25 hour at room temperature, and 22.5 hours in a humidity cabinet at 49°C and 85 percent relative humidity. Other variations of this test include the above plus a weekly freeze/dry cycle, or dusting the panels with kaolin powder before testing, or a temperature of 60°C in the humidity cabinet.

Tooke's cycle [60] consists of rotating panels in a chamber equipped with ultraviolet lamps and nozzles for spraying synthetic seawater solution [22]. The UV light in Tooke's cycle is on for 40 minutes and off for 40 minutes. Panels are also sprayed for 30 seconds every 15 minutes. Alumbaugh and Hearst [61] developed a cyclic test immersing specimens in aerated synthetic seawater for 1 1/2 hours and drying them in warm air (50°C) for 1 1/2 hours.

Another cyclic test (ASTM D2933-74) [62] combines 4 hours testing in a salt spray, 18 hours at 37.8°C and 100 percent relative humidity and 2 hours in a freezing chamber at -28.3°C. Sakae, et. al. [63] describe several sequences of tests for evaluating corrosion control coatings. These cycles usually include exposure to a carbon arc or xenon arc light, exposure to a salt spray, and exposure to an SO_2 environment. The Port Authority of New York uses a nine step cycle test which includes: 1) 168 hours in a xenon arc accelerated weathering machine, 2) 15 freeze/thaw cycles, 3) 16.5 hours salt fog, 4) 72 hours accelerated weathering, 5) 15 freeze/thaw cycles, 6) 5.5 hours salt fog, 7) 120 hours accelerated weathering, 8) 5.5 hours salt fog, and 9) 120 hours accelerated weathering. They report being able to distinguish some performance differences not distinguishable with salt spray.

3.3.2 Extent of Usage

Most of these tests are relatively new and not standardized; usage is very limited.

3.3.3 Time to Failure

In the prohesion test, primers are tested for 48 hours; complete systems are tested for 2000 hours [59]. In Tooke's [60] accelerated environment, alkyd primers usually failed (ASTM scribe rating of 5) between 400 and 1000 hours. Hospadaruk et al. [38] report their cycle with kaolin dust caused failure (25 percent surface rust) in 600 hours for a maleinized oil primer and in 2000 hours for an epoxy primer. Alumbaugh and Hearst [61] report vinyls and epoxies failed in their test cycle between 700 and 4500 hours. In the Michigan Department of Transportation, cyclic test coatings are typicaly exposed for 300 hours.

3.3.4 Modes of Failure

Since some of the cycles described in this section include ambient environmental exposure, as well as exposure to high humidity, light, and variable of temperature, many failure modes are observed. Typical failures include blistering, rusting, undercutting at the scribe, chalking, and loss of gloss.

3.3.5 Properties Measured

Properties measured after sequential testing are similar to those measured after salt spray and cyclic testing. Coatings and substrates are evaluated for indication of rusting, blistering, flaking, undercutting at the scribe, chalking, and loss of gloss.

3.3.6 Assessment

No specific information pertaining to the assessment is available for this or the following tests. The previously made comments about lack of information on reproducibility and correlatibility apply here and to the following accelerated tests.

3.4 CONDENSATION TESTS

3.4.1 Description

In this test, specimens are exposed to 100 percent relative humidity at a constant temperature. This is often done by exposing the coated side of a test specimen to warm, moist air while keeping the back side of the panel at ambient temperature. Condensation must cover the coatings at all times. Corrosion is dependent on the time of wetness [65]. The temperature prescribed in ASTM D2247-68 (1973) [66] is 38 ± 1°C. Sometimes temperatures of 49°C or 60°C are used [38, 67]. Increasing the temperature from 49°C to 60°C increases the rate of corrosion 150 to 200 percent [38].

Van Laar [68] varied the humidity test by making the atmosphere rich in HCl, H_2SO_4, or CH_3COOH along with high humidity and elevated temperatures. The HCl atmosphere was the most corrosive, followed by H_2SO_4 and CH_3COOH.

3.4.2 Extent of Usage

This test is frequently used by industrial laboratories for testing coatings for corrosion protection. Several highway departments use a humidity testing method as part of their evaluation procedures. One highway department places coated panels in a concrete curing chamber at a high humidity (95 percent) and elevated temperature 65°C for 300 hours.

3.4.3 Time to Failure

For high build vinyl coatings, Pila [33] found no blistering or corrosion after 800 hours humidity exposure for most pigments tested. Geld [69] reported slight surface deterioration for vinyl or coal tar coatings after 1400 hours of room temperature exposure to 100 percent humidity. However, considerable rusting of substrate surfaces was found after the coating was removed. Several experimental acrylic and alkyd thermosetting coatings failed in 300 to 400 hours [70]. A coal tar epoxy was found to protect the substrate for 1000 hours [71].

3.4.4 Modes of Failure

The conditions in a humidity cabinet are favorable for water permeation, leaching of soluble components, softening, and swelling of coatings. Diffusion of water through coatings occurs rapidly. This reaction is driven osmotically by the presence of soluble components at the coating/substrate interface. Soluble components include contamination present before coating application, diffusion of ions or gases which diffused through the coating, and trapped solvent. The presence of those contaminants can lead to blister formation and rusting.

3.4.5 Properties Measured

The specimens are usually evaluated using ASTM procedures for blistering and rusting. Additional information can be obtained if the coating is removed after testing and the substrate examined.

3.5 IMMERSION

3.5.1 Description

An immersion test for organic coatings on structural steel is described in ASTM D870-54 (1973) [73]. The test specimens are partially immersed in the test liquid (i.e., distilled water, salt solution, acid, base, etc.) and maintained at a temperature of 37.8 ± 1°C. The test liquid is changed as required to avoid contamination. Temperature is often a variable.

3.5.2 Extent of Usage

Immersion testing is conducted on coatings that will be subjected to immersion in service.

3.5.3 Time to Failure

Some experimental one-pack epoxy primers immersed in distilled water started blistering in less than 150 hours. However, rusting occurred only after 150 hours [32]. Two-pack epoxy primers protected the steel substrate for over 2000 hours. Vinyl coating systems showed no rusting after 6190 hours [31]. Linseed oil and linseed oil alkyd coatings have also been reported to show little blistering after 350 hours [71]. Some phenolic and two-part epoxy coatings showed little rusting or blistering after 600 hours [32]. Vinyl coatings showed no blistering after 5700 hours immersion in seawater [31].

3.5.4 Modes of Failure

The modes of failure of coatings due to immersion are similar to those in the humidity cabinet. Water permeates the coating causing swelling, leaching of soluble components, and loss of adhesion. Rusting is probably controlled by the availability of oxygen.

3.5.5 Properties Measured

As with corrosion tests, coatings are examined for blistering and corrosion. Sometimes coatings are stripped so that the substrate can be examined. Tooke and Montalvo [74] followed the loss of adhesion as a function of time of immersion. Adhesion for all primers studied (oil, oil alkyd, alkyd, and melamine alkyd) fell off rapidly with immersion time.

3.6 KESTERNICH TEST

3.6.1 Description

This test was designed to simulate weathering in industrial environments. The stresses include elevated temperature, 100 percent relative humidity and SO_2. The Kesternich test cycle is described in standard DIN 50018 [75]. Samples are placed in a cabinet in which water and SO_2 are introduced and the cabinet is heated to a 40°C. After eight hours of exposure, the door of the cabinet is opened and the specimens are exposed to room conditions for 16 hours.

3.6.2 Extent of Usage

Although often reported in the European literature [76, 77], the test is not widely used in the United States.

3.6.3 Time to Failure

Kesternich testing is usually conducted for 240 to 1000 hours. At the end of the exposure time, the panels are evaluated. After 240 hours, Chess [76] reported that coatings on galvanized steel showed partial to total deterioration.

3.6.4 Modes of Failure

It has been shown that SO_2 permeates free paint films [12]. It is, therefore, possible that ions may be formed at the coating/substrate interface by the reaction of water and oxidizers with SO_2. Chemically, ions on the metal surface would cause an increase in osmotic pressure and interfere with passivating properties of inhibitive pigments, thus promoting corrosion.

3.6.5 Properties Measured

As with the salt fog test, panels are evaluated for blistering, rusting, and undercutting of the coating at the scribe or edge.

3.7 CATHODIC TEST

3.7.1 Description

Cathodic tests, often called "bullet hole" tests [78], are designed to test the protective qualities of sacrificial coatings. The test specimens are prepared in such a way as to leave an uncoated circular or rectangular area in the center of the panel. Exposed edges of the panel are frequently coated with wax to prevent corrosion. The specimen is then immersed in a liquid (such as synthetic seawater or 3 percent NaCl) at room temperature until corrosion is observed in the uncoated area, the "bullet hole." For zinc rich coatings, the zinc becomes the anode, while the exposed steel substrate becomes the cathode. As long as an anodic reaction does not occur on the steel surface, corrosion is prevented.

3.7.2 Extent of Usage

This test is sometimes used by coating manufacturers to assess the ability of sacrificial coatings to provide cathodic protection. It is to be included in specifications developed by the Navy and is being used in the evaluation of zinc rich coating extenders.

3.7.3 Time to Failure

These tests are usually carried out until corrosion occurs in the "bullet hole." The varying specification requires that coatings shall prevent corrosion in the base metal area for a minimum of 30 days immersion in synthetic seawater.

3.7.4 Modes of Failure

Failure occurs when the zinc is consumed. The steel substrate then becomes anodic and rusting occurs. This test does not take into account the protective coating formed by the zinc reaction products.

3.7.5 Properties Measured

Only the time for rust to appear in the "bullet hole" is measured.

4. MEASUREMENT TECHNIQUES FOR EARLY CHARACTERIZATION OF DEGRADATION

The accelerated test methods described in chapter 3 have many shortcomings. One of the most significant is that the relationship between performance in the accelerated weathering environment and service environment is not well defined. Currently, more sensitive evaluation techniques are being developed. These techniques include measures of adhesion, electrical properties, permeabilities, mechanical stress, and chemical changes.

4.1 ADHESION

4.1.1 Significance of Property

Since it is thought that corrosion does not proceed to any extent as long as the coating adheres firmly to the substrate [12, 18], changes in adhesion should relate to durability. However, these measurements must be done carefully and under controlled conditions as adhesion of coatings to a substrate depends on environmental conditions [85]. Adhesive strength usually decreases when coatings are in a humid or wet environment [81, 82] and recovers to some extent after the coatings are placed in a dry environment [86]. The ability of a coating to maintain good adhesive properties under wet conditions is thought to be very important with respect to its ability to provide corrosion protection [12].

4.1.2 Measuring Techniques

Bullett and Prosser [87] have recently reviewed the available adhesion measuring techniques. Among these, two are ASTM standard test methods -- ASTM D2197 and 3359. ASTM D2197-68 (reapproved 1979) [88] covers the determination of adhesion by a scrape tester method or by a parallel groove adhesion tester. In the scrape tester method, adhesion is determined by pushing the coated panels beneath a rounded stylus or loop which is loaded in increasing amounts until the coating is sheared from the substrate surface. ASTM's precision statement says that the results agree well with other qualitative evaluation methods. In the parallel groove method, adhesion is evaluated in terms of the closeness with which parallel grooves can be cut through the coating before the intervening film is lifted from its substrate. ASTM's statement of precision says that 95 percent of the time the same operator should be within two microknife adhesion units for duplicate tests; measurements made by different operators in different laboratories should be within four units.

Tape test methods (ASTM 3358 [89]) are commonly used in the industry for measuring adhesion. In one, an x-cut is made through the coating over which a pressure sensitive tape is applied and removed; adhesion is assessed qualitatively on a scale of zero to five. In the other method, a matrix pattern, using six or seven cuts in each direction is made through the film. Pressure sensitive tape is applied over the matrix and removed. Adhesion is evaluated by comparison with descriptions and illustrations on a zero to five scale. Both methods are repeatable to within one rating and reproducible to within two ratings at the 95 percent confidence level, according to the ASTM statement of precision.

The most commonly used measure of adhesion, which gives a measure of the force needed to remove a coating, is a tensile or pull-off method. Standard methods for pulloff adhesion tests are described in ISO 4624-1978 (E) [90] and DIN 53232 [91]. In both standard test methods, two different test assemblies are described. In one test, a coating is applied to the top of a rigid cylinder (approximately 1 cm in diameter) to which a second cylinder of the same size is adhered. In the other test, a rigid cylinder is glued to a coated panel having greater dimensions than the cross-sectional area of the cylinder. The amount of force needed to pull the test assemblies apart is measured and the mode of failure is noted. For both procedures, results are invariant with cylinder diameter ranging from .6 to 2.5 cm.

For these two tests, the stress distributions are different [92]. Edge effects in the second test contribute to an apparent lower adhesion value and to a greater experimental variation.

The Joint Service Research and Development Committee on Paints and Varnishes [93] sponsored an extensive study carried out to investigate the direct pull-off techniques. Surface preparation, paint application, and temperature were factors affecting interlaboratory reproducibility. Proper alignment and rate of loading also affect variability. Sickfield [92] reports a range of 5 to 15 percent from the mean for coatings tested between two cylinders and a range of 10 to 30 percent of the mean when the cylinder is glued to a panel. Others report similar variations in test results [94].

Two field tensile testers are the Elcometer[1] and the torque wrench. The Elcometer exerts a tensile stress through the action of a spring. Experimental results for this tester often display high variations. The torque wrench or spanner method involves gluing a rigid test cylinder to the coating and measuring the torque necessary to remove it [95]. Breaking strength values for both procedures are of the same order of magnitude and have similar failure characteristics.

4.2 ELECTRICAL MEASUREMENTS

4.2.1 Significance of Property

Electric properties relate to the corrosion protective qualities of the coatings. Some correlation between corrosion protection qualities of the coatings and electrical properties has been found. Limited information on the mechanism of corrosion of a coating during immersion can be obtained from electrical measurements [102]. Leidheiser [96] recently reviewed electrical measurement procedures.

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[1] Elcometer is a brand name adhesion tester. Recognition of a specific commercial product is not meant to constitute an endorsement by the National Bureau of Standards.

4.2.2 Measuring Techniques

4.2.2.1 D. C. Resistance Measurements

Bacon et. al., [97] measured D. C. resistance of over 300 organic coatings on metal substrates immersed in electrolytes over a period of 150 days. In cases of good protection (determined visually), the resistance of the film exceeded 10^8 ohms/cm^2. When corrosion occurred, the resistance was less than 10^6 ohms/cm^2. Coatings having resistances between 10^6 and 10^8 ohms/cm^2 were sometimes good and sometimes not.

Mayne and Mills [98] demonstrated that the electrical properties of a film vary greatly with location on the film. They found a correlation between film resistance and corrosion. D.C. resistances of films were also shown to change after immersion in KCl [98, 103, 104]. Films increasing in resistance did not corrode, while films decreasing in resistance did. Increased resistance was thought to be associated with increase in cross link density. The authors suggest that improved protection may be obtained by uniformly increasing crosslink density over the film.

Equipment needed to carry out these measurements is described by Brown [105]. Included is a calomel or Ag/AgCl electrode, an electrometer with a high input resistance, and two potentiometers to provide added potential for high resistance measurements or to charge panels having a long time constant.

4.2.2.2 A. C. Resistance Measurements

A.C. resistance measurements can provide the same information as that obtained from D.C. measurements. In addition, A.C. measurements have several advantages over D.C. measurements. The most important one is the ability of measurements to be made as a function of frequency. Processes occuring in the coating can be distinguished from those at the interface by obtaining data over a wide range of frequencies [107, 108].

4.2.2.3 Capacitance Measurements

Changes in the capacitance of coatings have been associated with the penetration of water into the film. Difference in water uptake, determined gravimetrically and by capacitance measurements, has been used to characterize differences in the mode of distribution of water in coatings as a function of pigment and polymer [111]. Models have been developed relating change in capacitance with change in depth of penetration of water into the coating [102, 112].

4.3 PERMEABILITY MEASUREMENTS

4.3.1 Significance of Property

Since water, oxygen, and ions are needed at the coating/substrate interface for corrosion to occur, the rate at which they permeate would seem to be related to the protective qualities of the coating. A great amount of work has recently been done to measure permeabilities of different coating systems to do the following: 1) water: as a function of relative humidity and temperature [113, 114]; 2) oxygen: as a function of temperature and the water absorption [115]; 3) sulfur dioxide: as a function of temperature [12]; and 4) various ions: [116, 117, 118, 119, 120].

It is generally agreed that the water permeation rate through a coating does not control the corrosion rate [12]. The rate of oxygen permeation is often a sizeable fraction of that needed for corrosion of unprotected mild steel [18, 115]; however, corrosion of coated steel, at least in the early stages of exposure, proceeds much slower. These ideas suggest that permeabilities to water and oxygen are linked with other protective mechanisms.

The permeability of coatings to ions such as Cl^-, SO_4^{-2}, and Na^+ are several orders of magnitude smaller than to water [12, 121]. Evidence exists that ion permeability and ion exchange properties of the coating may be related directly to the protective quality of the paint [118, 122, 123].

4.3.2 Measuring Techniques

Free films are used in obtaining measurements of permeability to oxygen and water.

Oxygen permeabilities can be determined using a pressure differential method. The free coating film of interest is positioned between a large and a small chamber. The large chamber contains oxygen at a pressure of 50 or 100 mm of mercury (6.5×10^3 to 13×10^3 Pa), while the small chamber is evacuated. Pressure rises are then measured. For nine different films, oxygen permeability was insensitive to relative humidity but very sensitive to temperature [115].

Sulfur dioxide permeabilities are measured by exposing one side of the film to humid air containing SO_2 and titrating the water leaving the film on the downstream side of the permeation cell for its acid content [12].

The measurement of ion permeabilities and ion exchange properties of films is much more difficult. Recent work by Ruggeri and Beck [121] identifies problems associated with measurements for films with very low permeabilities and ion concentrations. Typical experimental procedures include radioactive tracer methods and use of special electrodes or specific ion titrations. These measurements are not routinely done for organic coatings.

4.4 MECHANICAL STRESS MEASUREMENTS

4.4.1 Significance of Property

Internal stresses of coatings have a strong influence on many physical and chemical properties of coating systems. Stresses arise during curing of the film because of shrinkage and crosslinking [124].

Changes in temperature and relative humidity cause changes in the internal stress. .The thermal expansion coefficients of some coatings are on the order of two to three times greater than that of metals. Hence, temperature decreases will increase film stress. If the additional stress is sufficiently high, the film can either become detached from the substrate or crack [129]. Water may also act as a plasticizer reducing the internal stress [126]. It can also leach out soluble products, which may result in increased internal stress in the film on redrying [125].

4.4.2 Measuring Techniques

4.4.2.1 Fixed Film

Internal stresses in coatings can be determined using a cantilever beam deflection method. A coating is applied to one side of a thin steel strip and deflection is measured microscopically [127] or mechanically [128] as the coating cures. Saarnak [127] reports that, if measurement procedures and environmental conditions are carefully controlled, satisfactory reproduction is possible. Croll [128] reports experimental errors of about 15 percent. Internal stresses of 5 MPa have been reported for freshly cured coatings.

4.4.2.2 Free Films

Mechanical properties of free films can be determined by stress-strain measurements, transient, and dynamic tests. In one type of dynamic test, an oscillating strain is applied at a constant frequency and the resulting stress and phase difference measured. Measures of both elastic and viscous response are obtained. When these tests are performed as a function of temperature, glass transition temperatures and brittle-ductile transition temperatures [130] are obtained. Loss tangent curves obtained from dynamic testing are related to impact resistance of the film.

Changes in mechanical properties after aging can often be related to coating durability [131]. Talen [132] found that alkyd resin varnish tensile results correlated well with outdoor durability. Tensile tests after outdoor exposure also revealed changes in properties sooner than visual changes.

4.5 CHEMICAL TECHNIQUES

4.5.1 Significance of Properties Measured

In order to improve coating systems, it is necessary to link changes in the coating microstructure to macrostructural performance changes. By making this connection, it is hoped that the causes of coating system degradation may be readily identified; thus, this would provide information for coating systems improvement. Analytical equipment capable of making microstructural change characterizations are described below.

4.5.2 Measuring Techniques

4.5.2.1 Ellipsometry

Ellipsometry is an optical technique which has been used for observing changes under transparent coatings at the coating/substrate interface. An ellipsometer detects phase and amplitude changes in visible elliptically polarized light when it is reflected from the metal surface. The changes can be related to the metal oxide film thickness. This technique had previously been applied to the study of corrosion of metals immersed in a solvent [133]. Film formation, film dissolution, and surface roughening were observed.

When electrochemical measurements are carried out simultaneously with the optical measurements, changes in electrical potential, and pH can be determined while observing changes in metal oxide film thickness. Ritter [134] used this technique to study iron coated with a transparent cellulose nitrate coating and with various inhibitors either in or under the coating. At least two stages of activity were noted during immersion in 0.05N NaCl. During the first stage, oxygen, water, and Cl^- permeated the coating causing localized breakdown of the oxide layer originally present on the metal surface. Active metal sites were exposed and became anodic areas while less active areas became cathodic areas and the pH increased gradually. During the second stage, a large decrease in one of the ellisopmetry parameters was noted as the pH increased. This appeared to be due to both oxide film growth and surface roughening corresponding to active corrosion. Both the detection of corrosion and the kinetics of the reactions can be determined with this technique. This technique may be useful in evaluating the performance of inhibitors as well as surface preparation methods and pretreatments.

4.5.2.2 X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy has been used to identify modes of failure at the coating/substrate interface [80, 135, 136] as well as to characterize surfaces of substrates before application of a coating [80]. For example, examination of the surfaces after cathodic disbondment has shown that saponified primer coating was present on the metal substrate [136]. Hence, failure was described as cohesive since some polymer remained on the surface.

These techniques appear to be very powerful in examining the metal surface and the metal/coating interface. The instruments are expensive and technical knowledge and skill is required for using these instruments, designing experiments, and analyzing the results.

4.5.2.3 Infrared Spectroscopy

Infrared spectroscopy is used to examine the top surface of coatings. Hearst [137] examined the surfaces of several kinds of coatings before and after atmospheric, xenon-arc, and mercury-arc weathering using a dispersive infrared spectrophotometer. The effect of exposures on the coatings was an increase in carbonyl content. However, the changes he observed in the surface did not correspond to durability in service. This is not completely unexpected since it is generally felt that changes in the surface of coatings do not influence performance unless the coating becomes very thin.

Very small differences in chemical composition can be determined using a Fourier transform infrared spectrophotometer. It is possible to determine the combined or individual effect of both heat and moisture on coatings by subtracting spectra. It is also possible to obtain spectra at varying depths from the surface and observe the changes in composition as a function of depth. The potential of this instrument is very great.

5. SUMMARY AND CONCLUSIONS

Prior to reviewing the literature, four criteria were established for evaluating accelerated aging tests for coatings over steel substrates. The four criteria were predictability, reproducibility, distinguishability, and extendability; it was felt, at the time, all accelerated aging tests should satisfy these criteria. After a cursory review of the literature, it became apparent however, that these are not the criteria upon which currently used accelerated aging tests were based. The predominant philosophy of current procedures is that of association or correlatability as opposed to predictability. Tests based on correlatability are termed comparison tests.

The most common comparison tests found in the literature and reported by coating laboratories were the salt fog, cyclic or sequential weathering, high relative humidity, cathodic, and the Kesternich tests. The salt fog is the most frequently used. Although the stress conditions in the above vary from test to test, a certain commonality exists. Each of these tests is designed to subject the coatings to a set of stresses or a sequence of stresses thought to be similar to those encountered in service. Typically, multiple coatings are subjected to a test and some of these coatings are controls (controls are coatings having whose durabilities are well known). After exposure to the test conditions, the performance of each coating is assessed and ranked against that of the controls. Correlations are then made relating the accelerated test rankings against those of the same coatings exposed outdoors.

In assessing these comparison tests, several serious problems have been noted. First, results from the analysis are measures of association, not quantitative service life predictions. This makes it difficult to distinguish between the merits of different coatings, makes the results difficult to extend to other possible service environments, and requires reliable long-term performance data for the control coatings. Second, the rankings from different iterations of the same accelerated aging tests are seldom reproducible. Finally, poor correlations exist between accelerated and outdoor exposure data. The end result of these deficiencies is that users and manufacturers of coating systems tend not to rely on the results of their short-term tests; instead, they depend heavily upon long-term outdoor exposure results and use their short-term results as supporting evidence. The obvious result of this lack of confidence is that the qualification times for new coatings are very long.

In conclusion, existing short-term test methods do not satisfy the four criteria outlined in chapter 2. Consequently, the methods are not fully adequate for reliably predicting service life of coatings.

6. RECOMMENDATIONS

The ultimate objectives of any accelerated aging procedure are to form the basis for the selection of the best coating for a given environmental and operating condition and to provide a method for assessing durability improvement for a coating system. These objectives can best be met if quantitative service life predictions can be made from the short-term or accelerated test data. It has been concluded that current short-term tests do not meet the need for quantitative service life data and that accelerated aging procedures having a more scientific base are needed. Specifically, we recommend:

1. Use of accelerated test procedures in which stresses are varied singly, but at multiple levels; e.g., exposing specimens to 95 percent relative humidity at each of four temperature levels -- 30°C, 50°C, 70°C, and 90°C. Initially, the response of the coatings to constant stress conditions should be accessed. Once this is accomplished, cyclic changes in a stress should be examined.

2. Application of analytical tools for quantitative characterization of the materials and material degradation processes as a function of exposure time. Included in this are non-destructive evaluation procedures useful in quantifying coating degradation.

3. Application of mathematical methods capable of relating material response to a wide variety of environmental and operating conditions. Reliability theory, as outlined in Appendix A, seems suitable.

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Appendix A. Reliability-Based Accelerated Aging Tests

The objective of accelerated aging tests is to make service life predictions at normal operating conditions from tests in which one or more of the stresses typically encountered in-service are operated at levels higher than normal. In operating at these high stress levels, it is presumed that the degradation process is accelerated but that the predominant failure mechanism is the same as that occurring in-service. Methods are available to verify these presumptions.

Mathematically, the accelerated aging process is stated as follows. Let Σ denote a vector of stresses to which the material is expected to be subjected in-service. Let S be any one of these stresses such that

$$S_0 < S_1 < \ldots < S_i < S_i + 1 < \ldots < \ldots < S_m. \qquad (1)$$

That is, the i^{th} level of this stress is less severe than the $(i + 1)^{th}$ level of stress; S_0 symbolizes the level of stress at normal conditions, and S_m symbolizes the most severe level of applied stress yet still obeying the imposed assumptions.

If now n specimens are randomly selected from a nominal population and subjected to stress level S_i, then each specimen will fail at some time T. Assuming all n specimens are exposed simultaneously, then the observed times to failure are ordered; that is

$$t_1 < t_2 < \ldots < t_2 < \ldots < t_r \text{ where } r < n.$$

These ordered times to failure form an empirical cumulative distribution function. To this empirical cumulative distribution function a theoretical cumulative distribution is fit such that the probability that a specimen will fail at or before time t is denoted by

$$F_{S_i}(t; \theta_i) = P_{S_i}(T < t) \qquad (2)$$

where

$F_{S_i}(t)$ is the cumulative distribution function of the random variable T for specimens subjected to stress S_i;

$P\,(\cdot)$ is the probability of the event in parentheses;

θ_i is a parameter vector for $F_{S_i}(t)$; and t is a time.

Assuming that the form of $F_{S_i}(t)$ does not change from stress level to stress level (the parameter vector θ is allowed to change) and assuming knowledge of $F_{S_i}(t)$ is available at two different stress levels, e.g., the i^{th} and the $(i + 1)^{th}$ stress levels, then an acceleration of the degradation process has occurred if for all $t > 0$

$$F_{S_i}(t;\ \theta_i) < F_{S_{i+1}}(t;\ \theta_{i+1}) \qquad (3)$$

where i = 1, 2, ...; m-1. Given Eq. 3, a function, $\rho(t;\ S,\theta)$, exists relating the cumulative distribution function at any elevated stress level I to that at normal conditions.

$$F_{S_i}(t;\ \theta) = F_{S_0}(\rho(t;\ S,\theta)) \qquad (4)$$

where $\rho(t;\ S,\theta)$ is the acceleration function relating the parameter vector θ to applied stress S. Commonly, the acceleration function is assumed to be independent of exposure time; that is,

$$\rho(t;\ S,\theta) = \Psi(S,\theta) \cdot t \qquad (5)$$

Examples of $\Psi(S,\theta)$ include the Arrhenius model, the Eyring model, the inverse power law; and the William, Landell, and Ferry type superpositions. Assuming the inverse function $F_{S_0}^{-1}(t;\theta)$ exists, then $\rho(t;\ S,\theta_I))$ can be determined by

$$\rho(t;\ S,\theta) = F_{S_0}^{-1}(F_{S_I}(t;\theta_I)). \qquad (6)$$

It is the mission of accelerated aging programs to determine the acceleration function $\rho(t;\ S,\theta)$. Knowledge of this function, along with any cumulative distribution function at an elevated stress level $F_{S_I}(t;\ \theta_I)$ permits estimates of the cumulative distribution function at the normal stress level, $F_{S_0}(t;\ \theta)$, (see eq. 4).

The obvious advantages of this procedure are that once $\rho(t;\ S,\theta)$ is known, then drastic reductions in the accelerated aging program can be made by conducting accelerated aging tests at the maximum allowable stress S_m obeying the assumptions. Large savings in time are also realized since estimates of $F_{S_0}(t;\ \theta)$ can be made without observing all of the failure times. Perhaps the most important advantage of using this procedure is that coatings having like performance under similar conditions can now be grouped into performance classes, hence, any improvement on one coating system from the class may apply to all coatings in the class, thus effecting great savings in research.

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11. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)*

This report presents the findings of the first of a two-phased study to aid the Federal Highway Administration in evaluating and selecting protective coatings for steel. The objectives of the study are to review existing short-term test procedures for selecting coatings, and to discuss analytical measurement techniques for characterizing coating systems and for monitoring coating degradation.

In assessing current accelerated aging testing procedures, several deficiencies became apparent. These included the reported lack of reproducibility in the rankings for different iterations of the same short-term test and the lack of correlatability between the rankings of short-term laboratory and long-term outdoor exposure tests.

It was concluded that, at the present time, coating manufacturers and users do not depend heavily on accelerated test results for making durability assessments. Instead, durability assessments are based on outdoor exposure performance. Recommendations are made to design future short-term test procedures using reliability theory.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

accelerated aging tests; coatings; corrosion; time to failure; predictability; reproducibility.

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