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An Investigation Conducted by
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Steel Structures Painting Council

NCEL WORKSHOP ON ACCELERATED TESTING OF PAINTS

Abstract An NCEL workshop, organized, conducted, and evaluated by the Steel Structures Painting Council, examined performance evaluation and durability of protective coatings for industrial structures. The workshop addressed three principal areas within the broad subject of coatings durability, namely:

- Accelerated Testing
- Statistical Methods and Evaluation
- Electrochemical Testing of Coatings

The findings are discussed in terms of the overall procedure for evaluating coating performance, which is divided into three mains aspects: inducing degradation, evaluating degradation, and design and interpretation of results.

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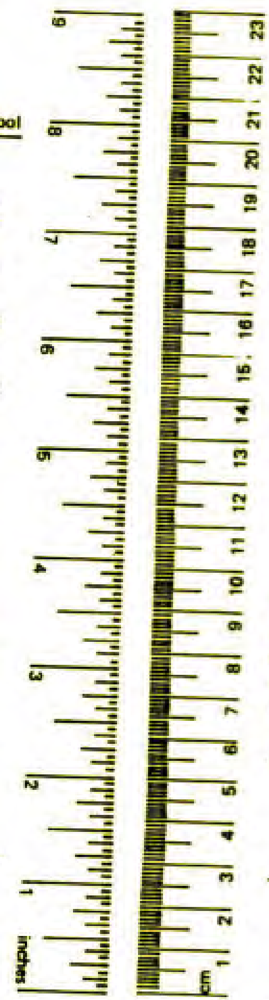
METRIC CONVERSION FACTORS

Approximate Conversions to Metric Measures

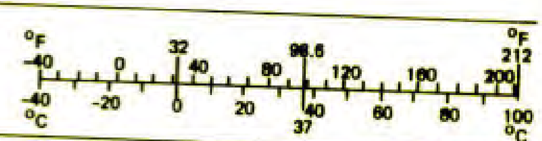
Symbol	When You Know	Multiply by	To Find	Symbol
		LENGTH		
in	inches	*2.5	centimeters	cm
ft	feet	30	centimeters	cm
yd	yards	0.9	meters	m
mi	miles	1.6	kilometers	km
		AREA		
in^2	square inches	6.5	square centimeters	cm^2
ft^2	square feet	0.09	square meters	m^2
yd^2	square yards	0.8	square meters	m^2
mi^2	square miles	2.6	square kilometers	km^2
	acres	0.4	hectares	ha
		MASS (weight)		
oz	ounces	28	grams	g
lb	pounds	0.45	kilograms	kg
	short tons (2,000 lb)	0.9	tonnes	t
		VOLUME		
tsp	teaspoons	5	milliliters	ml
Tbsp	tablespoons	15	milliliters	ml
fl oz	fluid ounces	30	milliliters	ml
c	cups	0.24	liters	l
pt	pints	0.47	liters	l
qt	quarts	0.95	liters	l
gal	gallons	3.8	liters	l
ft^3	cubic feet	0.03	cubic meters	m^3
yd^3	cubic yards	0.76	cubic meters	m^3
		TEMPERATURE (exact)		
°F	Fahrenheit temperature	5/9 (after subtracting 32)	Celsius temperature	°C

*1 in = 2.54 (exactly). For other exact conversions and more detailed tables, see NBS Misc. Publ. 286, Units of Weights and Measures, Price $2.25, SD Catalog No. C13.10:286.



Approximate Conversions from Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
		LENGTH		
mm	millimeters	0.04	inches	in
cm	centimeters	0.4	inches	in
m	meters	3.3	feet	ft
m	meters	1.1	yards	yd
km	kilometers	0.6	miles	mi
		AREA		
cm^2	square centimeters	0.16	square inches	in^2
m^2	square meters	1.2	square yards	yd^2
km^2	square kilometers	0.4	square miles	mi^2
ha	hectares (10,000 m^2)	2.5	acres	
		MASS (weight)		
g	grams	0.035	ounces	oz
kg	kilograms	2.2	pounds	lb
t	tonnes (1,000 kg)	1.1	short tons	
		VOLUME		
ml	milliliters	0.03	fluid ounces	fl oz
l	liters	2.1	pints	pt
l	liters	1.06	quarts	qt
l	liters	0.26	gallons	gal
m^3	cubic meters	35	cubic feet	ft^3
m^3	cubic meters	1.3	cubic yards	yd^3
		TEMPERATURE (exact)		
°C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature	°F



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An NCEL workshop, organized, conducted, and evaluated by the Steel Structures Painting Council, examined performance evaluation and durability of protective coatings for industrial structures. The workshop addressed three principal areas within the broad subject of coatings durability, namely:

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- Statistical Methods and Evaluation
- Electrochemical Testing of Coatings

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I. EXECUTIVE SUMMARY

An NCEL workshop, organized, conducted, and evaluated by Steel Structures Painting Council, examined performance evaluation and durability of protective coatings for industrial structures. The workshp addressed three principal areas within the broad subject of coatings durability, namely:

- Accelerated Testing
- Statistical Methods and Evaluation
- Electrochemical Testing of Coatings

The findings are discussed in terms of the overall procedure for evaluating coating performance, which is divided into three main aspects: inducing degradation, evaluating degradation, and design and interpretation of results.

Methods for Inducing Degradation

The essential components of a test to simulate exterior exposure environments are moisture, temperature effects, UV radiation, salt and other contaminants, and cyclic variations of these factors. Thus, cyclic accelerated tests are inherently superior in principle to conventional accelerated tests such as salt spray. Several proprietary cyclic test have shown great promise in increasing numbers of experiments. More definitive evaluation, however, is needed to determine the general suitability of this approach. A major goal is a standardized test procedure.

Exterior exposure tests on outdoor fences or actual structures are still considered the most reliable coating performance evaluation indicators, in spite of significant variations within and among test sites. New approaches have been developed for eliciting information in a shorter period of time than would be required for conventional coating failure. One innovative approach is to accelerate the exterior degradation rate by periodically spraying salt water or acid rain on the panels. Again, though promising, substantial additional testing is needed to determine quantitative benefits and possible limitations of this method.

Evaluating Degradation

Conventional evaluation by visual methods is subjective and observable only at advanced stages of degradation. Numerous evaluations and characterization techniques have been developed based on electrical, mechanical, chemical, and spectroscopic properties of coatings systems. Effective practical evaluation techniques should ideally possess the following attributes:

- Portable and easy-to-use equipment.
- Rapid and non-destructive measurements.
- Reliable and repeatable measurements.
- Provide early detection of degradation
- Type of degradation detected should be a valid indication of failure.
- Reasonable cost.

Based on these criteria, electrochemical impedance spectroscopy (EIS) is considered the most promising technique for evaluating protective coatings. Field versions of EIS are being developed and evaluated. EIS measurement is fast and reliable, and can be non-destructive. Equipment is moderate in cost ($15,000 to $50,000 for a complete setup) and can be operated by a technician under the supervision of an electrochemist. The method is able to detect certain early signs of degradation. An important question remains, however, about the true significance of EIS data, although some criteria have been established. For example, the break point frequency and the magnitude of impedance can be indications of whether a coating is good or poor.

EIS is apparently not suitable for permeable coatings such as latex, or those with pores or defects. Also, the signal is very sensitive to film variability. Relatively little work has been done on EIS for protective coatings, but the literature is growing and the potential seems enormous.

Experimental Design & Analysis

The last few years have seen a few new approaches for designing and analyzing experiments. Most notable is a procedure, reliability analysis, which uses large replicate sets (20 or more) to derive failure distribution curves and propose degradation models of coatings.

Most coating evaluators, however, have done a very poor job in statistical design and analysis. Major emphasis needs to be placed on better use of standard statistical procedures.

Specific areas addressed regarding experimental design and analysis include test panel design, characterizing exposure environments, laboratory and field evaluation techniques, and reference standards for coatings.

Major variables affecting coating performance at a test site are: level of contaminants (i.e., salt or sulfur dioxide), ultraviolet, temperature, humidity, and configuration. Standard tests are available or are being developed for parameters such as corrosivity by wire-on-bolt specimen, airborne chloride by candle method, and time of wetness.

Innovative field evaluation techniques include grid method for quantitative visual evaluation and infra-red and visual imaging. Improvements are sought in distinguishing rust from rust staining and examining underfilm phenomena.

An important need of industry, endorsed by all three work groups, is that of standard reference coatings. These would consist of coating materials which could be reproducibly formulated and which have known performance histories. They would be used as benchmarks for evaluating new coating materials by manufacturers and end-users.

A theme underscoring many of the technologies and test methods addressed by the workshops is the need for non-destructive testing and evaluation (NDT) of coating performance. As this topic cuts across all three workshop sessions, and is an inherent component of the existing Navy program of coating research, an entire chapter is devoted to the subject of NDT methods of coating degradation assessment. NDT methods development particularly in the areas of thermal image analysis and field use of electrochemical impedance spectroscopy was strongly recommended

Recommendations for Future Projects

Top-rated projects based on a consolidation of the three work groups are as follows:

- Discourage indiscriminate use of salt fog testing.

  Better procedures, including a battery of accelerated tests, careful use of cyclic testing, and utilization of exterior testing, along with other tenets of good practice, would result in considerably improved results and savings of money compared to the currently over-used and misused salt fog test.

- Develop and implement standard reference coatings for industrial maintenance applications. The use of standard reference coatings would provide uniform materials against which to test new products and provide a "level playing field."

- Assess and evaluate cyclic test methods. Based on the favorable reports of cyclic accelerated tests, there is a need to determine the validity and appropriate test procedures.

- Guide for Coating Performance Testing. This would provide coating evaluators direction on testing, evaluating, and procuring paints, and provide improved results and lower overall costs.

- Standard procedure for accelerated laboratory and field testing. In order to promote greater use of these methods, ASTM-type standards need to be developed.

- Field device for electrochemical impedance spectroscopy. To take full advantage of this technique, a field portable device must be developed and evaluated to determine best means for performing AC impedance on coated industrial structures.

- Improved field imaging procedures. This project would build on the innovative work done previously to establish guidelines on equipment, and measurement and analysis of data for these techniques.

- Develop standard methods for EIS on coated metals. In order to make this technique more accessible to coating laboratories and the results more meaningful, a standard procedure is needed for measuring and calibrating AC impedance.

Source of Funding

To accomplish the projects enumerated above, and effect major improvements in the science and practice of performance testing will require a coordinated industry effort in the next 5 to 10 years and funding support at approximately $2 to $5 million. To help generate these funds, a coating performance evaluation consortium should be established to bring together government agencies, manufacturers and suppliers, end-users, and technical and trade associations which have a stake in the performance of industrial maintenance coatings.

II. PURPOSE AND STRUCTURE

A. INTRODUCTION & BACKGROUND

Protective coatings are a major concern of owners of military, public, or private structures and facilities. They represent a significant portion of the cost of new structures, and an even greater proportion of the cost of maintaining those structures.

The cost of protection has been increasing dramatically in the last several years. The major factor has been restrictions and elimination of conventional coating materials, requiring owners to utilize very recent, untested coating systems on critical structures. Other factors affecting the increase in costs include the aging of the facilities as part of the national infrastructure and the lack of proper maintenance in the past.

Traditionally, coating systems are developed and evaluated and introduced over a period of years. The new environmental regulations and the need for better-performing systems has made it necessary, however, to condense the development and evaluations to a much shorter period of time. Thus, a key need for owners of these facilities is valid techniques for coating performance evaluation. Protective coatings are typically expected to last 10-20 years before requiring maintenance. Therefore it is imperative that facilitiy owners along with manufacturers have available short-term methods for evaluating the long-term durability of these systems.

Historically, the coatings industry has not had available adequate means for short-term or accelerated evaluation of coatings. This deficiency has been widely publicized and recognized. Organizations like Naval Civil Engineering Laboratory, Federation of Societies for Coatings Technology, and Steel Structures Painting Council have identified this problem and initiated various programs to address them. NCEL has been investigating this problem for 5 years or more and has become one of the major sources for developing and implementing new technological developments.

B. PURPOSE OF WORKSHOP

Considerable efforts have been expended by the above groups and related organizations such as National Institute for Standards and Technology, paint manufacturers, raw material and equipment suppliers to develop improved techniques and procedures for evaluating coating performance and durability. These activities have addressed diverse topics and approaches including fundamental studies of mechanisms of coating degradation, statistical approaches to modeling and failure analysis, new devices for characterizing and evaluating coatings, and sophisticated laboratory test chambers. It has become evident from a scanning of the technical literature that considerable progress has been made in several of these different projects. There has been, however, little effort to coordinate these programs or to identify approaches for how these users and manufacturers can take advantage of these developments.

NCEL, recognizing the benefits to be derived from greater communication and coordination of the technology, issued an RFP to organize a workshop. The workshop objectives were severalfold:

- Review and assess current research and development in coating performance evaluation and durability.
- Identify key areas where recent and anticipated breakthroughs could improve the ability to predict performance.
- Identify and delineate R&D needed and propose approaches for accomplishing.
- Organize and assemble the technology for performance evaluation and durability.

Based on earlier projects, NCEL had identified three key areas of technology which warranted in-depth analysis. These are:

- Accelerated testing of coatings
- Statistics and prediction modeling.
- Characterization techniques.

For each of these areas the goal was to identify and discuss the primary technical issues, to assess the current status of the technology, and to identify areas and approaches for future development work.

C. ORGANIZATION OF ACTIVITIES

The project to organize and implement these workshops was awarded to SSPC in August 1990. The SSPC scheduled the workshops as part of a major industry-wide conference on "Coating Performance Evaluation and Durability." The conference included the following components:

1. Two full-day concurrent tutorials addressing

   "Developing a Coating Performance Evaluation Program"
   "Advances in Coating Characterization Technology"

   The tutorials are extended lectures given in a classroom setting to provide in-depth information on specialized topics.

2. A two-day seminar of technical papers and discussion

   Seminar sessions included the following:
   - Session 1: Novel Approaches for Evaluating Coatings
   - Session 2: Accelerated Laboratory & Field Testing
   - Session 3: Statistical Methods & Evaluation Techniques
   - Session 4: Electrochemical and Other Characterization Methods

This part of the program was open to all attendees. It provided data and information on a very broad range of topics relating to evaluation of coatings.

3. A concurrent exhibit of products and services for the industry, including testing equipment, technical information services, and materials. The exhibits facilitated informal interactions among the conference attendees.

4. One and one-half day workshop divided into three working groups as follows:

- Accelerated Testing of Coatings
- Statistical and Evaluation Techniques
- Electrochemical Corrosion Techniques for Coatings

There were several benefits for co-scheduling these events. The spectrum of topics could be presented to provide a broad overview of the technology. Moreover, by presenting these papers at the seminar, the Work Group times could be devoted to discussions rather than lectures or presentations. Finally, most of the workshop participants had another reason for attending and did not require financial support.

Workshop attendance was by invitation only, in order to limit the size of the workshop and to provide a balanced group for discussion.

For each Work Group, three individuals were selected as follows:

- Leader: responsible for keeping discussion moving and eliciting a broad input.
- Instigator: responsible for bringing up diverse points of view and playing "devil's advocate"
- Tracker: responsible for keeping record of discussions and insuring that discussions keep essentially to subject and that objectives are achieved

In addition, several individuals were designated as "floaters" to maintain contact among the groups.

Also, a series of "Issues and Questions" was prepared for each group to stimulate discussion and provide a basis for their recommendations.

The work groups met together initially to review the general protocol and objectives and also at the conclusion to review the individual group findings and discuss areas of common concern.

Following the workshops, SSPC in conjunction with the group coordinators, prepared a summary of the findings and recommendations. This was circulated to the work group members for comment and fine-tuning. These findings and recommendations were presented to NCEL in August 1991, where SSPC was provided additional recommendations for preparation of the final report.

III. DISCUSSION OF WORKSHOP FINDINGS

Performance Evaluation and Coatings Durability are the subject of the report and the workshop. It is a broad and complex subject. The problems can be expressed succinctly but the approaches are very diverse, encompassing the deficiencies in understanding mechanisms, in developing and applying new technology, and in promoting and utilizing existing technology. The Workshop is considered part of a continuing industry process to evaluate and assess existing technology. An important goal of this process is to determine directions for future efforts and to initiate and encourage specific implementation projects.

The protective coatings industry has long recognized the deficiencies of techniques and procedures for evaluating performance. Recently, restrictions of many currently used materials and techniques, tightening budgets for maintenance and new construction, and the growth in new materials and techniques have intensified the need and interest in establishing and utilizing more reliable procedures.

Within the broad subject of improving performance evaluation, the Workshop focused on three specific areas: accelerated testing, statistical analysis and evaluation, and electrochemical testing. These three topics by no means cover the entire subject of performance evaluation. The three are not even directly comparable, as will be discussed subsequently. However it was felt necessary to provide some external focus in the workshops. This focus helped to attract the necessary expertise and to force the participants to keep within a defined scope. The treatise will review the discussions in each workshop within the larger context of performance evaluation.

Performance evaluation of coatings is needed by coatings manufacturers as well as coatings users. The manufacturer of coating materials must be able to demonstrate that the product can provide its intended service life or function. The owner or specifier must also be convinced that the coating performs its intended function. In addition, the owner is concerned about quality control to verify that the product furnished is the same as that product originally tested.

It is useful to divide performance evaluation test procedures into four components: preparing specimens, inducing degradation, evaluating degradation, and analyzing results. In this discussion, the first and last will be combined and labeled as "designing and analyzing experiments." These three aspects will be discussed in relation to the three workshop topics.

A. METHODS TO INDUCE DEGRADATION

1. Accelerated Laboratory Testing

The need for rapid, reproducible, yet representative means for inducing degradation is a major goal of accelerated testing. The group on cyclic accelerated testing focused on the value and validity of using various cycles to simulate the exposure conditions and the degradation which occurs under "natural exposure."

It has long been recognized that no artificial exposure can entirely reproduce even an idealized exterior exposure. Therefore, certain aspects must be compromised, e.g., combinations of exposures, certain low-level pollutants, speed of cooling and drying (time of wetness).

Proponents of cyclic accelerated tests have identified several specific objectives:

a. To determine if cyclic tests provide a reasonable simulation of exterior exposures.

b. To identify the principal variations and parameters of cyclic testing.

c. To identify the appropriate tests to corroborate preliminary conclusions of the merits of cyclic testing.

d. To determine the overall value of cyclic accelerated testing compared to conventional testing and compared to the needs of the protective coatings industry.

Conclusions regarding accelerated testing derived from the workshop are as follows:

a.. Current methods (principally salt fog) are entirely inadequate for evaluating coating performance and their use should be discouraged.

b. To simulate an exterior environment, one should include the following parameters as a minimum:

- moisture
- temperature effects
- ultraviolet radiation
- salts or other contaminants
- cyclic variations of above

c. Cyclic corrosion tests have shown great promise in preliminary evaluations by groups in the U.K. and the U.S. However, substantial additional evaluation is needed to determine the general suitability of these methods and to establish test parameters and recommended cycles. A proposed industry testing program is included under the Recommendations.

d. An important goal of the industry should be to develop one or more standard procedures, using cyclic testing. This would provide a large number of users with a valid means to compare alternative coatings systems.

2. Exterior Exposure Testing

Exterior exposures for performance evaluation also have disadvantages. Substantial variations occur in the exterior environment from one location to another and at different times within one location. In addition, the time for degradation for well-formulated high-technology coatings is quite lengthy, often 5 years or more.

Some discussion was held regarding the variability of the exterior exposure testing. A seminar paper presented by Will Kirk identified means for characterizing exterior environments. Major parameters are time of wetness, chloride level, average temperature, distance from pollution sources, and types of metal. It was pointed out that sophisticated means of characterizing environments are available but are not widely used by the protective coatings industry.

An important conclusion is that because of seasonal and year-to-year variations, results of short-term exterior exposures (one year or less) should be viewed with caution. Very little work has been performed on the effects of varying external environments, on performance evaluation, and on relative ranking of corrosion protective coatings. (This is contrasted to the subject of appearance properties of automotive and coil coatings for which a considerable amount of work has been reported).

At the seminar, SSPC reported on work comparing the salt fog test with short- to medium-term field exposures. It was demonstrated that an exterior exposure tests of 2 years was markedly superior to salt fog testing in predicting the ranking of a series of coatings exposed under long-term exterior conditions. The results are consistent with the findings of Kirk of LaQue. Interestingly, 2 years is also the minimum time period typically recommended for evaluating gloss, color, and other appearance properties in exterior testing for automotive and coil coatings, often done at Florida or Arizona sites. A more detailed discussion of non-destructive testing is presented in Chapter IV.

3. Accelerated Exterior Exposure Testing

A related method, which combines some of the attributes of accelerated testing and exterior exposure testing is that of accelerated exterior testing. This is a procedure, reported previously, in which test specimens are exposed at exterior facilities and periodically sprayed with salt water, acid rain or other aggressive species.

Other variations include enhancement of solar radiation, periodic immersion or exposures to high levels of SO_2. Unfortunately, the group did not devote much discussion to this subject, probably due to lack of specific experiences and lack of time.

A recent article in *JPCL* described an experiment in which periodic spray on exterior panels resulted in a rapid degradation rate of coatings applied to hand-cleaned steel in a marine environment. Significantly, the coating degradation occurred almost as rapidly as in salt fog, with greatly improved accuracy, according to the authors.

This method definitely merits further study. It would be of great interest to use some of the statistical evaluation techniques (i.e., using large numbers of replicates) to determine the enhancement factor for these sprays. Variables include the frequency, type, and concentration of sprays, along with the other types of acceleration factors. Some limited work has been undertaken by SSPC, with preliminary reports expected to be available in 1992.

B. EVALUATING DEGRADATION

Conventional approaches to evaluating coating degradation involve recording and tracking of visual evidence of physical defects, such as rust, blistering, fading, cracking, and undercutting at the scribe. These methods suffer some substantial disadvantage including:

- Non-quantitative and subjective
- Only can be observed at relatively advanced stages of degradation

Numerous other characterization methods, including both destructive and non-destructive, have been developed and evaluated over the last two decades. These include electrochemical, mechanical (torsion braid, cantilever beam), physical methods (infra-red thermography, acoustic emissions, free-volume microprobe), different types of spectroscopy (nuclear magnetic resonance, electron spin resonance, infrared spectroscopy) and related methods including scanning elelctron microscope (SEM) and Auger spectrometry. These methods examine the metal surfaces, the bulk film, or the interfaces between the metal and the coating or the coating and the environment. Most of these methods have not been developed or evaluated for industrial protective coatings, but rather for automotive or coil coatings, or coatings in general.

Each group or individual technique could be the subject of an entire workshop on its own. Thus detailed discussions on these techniques was beyond the scope of the current workshops. Several of these techniques were described in the tutorial portion of the conference to provide attendees with at least an idea of the existence and typical uses of these techniques.

The following are considered the most important requirements for an evaluation or characterization technique for corrosion protective industrial maintenance coatings:

1. Requirements for Evaluation Equipment

- Portability of Equipment

Industrial maintenance coatings are used on structures such as bridges, storage tanks, and electrical utility structures. Coatings are typically tested on small metal panels which are exposed or placed on structures or in laboratory chambers. The evaluation/characterization of coating performance is ideally conducted at or near the location of the exposure test. Thus, if it is desirable to monitor the coating performance on the structure, the device should be capable of being brought to that structure to make the measurement.

Current visual methods of evaluation are capable of being utilized on any configuration or structure. Most characterization methods, however, are not very portable and require the specimens to be brought to the testing device. These methods cannot even be readily used at a test fence exposure site. A technique which could be brought to the field (e.g., infra-red or optical camera) would have great utility.

Also of importance is the nature and size of the specimen required for testing. Coating evaluators typically use 4- by 6-in (100- by 150-mm), 3- by 6-in (75- by 150-mm), or 4- by 12-in (100- x 300-mm) metal panels for both test fences and laboratory chamber tests. The evaluation techniques will have a definite advantage if these types of specimens can be evaluated directly. If not, then special specimens must be prepared, which could greatly increase the time and effort for testing and decrease the utility of the method for most users.

- Rapid Measurement

The quicker the test, the more specimens can be measured in a given time. A rapid test allows evaluators to include more replicates in the experiment and to perform more tests on a given specimen. A rapid test is also a great advantage when specimens are being removed from a chamber or retrieved from a test rack.

- Costs

There are several costs that must be considered, including capital costs, operating costs, and maintenance costs. Equipment which requires an investment of several hundred thousand dollars will be limited to a small number of research institutions, large manufacturers and raw materials suppliers, and very large end-users. Equipment priced under $100,000 could be in the range of many small to medium-sized paint companies and materials suppliers, depending on the percieved value of the equipment. However, it should be recognized that currently used equipment for coating performance evaluation ranges in price from $5,000 to $15,000.

- Operation of Equipment

This item is related to the cost and the speed of measurement. The qualifications and training needed to operate and maintain equipment and to interpret the data vary widely among evaluation techniques. Also important is the time required to set up the equipment and allow it to equilibrate or be prepared for a measurement. Another factor is the proportional down-time requiring vendor-supplied services.

- Reliability and Repeatability of Measurement

An axiom of scientific experimentation is the necessity of repeating measurements with an acceptable and measurable precision. Unfortunately, for commonly used visual methods, precision is often not determined or recognized in the interpretation of the results. For many of the newer characterization methods, repeatability for a particular device is quite high. However, there may be variations from day to day or week to week based on systematic errors. Often, in addition, there is little or no data on reproducibility among laboratories or between similarly built devices. A related matter is the availability of standard reference materials for calibrating characterization methods.

2. Early Detection of Degradation

An important requirement of the method is that it be capable of detecting degradation at an early stage (before these changes are manifest visually). Otherwise it would have little advantage over currently used visual methods (Note: some advantage would still be gained from a technique which gave quantitative and reproducible evaluations over the same time frame as current visual methods).

3. Valid Indicators of Failure

Probably the most important criterion for an evaluation technique is that it provide a valid indication of the ultimate degradation leading to failure of a coating system.

The practical goal of any method developed and evaluated is to establish a technique which will benefit the facility owner and the manufacturer. The facility owner needs to determine when the coatings will fail (no longer able to serve its intended function) to make decisions about repainting or replacing the coating system. The manufacturer needs the same information to determine the best formulation for the specific end-use.

Thus, just because a method is capable of detecting degradation at a fairly early stage, it does automatically follow that the method can predict failure. The mechanism of degradation and failure are extremely complex. Loss of a property such as flexibility or change in cross-linked density may be highly predictive of failure for one type of coating but insignificant for another. Unfortunately, the coatings industry has undertaken relatively little basic research on such subjects (see discussion about additional research needed). Consequently, the primary procedure for determining whether early degradation results in failure are empirical comparisons and correlations. Thus, work on examining and characterizing early degradation must at some point be accompanied by exposing those coatings in conventional exposure locations for a long enough time to produce macroscopid failure. This would enable the researchers to ascertain the relation between early degradation and coating system failure.

4. Non-Destructive Testing

To monitor performance as a function of time, one can periodically remove the specimen from the chamber. To avoid disrupting the tests, the characterization should be performed quickly, preferably within a couple of hours or less. Otherwise the measurement itself could affect the performance. It is also important to avoid any significant stress (e.g., heating) during the evaluation. A non-destructive technique is preferred, otherwise the evaluation would require large numbers of replicate specimens to derive information of performance versus time. A non-destructive test is also required for any testing to be performed on a structure at a test fence (see Chapter IV).

C. MERITS OF ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS)

As corrosion is an electrochemical process, the onset and progress of the reaction should be amenable to electrochemical investigation. Initially, researchers measured DC polarization and film resistivity. However, in recent years, electrochemical impedance spectroscopy (EIS) has become the dominant and preferred method. It is considered a rapid, reproducible, and reliable measure of the basic electrochemical properties.

An examination of EIS using the criteria described in Section B above is as follows:

- Early Detection of Degradation

EIS detects electrical properties (impedance properties, breakdown frequency) which have shown very early changes in various coating systems. There is general consensus that an impedance of greater than 10^7 ohms indicates good performance, while a value of less than 10^5 ohms indicates significant film breakdown. Of course, these are generalizations, and do not apply to all films or exposures. They do suggest that with additional study and development, certain electrochemical properties can be the basis for more precise prediction.

- Degradation Leads to Failure

This question is more difficult to answer because only a small amount of work has been performed. Some evidence shows that loss of resistivity or impedance leads to blistering and corrosion. Establishing this connection is one of the great challenges to EIS (or any other) experimental technique. It will require evaluation of different generic coatings over various times, considering a number of variables, such as differences within a generic class, examining defective and defect-free coatings, and evaluation in a number of exposures (e.g., accelerated testing and exterior exposure)

- Rapid Measurement

EIS measures response over a range of frequencies. Measurements at high frequencies are very rapid, while those at lower frequencies can take hours or days. The favored approach is one which primarily uses high and middle frequencies, with the loss in precision or accuracy due to lower frequency cutoff a trade-off needed to make this technique more practical.

- Portability and Size of Equipment

Traditionally, EIS and other electrochemical measurements utilize equipment designed primarily for the laboratory, including potentiostats, frequency generator, frequency analyzer, computer, and test cell. Based on work discussed at the workshop, it is evident that equipment can be made for field use (e.g.,on a structure). Such a device has been marketed by a Japanese firm. Here again, some trade-off would likely be needed regarding the number of frequencies and amount of noise generated. The clear consensus of the EIS working group is that the techniques are available today but require additional development. These development efforts will focus on improving the precision, accuracy, ease of operation, and reduction of cost. In addition, industry must start generating and analyzing the data to come up with appropriate techniques.

- Cost

Present cost for a full set-up is estimated at $15,000 to $50,000. Though not insignificant, this cost by no means prohibitive for a group interested in coating performance evaluation. It is observed that the industry spends considerable sums on routine laboratory and field evaluations that have provided very little useful data to the sponsors.

- Operation of Equipment

The design and set-up of the equipment will likely require an electrochemical professional. The operation, maintenance, and routine collection of data can be performed by a trained technician, one not necessarily highly experienced in electrical circuitry or electrochemical testing. The consensus of the group was that an electrochemist was still needed for interpreting data and to modify sample procedures and experimental procedures as necessary. This situation may change as equipment becomes more standardized and standardized procedures are written for how to conduct the experiments.

- Reproducibility and Reliability of the Measurement

EIS is considered to be an extremely reproducible technique based on the equipment itself. The signal is highly sensitive to minor variation in the film itself (e.g., film inhomogeneities, presence of pores, thickness variations). This variability must be considered when establishing reference samples for use in proposed ASTM standard procedures. The same variabilities could also be a factor in determining the number of samples to use and the number of measurements required for a sample.

Based on the above criteria, EIS is judged to be the most useful electrochemical technique for evaluating coatings for exterior exposure.

D. EXPERIMENTAL DESIGN AND ANALYSIS

1. General

Experimental design and analysis is a well-studied field of engineering and mathematics. The coatings industry has not followed good practice, however, in these areas. Most coating performance evaluation experiments are poorly designed, with little regard for statistical significance.

Often the goal of the study is not stated in objective terms. Rather, experiments are frequently designed to prove the superiority of one product or technique (the sponsor's) over another (the competitor's) which can bias the results. A *research program* may have as its overall goal that of developing or demonstrating superior performance, but a *product evaluation* should be performed in an objective manner without bias and without knowledge of the identity of the specimens being tested.

The analysis and interpretation of data is equally deficient in the coatings industry. Use of statistics is the exception, with 90% of respondents to a recent survey indicating no use of statistics at all. This may be partially attributed to the poor experimental designs which do not build statistical validity in the first place. When statistics are reported, they are often misused, with further analysis showing a bias or lack of statistical significance of the results.

For the majority of the experiments, coatings are rated or ranked and selected or discarded based on non-statistical methods. There are often no definite criteria for when coating A will be judged better than coating B or when it is determined that there is insignificant data to do so. Adding to the problem is the general approach for utilizing a single replicate for each coating system in a given exposure. This approach is extremely risky because of the inherent variability of coating behavior as has been demonstrated in recent publications.

Within the last several years, there have been some articles published on new design and statistical and analytical approaches for coatings evaluation. Mostly these have involved applying methods used in other industries to the protective coatings industry.

T. Rehfeldt of Sherwin-Williams presented a paper at the SSPC seminar on a statistical approach to calibrate the rating scheme for non-linear measurements. This procedure would require an initial calibration using six or more judges to establish the rating criterion, but would go a long way to avoiding systematic errors in rating quantities such as rusting or cracking.

One new innovative approach has been presented for design and analysis of coating evaluation experiments. The technique, known as reliability life analysis, has been promoted and pioneered primarily by Jon Martin of NIST, who presented his ideas at the tutorial preceding the workshop. Briefly, this method involves using large numbers of replicates to develop the statistical distribution of failures based on a defined failure criterion of a given property. The very concept of failure distributions is itself a major advance. It recognizes the variability of coating degradation and allows more meaningful comparison of coatings or conditions. Beyond this, Martin has used this technique to propose models and mechanisms for coating degradation and failure.

Major improvements in the quality of coating testing and evaluation can be achieved by better use of available practices. Accordingly, the work group on statistical methods focused on these factors.

2. Experimental Design

A good overview of an experimental design for a coating evaluation program was given at the tutorial on Developing a Coating Evaluation Program, presented by SSPC. Additional information, including an outline is available from the authors of this report. Another important area concerns the number, type, and size of panels. A single replicate is never adequate, but there may be difficulty in using the 15 or so required by statisticians. Five or six replicates may be a reasonable compromise for practical considerations.

The group recommended that both flat areas and structural configurations (e.g., edges, corners) be utilized when evaluating coatings for these types of structures. Scribing to produce deliberate damage is often needed to produce earlier degradation results. However, the scribe can be a source of non-uniformity and should be prepared very carefully. Other variables that can be introduced in the coated panel include the surface preparation (e.g., type of abrasive, possible contaminants) and application methods.

3. Characterizing Environment

The group reviewed the major variables affecting corrosion rate and coating performance. These include the levels of chloride, sulfur dioxide and UV radiation, temperature, humidity, and general weather factors. Surface factors include the presence of salt or other contaminants, and the time of wetness (shown to have an important effect on corrosion rates).

There are numerous methods and standards for characterizing the environmental variables. A relatively new method, which has not been used in the coatings industry, involves measurement of loss of metals from a wire attached to a bolt. ASTM is developing a standard test around this method, and has previously developed standards for atmospheric chloride, time of wetness, and corrosion rates of bare metal. Standards are still under development for measuring atmospheric SO_2, and surface salts.

4. Laboratory and Field Evaluation Methods

The group reviewed some of the parameters and methods for evaluating performance of coatings, which is an important part of the experimental design. The emphasis was on methods that can be used in the field as well as in the laboratory. The current standard visual methods (e.g., ASTM D 610, D 714, and D 1654) were described. Because of the lack of uniformity of degradation of structures, techniques are needed to apply visual methods to large areas. One approach is to divide the area into sections and rate each section with an overall or weighted average produced. Also available are grid methods, which divide the test area into a large number of very small areas, and some recently developed methods from ASTM based on shipyard inspection.

Problems in distinguising rust from rust staining were also discussed as a possible source of error in field evaluation. Of special concern is the effect of lighting and other variables when rating panels or evaluating the appearance. Another major source of variability is the operator. It was recommended that industry look into the need to certify or qualify evaluators to ensure that they are interpreting the standards correctly and provide consistent results. Techniques for investigating underfilm phenomena were briefly reviewed. It was pointed out that this almost always requires a destructive test. One exception is infra-red thermal imaging, which allows detection of blisters or rust spots underneath the film. This method has also been pioneered by NIST. It could become more widely used because of reductions in costs of software and hardware used to obtain and analyze data. Typically coatings are removed from the substrate using methyl ethyl ketone or other strong solvents, and the underlying film evaluated by visual means. The group suggested developing a standard for stripping the coating to improve validity of results.

5. Reference Standards

An important need of the industry addressed by all three groups is that of reference standards for coating evaluation. These standard would be protective coatings which could be reproducibly formulated and which have known histories of performance. They would be used by coating manufacturers, raw materials suppliers, and end-users as benchmarks for evaluating the performance of newly developed coatings. A feasibility study on reference coatings was undertaken for the National Civil Engineering Laboratory, with the work being done by SSPC (see report SSPC-91-02, "Investigation of Standard Reference Paints for Improved Performance Evaluation.") More widespread dissemination of the information in that study would help to alleviate misconceptions held by many about the use and intent of reference standards. Certain existing coatings such as MIL-P-24441 or Federal Specification TT-P-86 are often used by evaluators as reference standard coatings, but most paint evaluators use their own internal standards or none at all.

IV. NON-DESTRUCTIVE METHODS OF DEGRADATION ASSESSMENT

One area of commonality between the three workshop groups was the need for better nondestructive methods of assessing the degree of degradation of a coating. In some instances, such as Electrochemical Impedance Spectroscopy, this was a fundamental aspect of the technology addressed by the workshops. Other non destructive methods of surface and coating interface analysis were also highlighted as talks and presentations within the tutorials and seminar sessions. These methods also figured heavily in subsequent workshop discussions.

Categories of non destructive evaluation methods can be subdivided into laboratory methods and field methods. Specific examples of individual technologies follow. They are characterized on the basis of field or laboratory use, maturity of technology and expense/sophistication of required equipment.

A. EXAMINATION OF THE COATING SURFACE

The surface of a coating is the easiest aspect to analyze. A large number of techniques suitable for field or laboratory use were discussed in the seminar sessions and subsequent workshops. The simplest of these techniques is quantitative visual assessment of degradation, often referred to as the grid method.

1. Grid Method

This technique was described in the tutorials on accelerated and field testing delivered by Drs. Bernard Appleman and Simon Boocock, it was also referred to by Mary McKnight of the National Institute of Standards and Technology during the seminar sessions. Briefly this method involves the superimposition of a finely divided grid over a test panel or coated surface. Anywhere within that grid that a defect of interest is noted, e.g. a blister or a rust spot, a count is made. Separate counts are made for individual defects. The separate cumulative counts represent the score for the system being analyzed. Previous work by SSPC and NIST for the National Shipbuilding Research Program and NCEL has demonstrated the viability of this method in providing earlier predictions of coating failure. This technique can be used in laboratory or field, it is inexpensive though more labor intensive than normal visual rating systems. Regardless the overall effort required is substantially less than traditional rating methods as results are obtained much earlier.

2. Surface Roughness Measurement

Referred to by Dr Brian Skerry in his paper on new accelerated testing methods this technique gives a measure of initial polymer breakdown, believed to be a progenitor of the onset of film breakdown at defect areas. The technique can be accomplished by using either loss of gloss measurements or by a profilometer. The instrumentation and skill required are within the scope of a trained inspector. The cost is low, $ 1000 - $5000, the technology is mature but the implementation suggested is new and not yet widely accepted.

3. Computer Analysis of Scanned Images

This method is presently in use by at least one commercial testing laboratory. It involves a computerized implementation of quantitative visual assessment. The high power and low cost of today's computers and storage media make this an attractive alternative to thermal or infra-red imaging, described below. This method was discussed in the accelerated and field testing workshop. The method is not mature, but only require a modest investment of time and effort to achieve maturity. The hardware involved, a scanner, image analysis software, storage media and computer, is mature and relatively cheap. The degree of skill required is expected to be minimal. The method will only give information about the coating surface and visible defects. This technique will likely be useful primarily in the laboratory.

4. Surface Analysis Methods

Grouped under this heading are a set of non destructive evaluation methods which are inherently expensive, sophisticated, demanding of the operator, and yielding potentially powerful information. All the methods referred to below were the subject of considerable discussion in either the seminars, tutorials or workshops.

Spectroscopic and Microscopic Methods

With the investment of considerable sums of money for instrumentation, sample preparation and operator personnel and training, a plethora of spectroscopic methods is available for analysis of the coating surface. Some are amenable to modification for use in assessing the entire coating film or the coating substrate interface. All are mature technologies subject to infrequent enhancements or improvements in resolution and sophistication. Every single one is a laboratory method of non destructive analysis. They are listed below.

Scanning Electron Microscopy - yields information about the coating surface, based on X-Ray Photoelectron Spectroscopy (XPS). Elemental constituents and oxidation states of film forming atoms can be determined. This oxidation state information can be used to assess the degree of polymer film breakdown.

Auger Electron Spectroscopy - this has deductive characteristics similar to XPS but is limited to a thinner film section, it has the advantage of providing more complete oxidation state information about the polymer film.

Infra-Red Spectroscopy - this is a potentially powerful technique capable of being modified to yield information about the coating surface, the coating film, or the coating substrate interface. Modifications demand custom sample stages for the spectrometer. This technique is really only useful when coupled to a computer capable of manipulating time domain measurements using Fourier Transform mathematics.

B. EVALUATION OF THE COATING STEEL INTERFACE

Perhaps more important than the assessment of degradation based on the coating film integrity are measures of corrosion or underfilm phenomena associated with the coating substrate interface. There are only really two non destructive means by which this aim can be accomplished, electrochemical impedance spectroscopy and thermal imaging.

1. Thermal Imaging

This method was described by two speakers at the conference, Mary McKnight of NIST and Dr. R.L. Thomas of Wayne State University. This method has also been subjected to close scrutiny by the NCEL staff. NCEL also played a lead role by providing funding for some of the NIST work.

The principle involves computer resolution of infra red images recorded using a special camera. Areas of blistering and underfilm corrosion yield a very different thermal signature from the intact coated areas of substrate metal. Though a field portable device was described by Dr. Thomas, certainly image analysis is usually conducted in laboratory. The technology is not deemed mature and hardware is expensive. Skill required for image manipulation is high. Despite these drawbacks the general principles of thermal image analysis are very attractive. Indeed, one iteration or another of this technology is quite likely to see further development. It is widely anticipated that as the hardware requirements are refined, a base set of the technology and associated computer/software requirements will be developed at substantially lower cost. The possible use of the technique in field is viewed as an exciting development and a sign of the future enhancements to be expected in this field.

2. Electrochemical Impedance Spectroscopy

Substantial discussion was given over to the benefits of this method. Previously applied to the corroding metal specimens this method has only recently seen use in analysis of coating failure mechanisms and degradation assessment. Much of the pioneering work in this field has been conducted at Navy laboratories such as David Taylor Research Center or with funding from the Navy to outside laboratories. The potential for this method is huge, the present use of this technique is minimal and restricted to the laboratory.

The reasons for minimal use are the high cost of the hardware, and the considerable level of skill required for complete interpretation of derived spectra. Both these barriers are likely to fall or become lower in coming years. Although the technique has heretofore been of use in the laboratory recent developmental work at DTRC along with independent development by industry vendors of the equipment promises to change this picture. An electrode system capable of field monitoring of in place structures was described by John Murray and Florian Mansfeld. A portable EIS instrument offering a subset of the techniques capabilities was described by Martin Kendig in the workshop on Electrochemical testing methods. The prospect of having a truly portable instrument offering nearly all the features of a laboratory set-up is not out of the question.

Despite the high current cost for the equipment EIS offers specific advantages which make it a good candidate for future development and analysis. Real time analysis of corrosion phenomena at the coating substrate interface is possible. Discrimination between failure modes can be made from skilled interpretation of the spectra derived. Still needed is information regarding the applicability of this method to a wide range of generic types of coating, particularly water-borne coating products.

V. RECOMMENDATIONS

A. TOP PRIORITY PROJECTS

The recommendations were derived from three groups which had separate agendas, yet met together sufficiently to provide substantial degree of interaction. The following is a review and consolidation of those recommendations, with a suggested order of priority.

1. Discourage Indiscriminate Use of Salt Fog Testing

Objective:

A program should be undertaken to inform users and suppliers of the significant deficiencies of salt fog testing along with available alternatives. The primary goal is to induce testers to stop relying on this as the ultimate corrosion test for coatings.

Approach:

The first step would be a few brief articles presented to a variety of publications, explaining the overall situation. For added authority, this article should be co-authored or at least endorsed by the workshop group or other recognized bodies such as ASTM, SSPC, or FSCT committees.

A second level of the project would be a detailed discussion of the deficiencies of salt fog with specific instances where it has given erroneous results. The treatise should also provide greater detail on alternative methods, such as a battery of accelerated tests, careful use of cyclic testing, and utilization of exterior testing.

Cost/Time:

The first series of articles could be accomplished with a very moderate cost (under $5,000) and completed within 3 months (not including the time needed for acquiring supporting authority). It is likely that existing bodies such as SSPC or FSCT would be willing to undertake this project with little or no external support.

The second stage would require a substantial amount of work of documenting and reviewing existing projects. Much of the data however is readily available. The work could be accomplished in 6 to 9 months at a cost under $10,000.

Benefit:

The major benefit would be a reduction in the amount of money wasted due to inadequate testing and possibly a higher level of interest in developing better test methods and methodologies.

2. Develop and Implement Standard Reference Coatings For Industrial Maintenance Applications

General Objective

Provide industry with a set of standard reference coatings to be used as benchmarks for coating performance evaluation.

Approach

This could be accomplished in two or more phases. A preliminary proposal was presented in a recent report sponsored by NCEL. The first phase would be to identify suitable coatings and prepare representative specimens for distribution to selected laboratories for evaluations. A second phase would be evaluation of the quality control aspects of the coatings and assessment of the effectiveness of these materials in various coating evaluation programs.

Cost/Time

The estimated cost for the first phase is $30,000 to $40,000 and a period of 1 year. The additional phase would attempt to make the program self-supporting, but would still require some additional funding of perhaps $60,000 to $100,000 and entail a development time of 2 to 3 years.

Benefits

The use of standard reference coatings would provide uniform materials against which to test new products. It would allow both coatings suppliers and coating users to use a "level playing field".

3. Assess and Evaluate Cyclic Test Methods

General Objective

Determine the validity and appropriate procedures for selected cyclic accelerated tests.

Approach

Select representative cyclic accelerated tests including specific cycles, considerations, and sequences. Evaluate a spectrum of coatings in the cyclic test as well as conventional tests and exterior testing to determine the relative merits. Use statistically valid sample sizes to ensure that results are significant. Prepare recommendations regarding the most suitable cycle, including reproducibility and other attributes of a good accelerated test.

Cost/Time

Total cost is estimated at $200,000 to $300,000, and the time would be 3 to 4 years. Major expenses are the following: preparing specimens --$50,000 to $75,000; conducting accelerated testing -- $75,000 to $100,000; field testing -- $30,000 to $50,000; analysis of data -- $30,000 to $50,000.

4. Guide for Coating Performance Testing

Objective

Develop a users guide for testing, evaluating, and procuring paints designed for corrosion protection and maintenance of appearance of industrial structures.

Approach

The guide would be intended to provide general information and specific recommendations for evaluating new products for specific structures and conditions and for replacing current materials. It would tentatively include the following types of subjects: introduction and background, review of industry practice, review of exposure conditions, description of conventional coatings, review of current laboratory and field testing methods, description of standarized reference paints, and discussion of performance levels of paints. Also included would be a step-by-step guide on how to conduct the coating evaluation covering design of the experiment, selection of coatings, preparation of specimens, physical and application tests, accelerated laboratory tests, controlled field trials, evaluation techniques, and data reduction and analysis.

Cost/Time

This project would cost $40,000 to $50,000 and be completed in 9 to 12 months.

5. Standarized Procedure For Accelerated Laboratory and Field Testing

Objective:

Develop standardized procedures for cyclic accelerated testing and accelerated exterior testing. Ideally these would be established through the interlaboratory testing consensus process of ASTM.

Approach:

Based on the results of well-documented studies of cyclic and other tests (e.g., see project #3) one or more accelerated test would be selected for standarization. For each of these, detailed information would be developed regarding description of equipment, operation and maintenance, and availability. Interlaboratory evaluations would be initiated to evaluate precision and develop additional database on typical evaluation times, cyclic conditions, etc.

Cost/Time

Because of the voluntary nature of ASTM, committee work, the study would require little external funding. One area where a small amount of funding ($5,000 to $10,000) might be required is in preparing the specimens and performing the analyses. The time required for this program would be 12 to 18 months.

6. Field Device for Electrochemical Impedance Spectroscopy

Objective

Develop and evaluate portable devices for performing AC Impedance (EIS) on coated industrial structures (e.g., bridges, tanks) and test fences.

Approach

Existing field devices for EIS would be acquired and evaluated on test fences and on several representative structures. Project would evaluate the affordability, ruggedness, ease of use, value of data obtained, reliability of data obtained, and relative time and cost to perform measurement. Based on this analysis, recommendation would be made for additional modifications to these devices to make them more beneficial to the users. Modifications might be required in hardware, software, or method of operation. Modification would be made either by the equipment manufacturers or as part of the study itself (perhaps in a third phase).

Cost/Time

The initial evaluations would cost $10,000 to $15,000 and be completed in 6 to 12 months. The second phase would be estimated at $15,000 to $25,000 and be completed within about one year. If additional work were needed to modify the hardware or software, additional costs would be incurred estimated at $30,000 to $50,000 and a time of 12 to 18 months.

7. Improved Field Imaging Procedures

Objective

Develop a procedure for use of imaging techniques to monitor and evaluate field performance of protective coatings. Procedure would establish the guidelines on the type of equipment to be used, the method and frequency of measurement, and analysis and interpretation of data for use in evaluating and predicting performance, and making decisions about repainting and replacing systems.

Approach

From review of currently available equipment, one or two units would be selected for the evaluation studies. Data on both visual and infra-red imaging would be compiled on coatings applied at test fences and structures over a period of several months to a year. Based on these experiences, procedures would be prepared on designing experiments, selecting hardware and software, selecting field specimens for evaluation, number of samples and frequency for imaging and data analysis routines. Guidance on interpretation of the data with regard to determining lifetimes would require longer-term evaluations and are best accomplished in a second phase.

Cost/Time

The total cost for the first phase is estimated at $75,000 to $100,000 with approximately one-third that amount allocated for purchasing the hardware and software. Time for the project would be 12 to 18 months. A second phase which would allow for longer-term evaluations would cost approximately $50,000 to $75,000 and be completed in 3 to 4 years.

8. Develop Standard Methods for EIS on Coated Metals

Objective

Develop a standard (e.g., ASTM) procedure for performing EIS measurements on coated metals. This would entail specific procedures, recommended basic hardware components, and identification of suitable reference materials.

Approach

An ASTM Task Group had previously developed a standard for electrochemical testing of other types of systems (ASTM G 106, "Practice for Verification of Algorithm and Equipment for Electrochemical Impedance Measurements.") A similar task group has been proposed for testing of coated metals. A procedure will be drafted and circulated among interested ASTM committee members. A task group or external project team would need to investigate and evaluate approaches for preparing uniform coating films on metal specimens. Suggestions include coil coatings or automatically applied structural steel coatings. The specimens, when determined to be sufficiently reproducible, would be distributed to participating electrochemical laboratories to develop a database for establishing a standard. Upon general agreement on the content of the standard, an interlaboratory test would be established using standard statistical designs and evaluations

Cost/Time

The development of the reference material would require external funding at approximately $8,000 to $12,000 and a time of about 6 months. The ASTM committee work would presumably be done on a voluntary basis by the participating laboratories. Again, some additional external funding ($3,000 to $5,000) might be required to prepare the final specimens and perform the analysis and other coordinating and handling needs.

B. OTHER RECOMMENDED PROJECTS

In addition to the above, a number of projects were recommended by the workshops. They are grouped according to the Work Group which made the recommendation.

Recommendations from Work Group #1, Accelerated and Field Testing

- Investigate mechanisms of coating degradation (All three groups agreed that there was a lack of effort within the coatings industry to study basic mechanisms of coatings degradation. No specific studies were recommended.)

Recommendations from Work Group #2, Evaluation Techniques and Statistical Designs

- Promote improved practice for experimental design
- Develop practical guide on need for and use of statistics in design and evaluation of protective coatings.
- Develop reference materials to characterize exterior exposure sites.
- Develop improved methods for site characterization and classification
- Develop composite visual rating methods to supplement existing ASTM methods.
- Develop reliable technique for evaluating adhesion of thick coating films.
- Develop standard parameters of deterioration for evaluating raters.
- Develop expert system for experimental design, evaluation, and analysis of data.
- Develop techniques for evaluating underfilm conditions and corrosion.

Recommendations from Work Group #3 -- Electrochemical Corrosion Testing

- Encourage use of electrochemical impedance spectroscopy by industry.
- Develop improved software for EIS of coatings
- Develop models for coating degradation and failure prediction (This item also addresses the need for more basic study by the industry on coating degradation)

C. CONSORTIUM PROPOSAL TO RAISE FUNDS

The projects identified will require a substantial sum over the next 5 to 10 years, estimated at $2 to $5 million. Sources for these funds are not readily identifiable. The protective coating industry must be able to justify the cost versus the perceived benefits to convince the industry to undertake this major investment.

It is proposed that a coating performance evaluation consortium (CPEC) be established to provide a broad base of support for generating funds and directing the program. The consortium would consist of individual companies, government agencies, associations, and others involved with protective coatings. Because of government reductions in R&D funding, the bulk of the support would be expected to come from industry. Government agencies could provide a significant role by seed funding and supporting specific aspects of the program considered to be directly relevant to the agencies' missions.

In order to provide the greatest benefits to the protective coatings industry, the majority of support should be derived from that industry, which includes over $1 billion per year in paint sales alone. This industry has traditionally been very competitive and spent relatively little on R&D. It is the challenge of the consortium to develop convincing arguments that the proposed projects are worth funding. They would improve the capability and competitiveness of the industry, along with other advantages to be enumerated.

Major players in the consortium would include trade associations such as ASTM, FSCT, SSPC, National Association of Corrosion Engineers, and American Iron and Steel Institute. Government activities involved would tentatively include Department of Defense (Tri-Services), Departments of Transportation, Environmental Protection Agency, and NIST. Industrial companies would include paint manufacturers, resin and pigment suppliers, and end-users such as state DOTs, oil or chemical companies, power generation facilities, and others.

In order to get started, the Consortium would require some seed money, perhaps on the order of $50,000. This would enable planning of the program, developing a mechanism, administration and bylaws, and preparation of marketing activities and research prospecti. The consortium would not have any dedicated facilities, but would assign work to various research labs and consulting organizations based on selection criteria and proposal solicitations. Initially the consortium could be housed in some external organization (e.g., a trade association) to minimize administrative and overhead costs.

Initially, it is proposed that the following three groups get together to discuss the first step: FSCT Corrosion Committee, SSPC, and NCEL, as these three groups have shown the greatest interest in these programs to date. Others which should be intimately involved are National Shipbuilding Research Program, Federal Highway Administration, and NIST.

D. NCEL ROLE

The Navy Civil Engineering Laboratory (NCEL) has an extensive program of research which is founded on improving the technology used in coating evaluation and durability assessment. This program has various elements, including short-term accelerated testing, coating characterization, and quantifcation of degradation. The NCEL program does not operate in a vacuum, rather it draws upon sources of known expertise in the coating technical community. This process helps ensure the relevance and feasibility, and advisability of implementing various technical improvements in the process of coating evaluation and durability assessment.

The NCEL program in coating evaluation and durability has several attractive elements. It is desirable that these elements be employed by the coatings industry. The NCEL program is in step with the needs of a broader technical audience encompassing coating users, specifiers, and manufacturers. The NCEL program provides a springboard from which further improvements in the technology of coating evaluation and durability assessment can be developed. The NCEL program has already provided a significant enhancement in the awareness of the technical shortcomings of past evaluation and testing methods. This awareness is becoming evident in efforts to describe improved methods for performance evaluation in documents issued by industry technical societies.

Appendix A: Findings from Work Group 1: Accelerated Testing of Coatings

1. Salt Fog and Other Accelerated Tests

a. Industry relies upon a few short-term accelerated tests for selecting coatings and predicting their performance. The most notable of these is the salt fog cabinet

b. The salt fog cabinet has been proven to be a poor predictor of coating performance for exterior exposure, including marine exposure. Salt fog accepts poor coatings (i.e., coatings that fail early in exterior) and it rejects good coatings (i.e., coatings that provide long term effective exterior protection.)

c. Salt fog tests may have some value as one of a battery of tests, or for quality control. However, the vast majority of laboratories do not recognize limitations and continue to use it in spite of its deficiencies.

d. Other widely used tests include condensation cabinet and immersion.

2. Exterior Performance Testing

a. The test considered most reliable as an indicator of performance is exterior exposure. Typically, coatings are exposed for 2+ years on one or more test fence locations.

b. A major deficiency in this approach is the lack of reproducibility of the exterior exposure site. However, it is generally felt that over a 2-year period at an exposure site, a coating will be subjected to a wide array of stresses and cycles. If a coating survives such an exposure, there is a high probability of a coating providing good exterior service.

c. Because of the variability in the environment, there is no absolute standard for exterior exposure testing. It is not advisable to compare coatings exposed at different times or in different environments.

d. The best comparison is obtained when multiple replicates (2 is absolute minimum) are exposed side by side. This type of testing will provide reasonably reliable indication of coating performance in similar exterior environments.

e. For highly aggressive environments (e.g., process area, offshore) this test should be supplemented with specialty tests such as salt water immersion, chemical immersion, or spot test.

3. Accelerated Exterior Testing.

a. This approach is considered a very viable means for reducing the time to acquire data in exterior exposures. It retains the essential desirable features of exterior testing and provides acceleration factors to obtain discrimination among coatings more rapidly.

b. This type of testing is most commonly done by spraying the specimens with salt water or acid rain. Overall, the industry has little experience with this technique, there are only a few articles published. A few commercial testing labs provide this service for their clients and have reported favorable results.

c. Some evidence suggests that degradation rates of the coatings will be increased by more rapid spraying (e.g., several times a day) Confirming data are not yet available.

d. UV enhancement and higher temperatures through a "black body" effect are widely used for testing automotive, coil coatings, and other systems for which aesthetics are critical. ASTM tests have been established and substantial literature exists describing these phenomena. Some facilities record and report the total irradiance, and compute therefrom an acceleration factor. This procedure is not universally accepted (see additional discussion under Accelerated Weathering).

4. Cyclic Spray Corrosion Testing

a. A major development over the last 10 to 15 years has been that of cyclic corrosion testing. The basic premise is to provide an environment which changes (cycles) between 2 factors (or imposing and relaxing a stress factor) .

b. It should be noted that this approach has been used in various accelerated weathering apparatuses. These devices tend to reproduce the diurnal cycle (i.e., condensation or water spray to simulate dew or rain and ultraviolet to simulate sunlight). The procedure has not been extended to corrosion testing (e.g., salt spray, immersion) except for a few laboratories.

c. The most noteworthy cyclic corrosion test is the Prohesion test developed in the U.K. based on some work in the 1960's by British Rail. The test is derived from the standard salt spray test, but differs in several significant ways.

d. The major difference is that unlike conventional salt spray, panels are periodically caused to dry out by using forced, heated dry air. This is claimed to induce wet/dry and hot/cold stresses and fatigue on the coating film. The extent of the stress depends on the extent to which the water permeates into and is released from the coating.

e. A second difference is in the type of solute which is sprayed. The Prohesion test uses mixture of ammonium sulfate with a very low concentration of sodium chloride compared to salt spray. Other differences exist in the temperature of the spray and the design of the cabinet.

f. The test is widely used in the UK and has received favorable accounts of work reported by the Paint Research Association and U.S. Manufacturers and has been reviewed and publicized by SSPC.

5. Cyclic Salt Spray with UV

a. Very recent work has indicated that UV radiation is a crucial factor in the degradation of coatings designed for exterior exposure. It has been hypothesized that the UV contributes to the degradation of the polymer and to the pattern of undercutting or other scribe-related failures. Thus the UV is not simply affecting appearance properties such as gloss and color retention.

b. Experimental evidence has also been presented that combining a cyclic salt spray with a UV cycle provides better simulation of exterior degradation patterns and coating ranking. The working group concluded that UV is a necessary component of corrosion testing programs.

6. Cyclic Immersion

a. Another recently developed test involved cycling between immersion (in various media) and dryout. The latter often includes UV exposure. Commercial apparatus is called "Enviro-Test." Typical cycle includes 2 to 3 hours immersion and 2 to 3 hours exposure to UV. The panels are placed on a wheel which rotates among 6 positions in a 360° arc.

b. This device provides for two important stresses: immersion and UV,. with the potential for a variety of media (including salt, seawater, acid and deionized water). However, there is very little data available on this method. The manufacturer and the users have not yet established a preferred or optimized cycle. Rather the cycle is tailored (somewhat arbitrarily) to a specific experimental objective.

7. Cyclic Condensation with UV

a. This test procedure was established 15 to 20 years ago by adding UV bulbs to the Cleveland Condensation cabinet. The condensation is caused by exposing the coated sides of the panel to heated water vapor, which then condenses on the surface. Many paint, raw materials suppliers, manufacutrers, and end-user laboratories have used this test for years as a measure of resistance to UV degradation. The condensation cycle was felt to accelerate the effect of UV.

b. The test has not been widely utilized as a measure of corrosion resistance, as the condensation cycle does not provide a very severe condition on high technology coatings. However it can be an effective way to determine the resistance to blistering.

8. Consensus on Accelerated Laboratory Testing.

The group identified various stresses that would be manifested in a coating exposed to exterior atmospheres. The following were considered essential for any accelerated test: moisture, temperature variation, UV radiation, contaminants (e.g., salt), and cyclic of these factors. The various stresses could be obtained using a single apparatus or by use of multiple apparatuses.

IB Group1: Recommendations: Accelerated Testing of Coatings

1. Best Current Practice for Performance Testing

Time Frame: Immediate
Priority: Urgent

a. Salt Fog Testing

The protective coatings industry should be strongly discouraged from continued reliance on salt spray as a major test for corrosion resistance and durability of protective coatings. Examples should be cited where this test has been proven to give erroneous conclusions which may be detrimental to the manufacturer or user's best interests.

b. Exterior Performance Testing

Additional use and reliance on this method should be encouraged as the most reliable proven method available. A minimum test time of 18 to 24 months is recommended at moderate to severe exposures. Earlier and/or more reliable results can be obtained by using techniques such as enhanced visual or infra-red examination, increased number of replicates or acceleration of the stresses.

c. Service Testing

The ultimate test of a coating's viability is its actual performance under service conditions applied withproduction application equipment. Service testing is recommended following screening by use of exterior exposure testing or if this is not feasible, a battery of laboratory tests (see discussion below). Because of the cost and risk factor associated with service testing, it is recommended that it be limited to 2 or 3 new coatings systems alongside a standard reference control coating.

d. Cyclic Corrosion Testing

- A laboratory testing program of protective coatings for steel should utilize a variety of stresses and conditions. As a minimum, coatings should be subjected to moisture, heat, dryout, UV, a contaminant such as salt, and cycling of the above stresses.

- None of the cyclic corrosion tests developed to date has been proven to provide consistent correlation with field results or to be capable of predicting long-term performance behavior. Thus, any of these tests are considered experimental procedures and should not be utilized for definitive coating performance evaluation or incorporated into specifications or other official documents. Among other deficiencies, these tests have not been evaluated for reproducibility or or repeatability, a major requirement of any test procedure.

- The cyclic test which has been most widely used, and for which some favorable published data are available is the Prohesion test. Most of the data reported are based on using the Prohesion test by itself, but some recent data have indicated improved ability to correlate with exterior exposures by use of Prohesion in conjunction with a UV cycle.

- A second test which has received some attention is the Enviro-Test, but there are no published data indicating its success in correlating with exterior exposures. Other means of producing cyclic environments, such as manual cycling, are also considered suitable means for producing these effects and are also being evaluated.

2. <u>Development of Coating Testing Guide</u>

Time Frame: Short Term
Priority: Definitely Needed

A Guide is needed on the current best practice for evaluating performance of coatings. The Guide should address the following subjects:

- Experimental design
- Panel preparation
- Testing of physical and chemical properties
- Accelerated laboratory testing
- Exterior exposure testing
- Analysis and interpretation of results

3. <u>Evaluation of Cyclic Corrosion Tests</u>

Time Frame: Short Term to Long Term
Priority: Urgent

A systematic program is needed to evaluate cyclic methods against conventional accelerated test methods and exterior exposure tests. Among the parameters to be investigated are the following:

- Cycle time (wet/UV plus dry time)
- Sequence of stresses
- Temperature of cabinet solution panel and control
- Source of UV
- Relative Humidity (rate of change and uniformity)
- Reproducibility Within and Among Cabinets
- Electrolyte Concentration
- Effect of Different Cycles on Different Coatings

In the absence of adequate funding to conduct a systematic evaluation of all these parameters, priorities should be established for different facets of the program. An example of a high priority is to determine the reproducibility of the panels in different locations inside a cabinet in repeated exposures in a single cabinet and among cabinets. ??? A preliminary proposal for a specific experiment will be developed as part of this report.

4. <u>Develop/Establish Standard Reference Coatings</u>
Time Frame: Short Term
Priority: Urgent

a. A vital need of industry is to establish a set of coatings which can serve as references or benchmarks of performance. These should be coatings which have known performance histories, and have been relatively widely used by different groups of industries.

b. Initially, a set could be based on SSPC and Navy control coatings, which include standards such as MIL-P-24441, TT-P-86, SSPC-Paint 25, standard vinyl system and others.

c. The utilization of standard reference coatings would require an organization to actually furnish liquid coating samples to various testing laboratories. Presumably this would be for a fee. A recent Navy/SSPC study discussed a number of concerns and questions about this approach, and provided a plan for implementing it. A summary is attached to the report.

5. <u>Investigate Mechanisms of Coating Degradation</u>
Time Frame: Long Term
Priority: Definitely Needed

There is also a need to better understand the mechanisms and causes of coating degradation and failure. Most of the previously listed programs and methods are based primarily on empirical observation of degradation. A fuller understanding of degradation would allow industry to develop better methods of characterizing degradation as well as to develop improved formulations to resist such degradation.

A variety of approaches and projects may be envisioned, including the following:

- Effect of UV and other stresses on T_g and permeability of coatings (EIS might be a useful technique to measure the permeability).
- Importance of defects on intiation and propagation of corrosion and blistering
- Characterization of corrosion products produced in scribe and under film under various exposure stresses, conditions, and time periods.
- Effect of pre-aging of coated panesl (prior to exposure) in accelerated chambers and exterior exposures.
- Influence of application and curing conditions (e.g., temperature and humidity) on ultimate performance of coatings.
- Influence of film homogeneity (i.e., pigment agglomeration, film cross-link density) on performance properties.

1C GROUP 1: ACCELERATED AND FIELD TESTING
Responses to Questions and Issues

1. What are the types and variations of cyclic corrosion testing available?

   This question was dealt with at some length, citations given included prohesion, envirotest, combination cycle experiments, ASTM cyclic salt fog testing, QUV testing, Weatherometer tests.

2. What data are available on coating degradation and cyclic salt spray and conventional salt spray?

   Limited data available, best data that reported at this conference, more data being developed by SSPC.

3. How do times for degradation compare in cyclic salt spray and conventional salt spray?

   Slightly longer in cyclic salt spray, attendees felt that accuracy of degradation was more important than time required.

4. What is the origin and significance of the Harrison/Timmins Solution used in prohesion testing?

   Independent work of Timmins, loosely based on J.E.O. Mayne's work. Intended to reflect actual industrial exposure.

5. How long a time is required for coatings to dry out between wetting cycles? How important is the dryout period? How is it affected by coating type, substrate, and color?

   Time needed about one hour, dry out period is critical portion of the cycle; can be affected by coating type, color, substrate thickness. Most important that rust in scribe dries out ?

6. What data are available on reproducibility of cyclic salt spray or immersion tests?

   Reproducibility data very limited, such data is being generated, Skerry, Q-Panel, Cleveland Society Coating Technology, SSPC.

7. What evidence is there to indicate different mechanisms of degradation in cyclic salt spray or immersion tests?

   Good evidence, much of which was reported here at this conference. Evidence for cyclic immersion presently limited but new data being generated by SSPC and KTA-Tator.

8. Is there a difference due to the type of substrate (i.e., hot-rolled vs. cold-rolled)?

   Some disagreement on this point. Austin holds that cold rolled steel will show representative earlier failure. Others believed it to be a wholly different type of substrate.

9. What approaches can be used for comparing accelerated test data with field data?

   Simple statistical tests such as Spearman rank correlation are informative. May need more careful examination of data to assure that false results are not being accepted.

10. What is the evidence for or against correlation of salt fog or cyclic salt fog with field data?

    Salt fog can correlate well with marine outdoor exposure - but yields many false negative results. It correlates badly with industrial exposure. Prohesion correlated with industrial.

11. What is the effect of UV on the rate and mechanism of degradation and the degree of correlation of accelerated testing with exterior exposure testing?

    Ultra violet exposure appears to be a critical component of a representative combined cycle experiment, maybe it should be a mandatory component.

12. How does one determine the number of replicates to be employed for accelerated experiments?

    We believe this is an appropriate question for work group two and that the answer depends on the statistical significance one hopes to demonstrate from the experiment.

13. What are the findings and conclusions from the AISI/SAE investigations of cyclic corrosion tests for automotive coatings ?

    None as yet, too early to make any clear call.

14. How misleading and detrimental is salt spray ? How strongly should its use be discouraged ?

    Salt fog alone is detrimental and misleading, but any single test of coating performance could also be held in question.

15. Should the coatings industry attempt to establish standards and criteria for reporting of accelerated test data ?

    Yes !

16. What are the advantages and disadvantages of standard reference paints and the prospects for establishing them ?

Advantages, providing controlled controls for experiments. Limitations, may not keep up with new formulation requirements, may be difficult to administer. may be costly.

17. To what degree does the validity of an accelerated test depend on the generic type of coating ?

Let us turn this question on its head, what is needed is a method applicable to the widest variety of coating materials.

18. What are the prospects for the industry to establish standard test methods in cyclic testing ? How could such standard test methods be established ?

Pretty good, desire is present, need is becoming more urgent. Could be done through a consortium of supporters with widespread industry backing.

19. What are some examples of accelerated field testing of protective coatings?

Norwegian, Volkswagen, US Auto makers, use of Q-Panels for earlier failure indication. Small scale SSPC efforts.

20. What is the evidence of success of these accelerated field tests in predicting extended term exterior exposures?

Pretty good for some auto programs. Probable need for reappraisal of SSPC efforts.

21. What is an appropriate length of time for conducting exterior or accelerated exterior exposure to distinguish between coatings?

Appendix B: Findings from Work Group 2: Evaluation Techniques and Statistical Design

(NOTE: Most discussions focused on exterior atmospheric exposures)

1. Experimental design

a. General

- Refer to notes from SSPC Tutorial 4/30/y1
- Laborary tests are primarily screening tests for exterior evaluation .

b. Number of Panels

- Group agreed that one is never enough, SSPC suggests 56, statisticians request 15 or more.
- More replicate panels may reduce exposure time, since as number increases probability of early failure increases.
- Risk associated with making an error in judging durability should be taken into account when selecting number of replicates; more panels increase probability of correctly characterizing coating durability as applied to a structure.
- Corrosion failures tend to be coating defect driven rather than related to surface or bulk properties, therefore more replicates are needed.

c. Panel Size and Configuration:

- Should reflect structure for which coatings are intended, e.g., for bridges, panel should include sharp corners, edges and bolts-usually most severe preferred.
- Use of stripe coat when stripe will be used on job.
- Flat panels for exterior exposure are generally 4 x12 inches, min. Often are 6x12. They need to be large enough to ensure that the coating performance over the edges does not affect the coating performance in the central part of the panel.
- Scribe: An important component of panel design, but may introduce additional variability.

*based on notes taken by Mary McKnight

- Steel uniformity: Fairly good, according to W. Kirk, degree of corrosion also influenced by degree of roughness, may depend on whether steel is made from virgin iron or recycled (latter may have impurities according to G. L. Tinklenberg).

d. Surface Preparation

- Consider type of abrasive that will be used, profile should be specified and characterized.
- Consider source and levels nd type of surface contamination.
- Include SP11 if that will be used on job.
- After blasting, further cleaning may be needed to remove contaminants. Procedures have been developed by SSPC (Swabbing), also KTA SCAT. Bresle test can be used for NOX, Cl - and S04.
- Consider applying coating the same day that panels are prepared VPI paper may affect coating performance.
- If using shot or other recycled abrasive, need to consider its condition.

e. Application Method

- Usually want uniform coating thickness, may have to prepare many panels to obtain desired range of thickness.
- Consensus that application method should be like that to be used in the field.

2. Characterizing Environment

a. Parameters measured

1. Atmospheric parameters

   - Chloride (wet candle)
   - SO_2 Weather Factors, including UV, temperature
   - Humidity, precipitation.

2. Surface Parameters

   - Salt or other surface contaminant
   - Ti me of wetness

3. Degradation of Standard Materials

- Wire on bolt test
- Corrosion rate of steel or zinc, degradation of coatings (e.g. undercutting at scribe)

b. Methods & Standards

1. Atmospheric chloride: wet candle procedure, under consideration by ASTM G3.
2. Atmospheric SO_2 measured routinely by various meteorological stations.
3. Surface Salts, SSPC, ISO, KTA (SCAT) have proposed methods.
4. Wire on bolt tests standard being developed by ASTM G1-07.
5. Time of Wetness: ASTM G82.
6. Corrosion rate of steel or zinc - ASTM G1.
7. Undercutting of paint: ASTM D1654, SSPC has data.
8. General site corrosivity - ASTM G92.
9. Others: See water immersion, ASTM G50.

Available Data

- G 104 data on corrosivity of exposure sites (Materials Performance, Sheldon Dean of Air Products).

- ALCAN data on welding wire, for aluminum1100 alloy. (Contact: Bud Loss, Armco)

Groups Involved

- ASTM (identify specific Task Groups) Aluminum or steel companies SSPC, ISO or other international groups. Current Classification Schemes SSPC exposure zones General terms: industrial, marine, rural, urban, etc. Variability of sites and data collection.

- Variations Among Sites: Many variables including wind direction, distance from ocean or other pollution sources, differences in amount of sunlight due to latitude, average rainfall, current pH of rainfall, etc.

- Variations Within Site: Great variability in corrosivity may occur within same major area, for example location on a test rack. Small steel disks can be placed throughout the area to characterize corrosivity. Ninety day test, minimum of 2 to 3 replicates recommended. ASTM G1 has developed cleaning procedures for removing corrosion products for steel disks used in corrosivity test.

- Variations Over Time: Researchers have found a very wide variability in the site characteristics from year to year, even within a given site. These data also have not correlated to corrosion or coating degradation rate.

- Panel exposure sites need to be free from shadows (i.e., BOLD exposure). However, also need to consider effects of sheltering for weathering steel. Sheltered panels may have significantly elevated corrosion rates.

g. Measurement Procedure

- Important factors include time and frequency of measurement and number of replicates exposed.

- Possibility of reference standards for characterizing exposure.

3. Exposure Sites

a. Types of Exposure

- Panels on test fence

- Panels on structures or at plant locations

- Coating directly on structure in service or process.

b. Exposure racks

- Rack placement - Severity of an environment can vary greatly within an industrial plant, near a salt water body, and the like. Some like to expose coatings in an environment similar to that in which coatings will be used. Others noted the need to prevent unnatural weathering effects, e.g., accumulation of blasting debris.

- Placement on racks should be at random. Randomness also desirable when coatings are tested on structures.

- Angle of orientation may affect results; in U.S. commonly used angle is 45 degrees. Should consider angle at which coating will be used.

4. Materials Characterization: Parameters and Methods

a. Visual methods

- Defining Measurement Areas: Divide the area into sections and rate each based upon standard visual methods, also can evaluate appearance, or film integrity.

- Standard visual methods: These include ASTM D610 D714, D1654, along with methods for appearance (e.g. chalking, cracking, etc.) Essentially address microscopic degradation properities Decorative plating ASTM committee, B8, has standards for rating appearance and coating integrity.

- Rust staining invoked considerable discussion, with note that volume of corrosion products is roughly 10 times that of the metal oxidized. Also noted the difference between coating deterioration and extent of corrosion. Level of protection may also be a useful concept.

- Non-standard visual evaluation methods: These include grid methods, imaging. (ASTM F25 methods essentially are non-standard, although there is a procedure written).

- Consider effect of lighting and other variables on rating, source of lighting, (e.g. sunlight, incandescent or fluorescent bulb) time of day, direct or indirect lighting, acuteness of vision, color and shadows).

- Sources of variability (material, operator, site)

b. Physical/Mechanical Methods

- Adhesion
- Impact
- Roughness
- Usually require a destructive test.

c. Chemical and electro-chemical

- Permeability
- A.C. Impedance
- Conductivity
- Most test need to be run in laboratory, some progress in field measurement techniques.

d. Under Film Phenomena

- Usually destructive test required.

- Knife test can be used to evaluate underfilm corrosion.

- Imaging is a promising approach.

- Standard needed for stripping coating (typically use MEK or other strong solvent).

e. Other Field Methods

- ASTM and NCEL test kits may give some information on generic type.

f. Qualifications of evaluators

- Evaluators become more consistent with experience. Is there a need to certify or qualify evaluators? Do we need standard deteriorated panels to help in characterizing evaluators?

5. Material characterization: Analysis and interpretation of data.

a. Reference standards for coating evaluation.

- Strong need seen by group.
- Some problems in reproducibility ofcoating materials.
- Feasibility study completed by SSPC (NCEL report being published by SSPC)
- Primarily use coatings such as MIL-P24441 and others which have wide history of performance and familiarility to industry.
- Undercutting of scribe can be measure of corrosivity as related to coating degradation.

b. Variability among different coatings

- Different generic coating may have different degradation modes and hence require different evaluation parameters and criteria (e.g. Waterbornes).

c. Time to failure

- Important concept (need to educate industry)
- Need definitions of failure and degradation

d. Statistical evaluation

- Need to be considered when designing experiment.
- Trade off involved in using increasing number of panels. This approach increases the cost, but can provide earlier information and increased degree of confidence.

Identified Needs for Additional Study

1. Experimental design
   - Expert system on experimental design, evaluation and analysis of data.
   - Testing of repairability of a maintenance coating.
2. Characterizing Environment Reference materials to characterize environmental site.

3. Exposure Sites

4. Materials Characterization: Parameters and Methods.

- Can impact tests be useful as field tests to assess adhesion? Noncontact profilimeter--can we get useful field information?

- Infrared/Acoustic Emission/ultrasound/eddy sound--what information can we get from technique?

- Field EIS device--how would it be used? How do we evaluate underfilm condition? How do we measure adhesion of thick films?

5. Materials Characterization: Analysis & Interpretation of Data

- New visual patterns, localized vs widespread (Could we use the ASTM F25 standards)
- Standard procedure for laboratory imaging and analysis?

- Reference materials for using as controls to include in test environments.

- Special needs for testing waterborne coatings.

- Standard panels of deteriorated coatings to use in evaluating operators who carry out visual ratings.

- Demonstration of statistics, e.g., more panels shorten exposure time, performance of coating on few panels may not be good representation of performance of coating on many panels or large areas.

- Correct use of subjective procedures (need brought about by information in Tom Rehfeldt talk.)

- Need statistician to writer a paper to describe, in laymans terms, important considerations, risk taken when certain assumptions are made, etc.

2 B GROUP 2: RECOMMENDATIONS: EVALUATION TECHNIQUES AND STATISTICAL DESIGN

The recommendations are organized according to the five major topics addressed during the Workshop #2.

1. Experimental Design

a. Guide to Testing of Industrial Maintenance Coatings
Time Frame: Short Term
Priority: Urgent

Industry should develop a general guide for performance testing of industrial maintenance coatings in the laboratory and in field or service. The SSPC tutorial and some recent texts would provide a good basis. The effort would probably be less than one year. The Guide would address factors such as experimental design, selection of coating systems, preparation of panels, selection and use of accelerated tests, exterior exposure tests, evaluation of coatings degradation, and analysis of data.

b. Promote Improved Practice for Experimental Design
Time Frame: Immediate
Priority: Urgent

This recommendation consists of informally applying some of the points discussed at this conference such as use of replicates, consistency in source of steel, and preparation and application methods, and various other techniques that are widely recognized but not uniformly observed.

c. Expert System for Experimental Design, Evaluation and Analysis of Data
Time Frame: Short Term to Long Term
Priority: Definitely Needed

The technology for expert systems is widely available, and some have been developed relating to selection of coatings and analysis of coatings failure. However, most specifiers, owners, and others are not familiar with the concept of expert systems, and have not been convinced of the value of the existing programs. Thus, a substantial amount of additional work would be required to develop a user-friendly, effective, and practical expert system. Demonstration of the usefulness and payback of such a system would require a separate implementation effort. Because of the complexity of the development (to establish a simple system), fairly major effort is anticipated, requiring several man-years of effort and a commensurate budget. Sources of funding may be problematic if currently developed systems cannot be adapted, or if a commercial (i.e., proprietary) system is not developed.

2. Characterizing Environments

a. Reference Materials to Characterize Environmental Sites

Time Frame: Short Term
Priority: Definitely Needed

Steel and zinc panels are used to some degree for this purpose, but there is no consensus on the length of exposure time needed, number of specimens needed, or the interpretation of the corrosion rates. An alternate approach is to use the rate of undercutting of a barrier coating, which has shown some promise in that regard in SSPC studies. It is also possible that undamaged coatings systems which are used a s standard reference coatings, could also be used to characterize the exposure site. However, in this case, it would be necessary to use some coatings with relatively poor protection properties in order to allow the site to be characterized within a practical length of time.

b. Adopting Improved Methods for Site Characterization

Time Frame: Immediate to Short Term
Priority: Definitely Needed

There are numerous guidelines for action such as rack design, placement on rack, randomization on racks, angle of orientation, which are very well known, but which many evaluators do not observe. There are other methods such as wet candle, wire on bolt, surface salt extraction, and time of wetness, which are not routinely measured by most evaluators. Some additional work is needed to assess the merits of these techniques, determine the extent of standardization and reproducibility, and demonstrate how they can be incorporated into an evaluation program.

c. Improved Exposure Site Classification Schemes.

Time Frame: Short Term
Priority: Definitely Needed

The SSPC classification scheme is not appropriate to many types of exposures, which have combinations of factors (i.e., chloride plus SO_2). Also, the SSPC schemes do not recognize acidity of precipitation as a major variable. The current scheme could be used as a starting point to develop a scheme which incorporates these other variables and possibly would include some type of quantitative measurements such as corrosion rates, amount of precipitation, time of wetness, etc. The need for this type of scheme was evidenced in the recent development of a performance specification for coating materials.

3. Materials Characterization: Parameters and Methods

a. Composite Visual Rating Methods

Time Frame: Imediate to Short Term
Priority: Definitely Needed

Because of the non-uniformity of corrosion on structures a number of groups have established composite rating schemes in which the section rated is broken down into smaller units and then the data from these small units (e.g., one-foot areas) or individual structural components (e.g., bridge top flange) are combined. The general concept and some examples could be presented and encouraged immediately, however the existing ASTM F-25 procedure is very cumbersome and an improved standardized method is needed. Some advances have been made by NIST, NCEL, and the CERL.

b. Use of Imaging and Quantitative Methods

Time Frame: Immediate
Priority: Definitely Needed

Quantitative visual techniques developed by NIST and SSPC are documented and easy to use and considered to be of definite benefit. Technolgy of scanning surfaces with visual or infra-red cameras is also well established and readily available. The price of equipment, particularly software and hardware, has dropped significantly in the past several years, thus these techniques can be applied immediately pending dissemination of the technology and benefits.

c. Development of Improved, Meaningful, Mechanical and Physical Field Tests

Time Frame: Short Term
Priority: Definitely Needed

The workshop identified several field techniques which could provide valuable performance information. These include water permeation tests, non-contact profilometer, and field impact tests. Additional development and evaluation work is needed to optimize the procedure, determine reproducibility, and determine the validity of data derived from these tests.

d. Application of More Sophisticiated Characterization Tests to Coating Performance Evaluation

Time Frame: Short Term to Long Term
Priority: Probably Needed

A number of techniques which are used for laboratory evaluation of materials may have application to field performance evaluation of coatings. These include infra-red or acoustic emission, ultra-sound techniques, Eddy sound techniques, and others.

e. Field Use of Electrochemical Impedance Spectroscopy

Time Frame: Short Term
Priority: Urgent

The workshop attendees felt that EIS devices could provide extremely valuable field data with some minor modifications of existing hardware and software. The recommendation is referred to the Electrochemical Work Group.

f. Develop Techniques for Evaluating Underfilm Conditions and Corrosion

Time Frame: Short TermT
Priority: Definitely Needed

It is important to observe underfilm phenomena such as underfilm corrosion, incipient blistering, or other defects. These phenomena often occur well in advance of visually evident degradation and thus can be used for early prediction of performance. A standardized method is needed for stripping coatings from panels, as well as for evaluating the condition of the underlying metal.

g. Develop Reliable Technique for Evaluating Adhesion of Thick Films

Time Frame: Immediate to Short Term
Priority: Definitely Needed

Some current ASTM methods (e.g., ASTM D 3359 and ASTM D-4541 describe adhesion tests which can be applied to thick film as well as thin films. However, there is lack of agreement on the meaningfulness or interpretation of the data. Thus for immediate purposes, the properties of these techniques can be promoted, but development work is warranted to identify an alternative test for adhesion. Also mentioned was a need for a non-destructive adhesion test.

4. Materials Characterization: Analysis and Interpretation of Data

a. Standard Reference Coatings

Time Frame: Short Term
Priority: Urgent

Control coatings are recognized as essential to any performance evaluation program to compare new candidate coatings with coatings of known performance history. Industry would benefit greatly by having available standard reference coatings which could be used by suppliers, testing laboratories, specifiers, and others for this purpose. Some de-facto standards such as the MIL-P-24441 or TTP-86 or SSPC-Paint 25 exist. Questions that need to be addressed include the reproducibility of the coating, supplies and production, quality control tests, and others. A preliminary proposal has been prepared by SSPC, but was not funded.

b. Develop Standard Parameters of Deterioration for Evaluating Raters

Time Frame: Short Term

Priority: Probably Needed

Many of the standards used (e.g., visual standards) are objective and differ from rater to rater. The proposal is to prepare a standard panels or photographs or other procedure for judging the rater's ability to assign proper visual ratings.

c. Demonstrate Value of Statistical Design and Evaluation

Time Frame: Short Term

Priority: Definitely Needed

This project would provide specific evidence from real studies along with theoretical back-up to demonstrate the value of using increased sample size and other statistical approaches. Also could address the need to use statistical sampling when rating (?) a structure.

d. Treatise on Uses of Statistics in Coatings

Time Frame: Immediate to Short Term

Priority: Urgent

A report or series of articles is needed to explain the use and importance of statistics in layman's terms. It would cover types of errors, statistical design, number of replicates, risks taken when certain assumptions are made, etc. Also of value would be to demonstrate the correct use of suggested procedures, for example, certain objective parameters such as rust ratings, blister ratings or checking may not be consistent with a linear scale as is currently used. This study would not require any new development work but would require someone who was familiar with coatings and statistics and knows how to communicate well to the coatings practitioner.

Appendix C: Findings from Work Group 3: Electrochemical Corrosion Testing

The group consisted mainly of Electrochemical Impedance Spectroscopy (EIS) users and interested parties.

EINDINGS

A general statement accepted by the group was: EIS is an important tool for measuring and defining (with the use of a generally accepted model) the state of a coated panel.

The topics addressed by the group consisted of the 17 questions and issues suggested by the Workshop organizers for consideration by the group and one additional item described generally as a competitive round-robin test. The list of 17 topics is included as an attachment. Discussion on each of the items varied considerably depending on the level of interest, information available and depth of controversy. Consideration of topics 1 and 3 yielded lengthy discussions which are treated separately below followed by a tabular treatment of all 17 topics.

Equipment. Costs and Level of Expertise (Topics 1 & 3)

Instrumentation for making EIS measurements is commercially available with a cost range of $13,000 to $50,000 depending on the level of sophistication required and consists of the following components:

- Cell - Normally simple designs, usllally made by investigator (less than $500). Usually a clamp-on cylinder filled with a test media (electrolyte) and includes additional electrode(s).
- Potentiostat - Required for 3-electrode configuration (typical R&D studies), not required for 2-electrode configuration. Several manufacturers. Price range $5,000 to $12,000.
- Frequency generator/analyzer - Currently 2 major manufacturers representing two differing technologies: A frequency response analyzer (FRA) and a lock-in analyzer (LIA). The LIA is limited in low-frequency response and is normally supplemented by a fast Fourier transform (FFT) technique for low-frequency measurements. Plice range: $10,000- $30,000.
- Computer - Not necessary, but very, very highly recommended for practical productivity levels. Price range: $2,000- $10,000.
- Data acquisition software - Currently 3 known sources. Price range: $500 - $3,000.
- Data analysis software - Currently 6 known sources. Price range: $50 - $3,500.

All typical systems are quite accurate within their working ranges of frequency and impedance limits. Time to acquire and analyze data is application dependent with acquisition times of 10 min to 48 h. Rudimentary data analysis and plotting require less than 10 min.

Minimum level of expertise required for operating the EIS equipment is: Laboratory Technician. Usually QA/QC data interpretation can also be performed by a trained technician although supervision by a knowledgeable electrochemist is highly desirable, particularly in the initial phases of setup. Interpretation of non-standard test results (new sample type or new test environment) is probably better left to a trained electrochemist.

Existing equipment models, although designed and intended for indoor use with AC power source, can be taken into the field for data accumulation and analysis. Simple alternative cell designs are available which are independent of orientation.

Equipment improvements for greater portability, higher measurement capability (higher impedance values at low frequencies, high frequency range), greater degree of sophistication in output format and lower initial costs are all desirable but not considered essential.

Tabulation of Results on All Topics

The discussions on all Workshop 3 topics were categorized into five areas which were summarized in Current Status (Table I) and Future Requirements (Table II). The five areas were:

1) The EIS technique.

2) EIS test results.

3) EIS results correlation with long-term alternative coatings performance evaluations.

4) Alternative electrochemical measurement techniques.

5) Miscellaneous, including identification of those formerly or currently active in electrochemical assessment of protective coatings.

TABLE I: CURRENT STATUS	
TOPIC OR AREA (Topic #)	**INFORMATION**
TECHNIQUE	
• Equipment (T-1)	In general, use is R & D oriented. Some quality assurance applications and field efforts in-progress. At least one field system designed for field use is available. Both 2 and 3 electrode approaches used.
· Test cell	Individual approach. Design guidelines published. Problems include high frequency response considerations.
· Test media	Related to cell design. Can be modified to evaluate chemical resistance of coating system.
· Potentiostat	Several commercially available ($5K-$10K). Not needed for 2-electrode configuration.
· FRA/LIA	Very convenient. Several (3-4) commercially available models. Alternative techniques can be highly manpower intensive.
· Computer	Wide selection available ($2K-$10K, and up).
· Operational Software	Commercially available from EG&G PAR or Solartron/Scribner. Custom programming in BASIC has also been developed.
· Analysis Software	Several programs available (Boukamp/PAR, Solartron/CIRFIT, Z-Plot/UVa-Scribner, J.R. MacDonald/CIRFIT, SPICE/PSPICE).
• Types of Samples (T-2)	Normally non-conductive organic coatings on steel (most often) substrates. Tests performed with reasonably conductive fluids.
• Samples W/WO Induced Defects (T-7)	Both utilized. Induced defect (scribe or drilled hole possibly useful for adhesion studies).
• In-situ Tests (T-9)	Laboratory or field evaluations of continuous immersion, immersed for measurement only or wetted samples. Problems with coated metal in concrete media.
• Quality Assurance Tests (T-11)	Both 2 electrode and 3 electrode measurements can be compared to a quality control database.
• Sample Limitations (T-17)	No thickness limit with large test cells.
• Frequency Range (T-6)	For research and development, use as wide as practical. For quality assurance or control, restrict to minimum requirements.
• Personnel required (T-3)	For research and development, trained electrochemist recommended. For quality assurance or control, trained high school level.
RESULTS	
• Types of Testing (T-4)	For immersed or wetted area: capacitance versus time, defect (pinhole, holiday) detection, damage development.
• Reproducibility (T-5)	Very reproducible with dummy (calibration) cells to 90% of system upper measurement limit.
• Standardization of Testing Coatings (T-12)	ASTM G-106 is adaptable for coatings applications. Draft of adapted method is in preparation.
• Detect Small Differences/Changes (T-16)	Need "standard" real coating for statistical comparisons. Potential materials under consideration.
DATA INTERPRETATION (T-8) and DATA CORRELATION (T-10)	Mainly 3 published studies: Blistering and rusting (Scully, Murray & Hack), Atmospheric degradation (Skerry), and Immersion study of architectural coating (Murray & Hack).
ALTERNATIVE ELECTROCHEMICAL MEASUREMENT TECHNIQUES (T-13)	Electrochemical Noise Spectroscopy, Fix-frequency capacitance measurements, DC resistance, Pulse measurements.
MISCELLANEOUS	
• Organizations Supporting EIS (T-15)	None. Scattered support for EIS as a component of research efforts. Department of Defense, commercial quality assurance and quality control programs.
• Organizations Disseminating Information on EIS & Related Methods (T-14)	The Electrochemical Society, National Association of Corrosion Engineers, ASTM, *Corrosion, Corrosion Science, Materials Performance, Brit. Corrosion Journal, J. Coatings Technology, J. Protective Coatings & Linings, JOCCA*, others.

TABLE II: FUTURE REQUIREMENTS	
TOPIC OR AREA (Topic #)	**INFORMATION**
TECHNIQUE	
• Equipment (T-1)	In general, NOTHING NEEDED. Optionally, useful developments would include a more field-compatible unit (light-weight, battery operated) and a higher impedance measurement capability at lower frequencies.
• Samples W/WO Induced Defects (T-7)	Additional consideration should be given to shape and type of induced defects.
• In-situ Tests (T-9)	In-situ atmospheric cell needed.
• Quality Assurance Tests (T-11)	Publish statistically valid databases for various coatings types.
• Sample Limitations (T-17)	Nothing currently needed.
• Frequency Range (T-6)	Redesigned potentiostat needed for 3-electrode systems ($f > 10^5$ Hz).
RESULTS	
• Types of Testing (T-4) • Reproducibility (T-5) • Standardization of Testing Coatings (T-12) • Detect Small Differences/Changes (T-16)	Needs: Standard panels (SSPC, ACT, Q-Panel or other); Recommended procedure (Kendig draft to committee;) Draft procedure to ASTM; Round robin tests should include EIS statistics & reliability, EIS versus long-term blistering and rusting, EIS versus other test methods and long-term field tests.
DATA INTERPRETATION (T-8) and DATA CORRELATION (T-10)	Need published long-term comparison studies for various environments including UV and non-UV, industrial, urban, rural, atmospheric, splash & spray zones, and immersion service.
ALTERNATIVE ELECTROCHEMICAL MEASUREMENT TECHNIQUES (T-13)	Low expense electrochemical noise spectroscopy and expert system for data processing may be beneficial.
MISCELLANEOUS	
• Organizations Supporting EIS (T-15) • Organizations Disseminating Information on EIS & Related Methods (T-14)	A consortium funded, coordinated effort would provide mutual benefits and resource savings.

Digression

A competition was proposed for efficiently and accurately ranking the performance of coated panels using EIS. While the Workshop participants did not come to an agreement on the final form of the contest, the essential elements can be acquired from the following description:

M. Kendig proposed a unique contest to determine the overall efficiency of EIS in ranking the performance of coated panels. Recognizing that the time to establish a rank may be as important as the absolute accuracy of the rank, the approach for the contest would be for each participant to receive panels and an intial fee for evaluating these (e.g., $6,000). The contest winner would be the highest scores based on

$$\text{Score} = \begin{bmatrix}\text{correlation}\\ \text{coefficient}\end{bmatrix}\left[\frac{1}{\text{Time of response}} + \frac{1}{3 \times \text{Labor Hours}}\right]$$

where the correlation coefficient would range from +1 (all correct) to -1 (all incorrect). Alternative factors were proposed for inclusion such as initial cost of equipment (normalized for inflation on a given date) ane cost of labor involved. A few of the participants would likely be efficient so that all funds would not be consumed and the winner would be awarded a flat fee (perhaps $10K) plus the remaining fund pool, which would be the contract fee to document the technique/approach in a report and journal quality paper.

Topics

1. What types of equipment (electrochemical, computcr ha}dware and software) are needed to conduct electrochemical impedance spectroscopy (EIS)? What are the approximate capital and maintenance and technician costs?

2. What type of systems are amenable to E:IS testing? knmersion in water, metal in concrete, metal in atmosphere?

3. What level of expertise is needed to design, conduct, and interpret EIS experiments?

4. What types of phenomena are most readily studied by EIS (i.e., water permeation film, delamination, mechanical stress, etc.)?

5. What data have been developed on the reproducibility of EIS measurements on coated specimens?

6. What are the advantages and limitations of using a small number of frequencies for EIS evaluation of coatings?

7. What are the advantages and limitations of studying defect-free coatings vs. coatings with induced defects?

8. How successful has EIS been in predicting whether or when a coating system will fail?

9. What are the prospects for *in situ* EIS measurements of steel in immersion, in concrete, or in the atmosphere?

10. What data are available for comparing EIS measurements to long-term exposures in water or other media?

11. What are the prospects for a coating manufacturer using EIS for routine comparative evaluation of new vs. standard coating systems?

12. What are the prospects for standardizing EIS measurements to the point where they can be performed by testing labs or by testing department of a coating company?

13. What other electrochemical techniques and tests are available for evaluating coatings? What types of systems have been studied? What type of phenomena has been studied? What are the advantages and limitations? What are the costs for these techniques?

14. What are the major groups, associations, periodicals for disseminating the work on EIS of coatings?

15. What are the major organizations or agencies supporting or conducting research and use of EIS?

16. How useful is EIS in picking up very small differences (e.g. in formulation or ability to withstand degradation) of coatings?

17. Are there any limitations on thickness of coatings or type of substrate (i.e., surface roughness or surface contamination) for using EIS?

3C: GROUP 3 -- ELECTROCHEMICAL CORROSION TESTING
Workshop Notes

NOTE: *The following are comments made during the May 2 meeting, derived from review of audio tape and organized according to categories shown. These are considered background notes.*

I. PROCEDURES

1. Hardware

- Some equipment doesn't work too well, but this is not well known. (e.g. FFT, Fast Fourier Transform).
- Question raised about whether to use two or three reference electrodes (three apparently is typical).
- One can also obtain impedance type data from noise.
- Cost for a fully equipped, off the shelf item ranges from $10,00-$50,000.
- Typical cost between $25,000-$40,000.
- Two electrode system OK for thick coatings in the field.
- For a standardized procedure, one should define the type of hardware used.

2. Software

- Some is available from equipment suppliers.
- Most good software still must be developed or modified in-house.
- Better software needed for routine interpretation of spectra.

3. Preparing Samples

- In some cases, it may be necessary to drill hole or otherwise make defect, because coatings may perform too well.
- Scribing is also commonly used.
- Damaged area may dominate the response. The size of the defect is important.
- Defects can make the coating disappear. Typical size should be 10^{-4} or 10^{-6} cm^2.

4. Reference Material

- Reproducible specimens (coated panels) needed.

- Concern about reproducibility of conventionally applied coating. Alternatives include electrodeposition or coil coating. Latter are then very uniformly applied coatings.

- ACT Company produces panels for automotive industry. They should be investigated regarding the reproducibility of their specimens and the possibility of their producing samples for EIS work.

- Also concerned about reproducibility of coatings from year to year.

- Industry needs reference samples for both high and low impedance coatings. (Possibility a high impedance coating with and without a defect).

- Relatively easy to produce a bad (low impedance) paint.

- Need method to verify reproducibility of panel. This is currently available for ASTM for steel rods, but may be more difficult for coating on steel.

- One way to verify reproducibility would be to distribute several replicates of a large batch to different laboratory groups for measuring EIS.

- Coil coatings are typically pre-treated and applied with a baked polyester.

- It will be useful to get samples which had a known performance in salt spray or other commonly used evaluation procedure.

- The group kept coming back to reference samples as a key to making EIS more widely useful and available.

5. **Designing Experiments**

- In response to question about the solution for a cell, it was explained that cells tried to simulate the exposure (e.g. acid rain, salt from marine).

- Conducting the experiment was relatively easy, but there was some question about interpreting the data.

- It was suggested that a dummy sample be run in parallel coated specimen (similar to the method proposed in ASTM G 106).

- One approach for experiment was to use replicate specimens for exterior exposure, with specimens being retrieved at six months, twelve months, etc.6. **Acquiring Data**

- At least one participant felt that data can be collected very routinely using high school students.

- Others felt that more experience is needed to insure that the data are reasonable and not simply a collection of numbers.

7. **Interpretation of Data**

- Question was asked, "What constitutes a good coating?" The response was a threshold of impedance or other measurements exist for a good coating, but cannot distinguish a good from a excellent coating.

- If one sees an increase in conductance (decrease in impedance), then it must be due to corrosion. In this way, EIS is better than DC methods.

- One participant stated that an electrochemist was needed to set up and interpret the data.

- It was felt that there is insufficient data base to determine how readily EIS can detect small differences in formulations. An example would be the ratio of polyamide to epoxy in a dried and cured film.

- Interpretation is relatively easy for high frequency responses down to the break point frequency or to 1 hertz.

- Certain phonemena were felt to be easy to interpret (i.e. routine), but no examples were cited.

- Information on mechanistic detail was where the electrochemical training was required.

- Example cited was Nippon Steel device for measuring EIS in the field.

- One individual stated that by using a black box approach,one can get at least the passive film resistance.

- The Group felt it was necessary to distinguish routine type experimental data from those requiring expert analysis.

- Testing should be done at various time intervals.

- Some experiments have been performed on EIS specimens exposed after 15 months exterior. Others have evaluated coating in long-term marine immersion.

- A double logarithmic plot of weight loss versus time (e.g. for zinc, steel or aluminum) is desirable.

- Note: A basic explanation is needed of why EIS is important and how it relates to corrosion (e.g. how loss of film resistance, i.e. impedance) is important.

- It is also important to plot AC impedance against other properties to establish correlations. Examples include ASTM-D610 and the condition of substrate after coating is removed, or loss of metal.

8. Reliability and Reproducibility

- It was felt that the major variability of EIS measurement would be in the coating or the panel rather than in the electrochemical technique.

- In other words, EIS can be used to determine the extent of reproducibility of the panels.
- The instrumentation is very precise, and it is a theoretically, very well defined measurement.
- Variation may also arise in In the location of the cell on the panel.
- Note: An inter-laboratory test would determine the extent of variance contributed by operator techniques, and specimen.

II. APPLICATIONS

1. Phenomenona Studied

- A question was asked, "Why is impedance important?"
- Impedance can detect degradation at the earliest stages (and quantitatively).
- Can see phenomena under film without accelerating the degradation.
- Coatings are true capacitors, thus one can determine the source of the impedance that is shutting off the capacitor.
- EIS can detect water pickup, change in pore resistance.
- Possibly can determine film delamination (Reference work by Steve Tait).
- Impedance needs to be correlated with other parameters.

2. Case Histories

- Some work on butadiene, observed corrosion at interface.
- One coating company measuring capacitance versus time.
- Note: Worthwhile study would be to investigate status of current use of EIS for protective coatings.
- Coating company has obtained straight line of EIS response versus rust. Observation made after stripping the panel.
- S. Tait study showed that one can detect differences in thick versus thin coating and obtain three different times constant (some are questioning whether this is a valid interpretation).
- One individual stated that if two coatings are in parallel, one should not get too time constant, but this is possible if they have different pore resistances.

- F. Mansfield was able to determine corrosion tendency of anodized aluminum in a few hours, versus 14 days for salt spray.

3. Limitations of AC Impedance

- Latex coatings have different kind of response, because they are designed to be water perennial (thus, EIS measurement may not be applicable).
- Certain types of failures (e.g. blistering) cannot be detected by EIS.
- Only one coating layer blister can be observed.
- Rustless blisters can be produced (from cathodic reaction which produces hydroxide).
- Paint can remain totally intact, (no pores) and one cannot see the delamination with EIS. One may even see an increase in the impedance at low frequency.

4. Field Applications of EIS

- It is possible to measure impedance at two frequencies but this approach is recommended only for field. In lab one would want to measure all frequencies. In field one would not need a frequency response analyzer.
- In field one requires simple equipment with fast data acquisition.
- One can take conventional EIS equipment to the field, although it is a little bit cumbersome.
- High frequency data is very easy to obtain.
- "Nippon" device can measure large number of frequencies in the field.
- In a ten second measurement time, one can get ten readings at one hertz or 10 thousand readings at a kilohertz.
- Another approach is to retrieve the panels from field exposure. One individual suggested doing this at a location near the lab site to avoid panel drying out during transit and to maintain good access.

5. Potential Uses of EIS

- Need to obtain more information on field devices for measuring EIS.
- Paint manufacturers have been using EIS. They are looking for guidance on size of area to investigate, equipment, and other practical aspects of testing.
- Question on testing *in situ*. Some work on EIS of bridge decks has been attempted, but there are some problems. Nippon has done some work, but not published.
- Improvements expected in five years, to allow collecting more field data.

- Paint manufacturers can benefit substantially from use of EIS, to improve product development. This would help generate an industry-wide data base.

- EIS also has the potential to detect defects in coatings (presumably unaged). A valuable tool that needs to be used more in this regard.

6. **Development Needs**

- Measurements should be taken inside and outside corrosion chambers, as well as panels in exterior. This would allow comparison of EIS with other evaluation methods (In a recent program, EIS ranked seven of eight coatings correctly, per B. Skerry).

- EIS could also possibly detect effects of UV weathering, because of that phenomenon's effect on transport and water uptake.

III. ROLE OF EIS IN COATING EVALUATION

1. **Quality Control versus Research**

- It is necessary to distinguish quality contrc test versus corrosion test. Most military specs use salt spray as quality control test.

- EIS can be used as a quality control test, to verify that a coating or specimen has the same properties as that originally tested. It can also be used to observe degradation or other phenomena in coatings.

- EIS can be utilized in product development (i.e. comparing coatings and their ability to achieve certain properties).

2. **EIS in Relation to Other Coating and Corrosion Test**

- "Goal should be to develop a philosophy" (possibly including a battery of tests) rather than trying to find a replacement for the Salt Fog Test.

- A rapid, quantitative test (one hour) is needed.

- EIS could be combined with other tests like cathodic disbondment.

- Only very small amount of data available to correlate EIS to exterior exposure (Scully, Murray, B. Skerry).

- Electrochemical testing should not be relied upon exclusively.

- EIS is fast and accurate, how can the industry be convinced.

- People may be convinced when they try it out and see the quality of the data.

3. Interactions and Communication of Technology

- New procedures need to be made more available to the coatings industry.

- Major organizations for disseminating information include; Electrochemical Society (Proceedings), ASTM (Seminar in November '91), American Chemical Society, *Journal of Coatings Technology, Corrosion Science, Progress in Organic Coatings*.

- Currently we have "bits and pieces" of information on EIS. Need to maintain dialogue between electrochemical and coatings industry.

- Possibly additional workshops needed to address more comprehensive issues. This workshop addressing a few selected critical issues.

- Individual agencies don't support development of a technique (e.g. Army, Navy, etc.). A consortium may be needed (e.g. like MTI).

- FSCT is also working to coordinate these types of activities.

- Montreal Automotive Association has test programs, which is using EIS. Details available from R. Granata.

4. Standard Method

- M. Kendig agreed to draft a standard procedure for performing EIS.

- It would be similar to method develop in ASTM G 106.

- It is not clear whether the various groups and industry would accept such as standard method, because of variations in how each laboratory conducts the experiment.

3B: GROUP 3 – ELECTROCHEMICAL CORROSION TESTING
Workshop Recommendations

1. Encourage Use of EIS by Industry

Time Frame: Immediate
Priority: Definitely Needed

a. General

Electrochemical Impedance Spectroscopy (EIS) has an extremely broad range of potential uses for evaluating and predicting the performance of industrial maintenance coatings and its use should strongly be encouraged

b. Potential Uses

Organizations seeking a rapid quantitative means for evaluating coating degradation should seriously consider investing in EIS. EIS has been used to study electrochemical behavior on a wide array of coatings on steel. There are several techniques that can identify and analyze defects, evaluate film resistance, determine times and rates of degradation and establish and verify degradation mechanisms.

c. Equipment Costs and Need

Complete instrumentation for conducting EIS including hardware and software is commercially available with a cost range of $13,000 to $50,000 depending on the level of sophistication required. All typical systems are quite accurate within their working ranges of frequency and impedance limits. Time to acquire and analyze data is user dependent, with acquisition time of 10 minutes to 48 hours. Rudimentary data analysis and plotting require less than 10 minutes.

d. Expertise to Acquire and Interpret Data

Minimum level of expertise required for operating the EIS equipment is a Laboratory Technician. Usually QA/QC data interpretation can also be performed by a trained technician, although supervision by a knowledgeble electrochemist is highly desirable, particularly in the intitial phases of setup. Interpretation of non-standard test results (new sample type or new test environment) is probably better left to a trained electrochemist.

2. Develop Practical Methods for Field EIS

Time Frame: Short Term
Priority: Definitely Needed

a. There is a need for well-defined, moderately priced, and easily performed EIS unit for collecting data under field conditions. Existing equipment models, although designed and intended for indoor use with AC power source, can be taken into the field for data accumulation and analysis. Simple alternative cell designs are available which are independent of orientation.

Equipment improvements for greater portability, higher measurement capability (higher impedance values at low frequencies, high frequency range), greater degree of sophistication in output format and lower in costs are all desirable but not considered essential.

b. Widespread field application of EIS is not expected until commercial units are developed. One alternative is for a government agency (e.g., Navy) to sponsor development of such a device which would then be available to all interested groups. Following development, a manufacturer would be required to package and market the government developed technology. An alternative to government development is development by a consortium of associations or private companies (to be addressed at general workshop conclusions).

c. The second approach is to allow market forces (i.e., a private equipment supplier) to do the development work to produce a field EIS unit. A few companies (EG&G Princeton, Gamry Instruments, Syncopel Scientific, and a Japanese firm) have commercialized some EIS equipment. The extent of the commercial market is still relatively small, with a strong potential for growth.

3. Develop Standard Method of Testing of EIS for Coatings on Metal

Time Frame: Short Term
Priority: Definitely Needed

a. The purpose of this standard would be to establish a uniform experimental procedure for conducting EIS on coated metals. Because of variations in specific system components and specimens, it is expected that the standard would be fairly broad in designating components. A key intent of the standard would be to provide a means for verifying that the electrochemical response from identical specimens was identical from lab to lab. The ASTM test would establish a means for determining EIS repeatability (within the lab) and reproducibility (among several labs). The method is expected to be modeled after the existing ASTM G 106 "Practice for Verification of Algorithm and Equipment for Electrochemical Impedance Spectroscopy." This draft is expected sometime in 1991.

b. One major concern which may hold up the acceptance of this draft is the problem of repeatability of the coated specimen itself (also see item 4.)

4. Develop/Establish Standard References (Coated Metal Panel) for EIS

Time Frame: Short Term
Priority: Definitely Needed

There was an expressed need for identifying and developing standard reproducible coated metal panels. The coatings would be made available to all testing groups using EIS as a means to verify the operations and equipment. Possible approaches would be to use coil coatings or electrocoating. Commercial supplier of coated specimens for the automotive industry should be contacted to determine the degree of reproducibility of these types of specimens.

5. Develop Improved Software for EIS Analysis of Coatings

Time Frame: Short Term
Priority: Needed

Improved software would provide the following advantages:

- Improved ability to interpret spectra
- More rapid and efficient comparison of different types of systems
- More individualized procedures could be used to analyze for specific coating effects.

6. Develop Electrochemical and Other Models of Coating Degradation and Performance Prediction Related to EIS

Time Frame: Long Term
Priority: Definitely Needed

Substantial additional R&D relating EIS and other electrochemical phenomena to degradation and durability of coatings is needed. Some examples of types of experiments are as follows:

a. What is the validity of rule of thumb criterion that an impedance of more than 10^7 ohms indicates a good performing coating?

b. Does a change in the break point frequency or Nyquist plot parameter indicate an early loss of adhesion or predict or correlate with other degradation properties of coatings?

c. Can EIS be applied to evaluate coatings of relatively low impedance such as acrylic dispersions?

d. Is EIS a valid method for detecting small changes among different batches of a coating or among coatings with slight formulation modifications?

e. Can EIS be used to determine the effect on the properties of the coated metals of accelerated tests like salt fog testing or cyclic corrosion testing or immersion?

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Advances in Accelerated Testing and Coating Characterization

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HIGH-PERFORMANCE VOC-COMPLIANT COATINGS for HYDRAULIC STRUCTURES

by Al Beitelman & John Baker

PART I. INTRODUCTION

BACKGROUND

The corps of Engineers has used solution vinyl paints for corrosion protection of hydraulic structures on inland waterways for many years. These coatings have an excellent service life, however,the liquid paint contains a high amount of solvents. Recently enacted volatile organic compound (VOC) style air pollution regulations put severe restrictions on solvents in paints by limiting the total amount of organic solvents that may be in liquid paint. Use of low solids paints, such as solution vinyl would violate these regulations while use of high-solids or 100 percent solid coatings would be in compliance with these regulations. Although these regulations are currently only in effect in selected portions of several states it is believed similar regulations will eventually be enacted on a wide basis. In order to develop a replacement system to comply with both existing and anticipated regulations, it is necessary to first evaluate potential proprietary coatings.

INVESTIGATION OBJECTIVES

The objective of this work was to develop a performance specification for the procurement of high solids coatings. These coatings would replace the existing solution vinyl coatings currently in use on Corps of Engineers locks and dams. A 4 part approach was used for the work:

a. Investigate generic high-solids and 100-percent solids coatings under laboratory conditions that simulate the exposures the coatings experience in use on hydraulic structures.
b. Identify coatings, based on their performance in laboratory tests, as candidates for field testing.
c. Obtain data to compare high-solids and 100-percent solids coating systems with some widely used conventional coating systems, such as the VR-6 and V-766 solution vinyl coating systems and the MIL-P-24441, type I, 2-package epoxy-polyamide coating system.
d. Provide data that could be used to write performance specifications for high-solids and 100-percent solids coatings.

METHODOLOGY

A literature search was conducted to identify generic high solids and 100-percent solids coating systems that had demonstrated desirable properties in either laboratory or field evaluations. This survey was used to identify coatings that would be good candidates for use on hydraulic structures. A telephone survey and a review of manufacturers' data sheets were used to select the

The Significance and Use of Water Vapor Permeability in Establishing Reliable, Practical Data on Coating Performance

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INTRODUCTION

The need to prevent moisture (and dissolved salts) from reaching the steel substrate is obvious: Water + Salt + Steel = Corrosion. To this end, protective coatings have been designed to act as barriers between the metallic surface and water. As a way of measuring a given coatings ability to prevent the migration of moisture to the steel substrate, test methods were developed to find the "permeability rating" of a product. In general, permeability can be defined as the ability of a given substance, either in liquid or gaseous form, to penetrate and diffuse through a coating. More specifically, ASTM D1653, "Water Vapor Permeability of Organic Coating Films" was developed as a standard test method for determining the ability of water in the vapor form, to penetrate thin films of protective coatings. This test method and others very similar to it, such as ASTM E-96 "Water Vapor Transmission of Materials" have been used to develop data on the permeability rating of various coatings. This data is used to compare protective coatings to one another as well as convince perspective buyers that a given product will perform better in a corrosive environment. This paper will examine the underlying assumptions and limitations of ASTM D1653, as well as, question the relevancy of data generated from this test method.

EXAMINATION OF ASTM D1653

ASTM D1653 "Water Vapor Permeability of Organic Coating Films" began as an offshoot of ASTM E-96 "Water Vapor Transmission of Materials" which was first published in 1953. ASTM D1653 recognized the need to develop a standard test method specific to thin film coatings. Two methods were adopted, Method A - Wet Cup and Method B - Dry Cup. Also included were three values which could be calculated from the data: Water Vapor Transmission Rate (WVT), Water Vapor Permeance (WVP), and Water Vapor Permeability (P).

Both the Wet Cup method and the Dry Cup method involve the use of desiccant typically anhydrous calcium chloride or anhydrous magnesium perchlorate, and distilled water or a saturated salt solution. In Method A water is placed inside the cup; In Method B desiccant is used in the cup. Method A allows for conditions of either very low relative humidity at 73°F (23°C) or 50% relative humidity at the same temperature. Method B allows for conditions of either 50% relative humidity at 73°F (23°C) or 90% relative humidity at 100°F (38°C). For both methods, it

Comparing Short- and Long-Term Testing of Coatings

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Presented at SSPC Conference on
Coating Performance Evaluation & Durability
April 30 - May 1, 1991
Pittsburgh, PA

This presentation is intended to provide a sampling of data comparing short-term and long-term testing of coatings for protecting steel in exterior atmospheric exposures. The data are taken from the SSPC research project PACE (Performane of Alternate Coatings in the Environment).

We are interested in determining long-term durability, i.e., how well a coating performs in a long-term atmospheric exterior test. There are several ways of doing this. First, we can actually perform long-term testing by placing test panels on exposure in aggressive areas or by applying coatings to chemical storage tanks, bridges, or other facilities. Exterior testing is considered the most reliable means of determining long-term performance, although there are disadvantages.

The second approach is to accelerate the degradation, commonly done with salt fog cabinets, humidity chambers, and UV-condensation cabinets. Here degradation (e.g., rusting, scribe undercutting, or blistering) will occur in a shorter time period, so in a matter of (say) 1000 hours instead of 5 years one can observe degradation. An important concern is: does that degradation reflect the degradation produced in an exterior environment?

Another approach is to try to detect the degradation early, rather than waiting for conventional means of degradation such as rusting and blistering. A prime example is using electrochemical means for early detection of degradation. There are other types of tests including water permeability or other electrochemical properties for detecting early degradation.

COMPARING PLANT AND LABORATORY ACCELERATED TESTING

Kevin Mallon and Bruce Rutherford, Mobay Corporation

Serious challenges face the coating specifier and end user in choosing high performance coating systems. New products and formulations are being developed at an accelerated pace to meet changing performance needs and regulatory requirements. Candidate materials for a particular application can be numerous, with assurances from each paint supplier that his product is right for the job. But it is the specifier who must choose the appropriate material.

Mobay Corporation is well known as a major manufacturer of polyurethane coating resins. But Mobay is an end user as well. It is a process chemical company with facilities at various locations that require coating for corrosion protection. In 1985, Mobay's Central Engineering Department with cooperation from the Mobay Coatings Division began a comprehensive testing program. This program utilizes a series of testing methods to measure relative coating system performance on a quantitative basis. The testing is intended to meet several objectives:

First, to establish a standard testing protocol for evaluation of potential coating systems and material suppliers.

Second, to demonstrate the application and performance characteristics of coating materials for new construction and maintenance painting.

Third, to compare paint systems developed in Germany by Bayer AG[1] with formulations utilizing American raw materials, and with commercially available paint systems.

An owner sponsored performance evaluation test program can provide the specifier with valuable data, which forms the basis for responsible material choices. This paper describes the three major portions of Mobay's test program: field application, field exposure of laboratory prepared panels, and accelerated laboratory testing.

[1] Bayer AG is the parent company of Bayer USA Inc., the management holding company that is the parent company of Mobay Corporation.

NAVY PROGRAM TO DEVELOP SHORT TERM PREDICTION OF COATING PERFORMANCE

OBJECTIVE

The objective of this program is to; 1) develop an accelerated aging methodology to rapidly test and evaluate new/old paints and coatings, 2) develop field instrumentation to test "fresh" (less than one year old) and "aged" (more than one year old) coating systems, 3) develop a materials screening test kit to test or screen coatings on site, and 4) apply these developments to wood and concrete.

PROBLEMS

The problems faced by the Navy user are that; 1) 95% of paints are never tested, 2) of those tested, only 25-50% meet all the specs, 3) 80% of the Navy's high performance coatings have been banned due to VOC legislation, and 4) complete testing can exceed some $2000.

CURRENT METHODOLOGY

The current method of predicting performance is based on limited atmospheric exposure. Exposure is usually 2 to 5 years (this is beyond what the manufacturer has already invested), sample population or size is minimal, and deterioration is based on visual standards which are subjective. Performance prediction ends up being based on operational history.

Laboratory methods of analysis focus on physical properties, chemical properties, and sometimes artificial weathering. No reliable link has been established between these properties and long term field performance.

Material acceptance relies on Certification of Conformation and visual standards. Field inspection of newly applied systems again relies on visual standards. Maintenance inspections require experienced personnel to identify the type and extent of deterioration and again relies on visual standards.

NEED

The Navy needs the capability of predicting long-term performance rapidly. We need to reliably accelerate the aging process and a failure prediction model to relate the accelerated aging to field performance. The Navy also needs to be able to rapidly and reliably test coatings on-site. The testing protocol must be for formulated (in the can) coatings, newly applied coatings, and in-situ (old) coatings.

TECHNICAL ISSUES

For accelerated aging: what will be defined as characteristic of

Thermal Wave Imaging for Nondestructive Evaluation of Coatings

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INTRODUCTION

In this paper we discuss the recent results of our infrared thermal wave studies of plasma-sprayed coatings and coatings on automotive metal panels. The purpose of this study is to develop a reliable NDE technique to assess the quality and test the integrity and bonding of these coatings . The experimental method is a pulsed heating and synchronous infrared thermal wave detection technique commonly referred to as box-car thermal wave video imaging.[1–4], shown schematically in Fig. 1. The thermal-wave technique we describe here utilizes time-dependent heating of the target, and simultaneously does real-time processing of the output video stream in synchronism with the time dependence of the heat source.

We use several variations of our technique, but a more-or-less generic version of a block diagram of the equipment is shown in Fig. 2. The system consists of an IR video camera (Inframetrics IR 600), a real-time image processor (Datacube), a computer workstation (Sun 3/160C), and various heating units with their associated electronic drivers and controls. In a typical application, an external function generator might serve as a clock to control the timing of both the heating signals and the operation of the image processor, thus providing the synchronization between the heating and processing functions.

THERMAL BARRIER COATED PISTON HEADS

The application of infrared thermal wave imaging to study the integrity of plasma sprayed zirconia thermal barrier coatings on metal piston heads has been described in detail elsewhere. [1–4] As an example of the results of this ongoing study, in Fig. 3 we show a comparison between an optical image of a piston after the engine test and a thermal wave image, taken with a gate delay time corresponding to the time required for a thermal wave to propagate through the coating to the metal interface and back to the surface. While the image shows a pattern of carbonization correlated with the positions of the fuel injector nozzles, there are no visible coating defects. The thermal wave image of the piston displays a clear subsurface delamination at the center of the piston and two weaker subsurface delaminations on the rim. The thermal wave image has been synchronously averaged over several repetitive pulses of the flash lamps used to heat the surface. A three- dimensional perspective plot of a thermal wave image of a second thermal barrier coated piston head is shown in Fig. 4. This piston showed visible damage in the form of spalled areas in the center. In the thermal wave image we can see additional damage in the form of delaminations around the spalled area at the center and three other regions on the rim.

The Use of XPS/SEM as a Means to Monitor Coating Degradation.

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Abstract.

Three fully formulated coatings systems: urethane, alkyd and latex, were exposed to an industrial environment and an accelerated corrosion/weathering test incorporating UV exposure and wet/dry corrosion cycling. Changes in the surface chemistry and morphology for each coating system, as a function of time in each environment, were followed using XPS and SEM. XPS detected changes in the surface composition of all three systems, for both environments, after short exposure periods. Changes in the high resolution C1s spectra were only observed for the alkyd and urethane systems. The SEM micrographs did not reveal any changes in morphology for these short exposures but substantial changes were noted after 15 months exterior exposure. Some of the trends detected with the exterior exposed samples were reproduced by the accelerated test, and possible reasons for differences are discussed.

Introduction.

The formulation of new coatings intended for exterior use, and improvements in existing coatings, usually involves exposure testing under accelerated and natural conditions to ensure adequate performance of the product in service. The shorter the time period for such testing the better as it enables the rapid transfer of new technologies to the market place; hence the practical importance of a good accelerated test method. Ideally the aim of an accelerated test is to produce modes of degradation that correlate well with those observed during exposure to natural environments, thus implying that the mechanisms of degradation under both sets of conditions are similar. However, many accelerated tests degrade paint systems in an unrealistic fashion, due to the incorporation of artificial conditions which do not occur in exterior exposures. An example of this is the use of light sources which overemphasise the more destructive short wavelength portions of the UV spectrum. Consequently, there is more reliance on natural exposure testing, which has the disadvantage of taking relatively long periods of time to produce useful results.

Recently, spectroscopic techniques such as X-ray Photoelectron Spectroscopy (XPS), Fourier Transform Infrared Spectroscopy (FTIR) and Electron Spin Resonance (ESR) have become available and can be used to monitor changes in bulk or surface chemistry of a paint system after short periods of exposure testing[1]. This paper presents some initial results from work emphasising the use of a surface sensitive technique (XPS) in conjunction with Scanning Electron Microscopy (SEM) to monitor the surface degradation of a paint film during accelerated and natural weathering. The eventual goal of this work is to correlate degradation of fully formulated paint systems when exposed to accelerated test conditions with degradation that occurs during exterior exposure to an industrial environment.

The accelerated test selected for this work was a cyclic corrosion/weathering test involving three major factors thought to play a significant role in the degradation of coatings intended primarily for corrosion control.[2-4] These factors are:

1) UV-condensation effects.

2) Wet/dry cycling

3) Exposure to a corrosive environment.

Experimental.

Materials and Sample Preparation.

Three coatings systems were used in this study: i) a high performance epoxy-polyamide primer with a high solids aliphatic polyurethane topcoat, ii) an alkyd primer/alkyd top-coat system and iii) an acrylic latex primer/acrylic latex topcoat system. In this text these will be referred to as the "urethane", "alkyd" and "latex" systems respectively.

The latex and polyurethane systems were applied to panels of cold rolled steel commercially treated with an iron phosphate coating. These panels were rinsed with methyl ethyl ketone (MEK) prior to painting. The alkyd

MONITORING THE CORROSIVITIES OF ATMOSPHERIC EXPOSURE SITES

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INTRODUCTION

The importance of atmospheric corrosion and its control from an economic, safety and aesthetic standpoint, among others, is well recognized. More structures and materials are exposed to the atmosphere than to any other environments. It is not surprising, therefore, that a vast body of literature exists on testing and performance of materials in the atmosphere and characterization of such environments. However, while much understanding and experience has evolved, on-going research and testing pertaining to atmospheric corrosion and its control is testament to the fact that many problems still remain to be resolved.

The desirability of accelerated testing, to enhance degradation of materials so that data can be obtained in the shortest possible time, has been espoused for a long time. However, the difficulties associated with accurately reproducing natural corrosion damage in accelerated tests have generally been found to be overwhelming. This stems from the dynamic nature of atmospheric environmental variables and their complex synergistic interactions. In other words, "natural" atmospheric environments are neither constant, nor reproducible, either from time to time or from one location to another. Despite the long exposure times often associated with atmospheric corrosion testing in natural environments, the related data almost always appear more credible because of their "real world" appeal. In light of this, it becomes highly desirable to characterize the corrosivities of atmospheric sites, be they for existing test locations, new ones being planned, or where new structures are to be built.

FACTORS AFFECTING CORROSIVITY AND MATERIALS BEHAVIOR

Atmospheric environments have often been classified into four broad categories, viz. marine, industrial, urban, and rural. Historically, these classifications were based on "geographical" location and particular airborne contaminants associated with them that contribute to their relative/respective corrosivities. For example, a marine environment is characterized by proximity to the ocean and salt-laden air that can produce very severe corrosion damage on many structural materials, enhance galvanic corrosion, and accelerate deterioration of protective coating systems/schemes. Specifically, the principal culprit in marine environments is the chloride (Cl^-) ion derived from sodium chloride. Industrial environments are associated with a host of industries producing atmospheric (pollutant) emissions, principally oxides of sulfur (SO_x, e.g., SO_2, SO_3); and smaller amounts of oxides of nitrogen (NO_x, e.g., NO_2), ammonia and its salts (NH_3, NH_4^+), hydrogen sulfide (H_2S), and so on. In urban environments, the principal contaminant is usually NO_x species from automobile exhaust fumes, possibly SO_x from long range transport and, infrequently, soot from home fuels. Rural environ-

ANALYSIS OF RATING SCALES IN COATING EVALUATIONS

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INTRODUCTION

In the coatings industry we do many careful, quantitative experiments to develop better coatings. The use of sophisticated experimental designs is increasingly important. We carefully analyze the data, which we obtain from experiments. We carefully measure the processing and composition variables during the experiment, and we make every effort to control variables. However, the responses which we measure for these designed experiments frequently take the form of subjective ratings on arbitrary scales. Such performance tests as solvent resistance, stain resistance, corrosion protection, salt spray evaluations, weathering, blocking, blistering, orange peel, etc., are based upon ratings.

The very nature of the rating process ensures that these scales are subjective. At best, the rating process produces ordinal rankings; but proper evaluation requires quantitative interval measures. The subject of this paper is a method for using the ratings to obtain the interval measures which are required, but which are only implied by the rankings.

PREVIOUS WORK

There have been attempts to overcome the problem of subjectivity in rating scales. Usually a reference material, whose properties are known, is included with the experimental materials. However, this does not ensure equal interval, repeatable, objective scales.

Rank order statistics are used to evaluate rating scale data [1,2,3,4]. Here the scale itself is ignored and the various paints under test are ranked from best to worst by one or several judges. Rank order calculations are used to equate the rankings of the various judges. These rankings usually work well; judges will rank a group of paints in the same order, subject to experimental error, and it is easy to tell which is the best and which is the worst.

However, the ranking techniques do not solve the problem of objective scales of measurement. The rankings show which is better but there is no way to tell how much better one coating is than the others. This is particularly troublesome in the middle range of the rankings, where discrimination is more important i.e., the greatest error occurs at the place where precision is most important. Another consideration is that one must always deal with a group of coatings and references; the usual rank order statistics do not provide an objective scale which can be used in subsequent testing.

---

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Evaluating Architectural Coatings in Immersion Conditions Using Electrochemical Impedance Spectroscopy (EIS)

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(Presented at the SSPC Coating Evaluation and Durability Conference, 1 May 1991, Pittsburgh, PA.)

Abstract

Five distinct architectural coatings have been immersed in ASTM substitute ocean water and tested using visual and EIS evaluation techniques. The data with respect to changes in coating capacitance, coating impedance, break point frequency as well as visual degradation results through the first eighteen months exposure are presented and discussed.

Introduction and Background

The objectives of this Naval Civil Engineering Laboratory (NCEL) sponsored study being conducted at the David Taylor Research Center (DTRC) are threefold. 1.) Demonstrate the applicability of the EIS technique to the study of five distinct types (physical and chemical) of organic based, anti-corrosion (AC) coatings on a steel substrate. 2.) Characterize the five coating systems using EIS with a minimally acceptable statistical base of 5 samples of each type of AC coating for up to 2.5 years. An additional sample of each type is to be evaluated in greater detail during the initial 30 days of exposure. 3.) Attempt to correlate EIS results to visual damage (rusting and blistering) over the long-term exposure periods and determine the earliest time when any EIS parameter(s) can be used to predict long-term coating breakdown.

The general approach to EIS testing of relatively thick epoxy AC coatings at DTRC has been discussed previously by Scully[1] and considerable detail regarding this study was recently disclosed[2]. The particular samples submitted for this evaluation were delivered from NCEL to DTRC and identified as presented in Table 1. The coating designation indicates the topcoat (first callout)/primer (second callout) chemistry.

The two layer alkyd and the urethane on epoxy coating systems were reasonably smooth, glossy and white or slightly off white in initial appearance. The Zn-epoxy primer (CR-6) contained metallic zinc powder in the epoxy base and a multitude of pores were initially observed throughout the topcoat. The pores are through the coating and exposed metal can be seen at the pore base, the metal presumed to be initially a zinc particle and not the steel substrate. The open pore area was estimated to be 1 %

DETERMINATION OF COATING DETERIORATION WITH EIS

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Abstract

Various parameters which can be obtained from impedance data such as the breakpoint frequency f_b, the magnitude of the phase angle minimum Φ_{min} at high frequencies and the frequency f_{min} of Φ_{min} are useful to estimate the degree of deteroriation of organic coatings on metals. Data obtained earlier for polybutadiene on steel have been reinterpreted using this concept. The delamination function Δ defined in this paper based on impedance data agrees very well with the degree of delamination determined visually according to ASTM D 610. An analysis of impedance data for marine coatings on steel suggests that the coating resistivity decreased significantly during exposure to NaCl. The concepts developed in this papers will form the basis for the design of instrumentation based on EIS for field testing of protective coatings.

Introduction

One of the most successful applications of electrochemical impedance spectroscopy (EIS) has been in the evaluation of the corrosion behavior of polymer coated metals. Kendig and Mansfeld have used the equivalent circuit shown in Fig.1 to analyze impedance spectra obtained for steel and Al alloys coated with polybutadiene (1 - 4). The effect of different pretreatments for steel on the resulting corrosion resistance of the coated steel during exposure to NaCl was characterized by the time dependence of the parameter R_{po} (Fig. 1), which was called "the pore resistance" (1 - 4). Large differences were observed for different surface pretreatments (Fig. 2) and it was argued that for less corrosion resistant surfaces the accumulating corrosion products would produce mechanical pressure on the coating which in turn would produce additional defects and decrease the experimental values of R_{po} (1 - 4).

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY: ONE LABORATORY'S EXPERIENCE USING IT TO PREDICT CORROSION BEHAVIOR OF INTERNALLY COATED STEEL CONTAINERS

W. S. Tait Ph.D., K. A. Handrich and J. A. Maier

Abstract

Internally coated steel container service lifetime (CSL) is significantly <1 year when coated steel container charge transfer resistance (R_{ct}) is $<10^7$ ohms·cm^2 within 100 days of exposure. At the other extreme, CSL is >2 years when R_{ct} is $> 10^9$ ohms·cm^2, and coating capacitance is < 1 nanoFarad/cm^2 after 100 days exposure.

Estimation of corrosion behavior for an entire coated container population (eg. one year's production) can only be made from repetitive samples, because of scatter in EIS data. In addition, it has been our experience that corrosion and coating parameters calculated from EIS data are not normally distributed. Consequently simple statistics can not be used to characterize data sets or for mathematical modeling.

Bode phase plots can be used to locate individual electrochemical events (or time constants) on corresponding Bode magnitude plots. Capacitance values are used to

Technology for Characterizing Protective Coatings

Some of the information presented in this tutorial can be found on the following pages. Tutorial instructors were:

John Murray, David Taylor Research Center
Jonathan Martin, National Institute of Standards & Technology
Reiner Holm, Mobay Corporation
Dwight Weldon, KTA-Tator
William van Ooij, University of Cincinnati

Electrochemical Techniques: A-C METHODS

General: Most of the D-C techniques for evaluating organic coated metal surfaces involve applying the voltage (or current) signal in only an anodic direction (or a cathodic direction). One can acquire a greater amount of information about a metal/solution interface or a coated metal/solution interface by applying a small alternating voltage and examining the resulting system impedance and phase shift as the values change with various applied frequencies. One can also apply a larger voltage range and examine the corresponding current and voltage wave form(s). The former technique has acquired the "popular" name of Electrochemical Impedance Spectroscopy (EIS) and will be discussed first. Many do not consider the latter technique as a true A-C test method, the general name being cyclic voltammetry. One certainly does apply an anodic and then a cathodic voltage to the surface which does result in a positive and then a negative current to the interface which should satisfy a definition of an A-C method. Two examples of the usefulness will be presented.

Electrochemical Impedance Spectroscopy (EIS)

Section Overview: Following a discussion of the generalities of the technique, the basics of the EIS theory will be presented followed by a look at dummy cell test results and then three applications.

EIS involves applying a small controlled cyclic voltage signal to an electrode/electrolyte system at a particular frequency, measuring the amplitude of the voltage and current and the phase shift, calculating the impedance of the system at that frequency, and then repeating the process over a wide range of frequencies. The impedance information can be analyzed using one or more data formats and the results are usually compared to the response from an anticipated equivalent electrical circuit model analog. By using a small amplitude signal (one to twenty millivolts) for the usual experimental time of about one hour, the sample is essentially unaffected and the test approach is considered to be a non-destructive technique. The frequencies examined with most commercial equipment will range from 10^5 Hz down to less than 10^{-2} Hz, the lowest frequency depending on the amount of time one wishes to spend using the equipment with any particular sample. Many of the experiments are performed with the sample potential cycled around the "native potential" or E_{corr}, although the evaluations can be made at any controlled potential.

Probing UV degradation of polymers and coatings by surface analysis and EPR spectroscopy

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Light stability and weather resistance are among the most important properties of plastics and polymeric coatings. The steady improvement of light stability and weather resistance means that accelerated and outdoor weathering tests now take much longer to complete, thus delaying research and development. Therefore, research efforts focus on methods suitable to get information about UV degradation mechanisms as well as to reduce test times. Both goals can be achieved by application of surface analysis techniques such as ESCA probing the very early stages and EPR quantifying radical processes in UV degradation.

Surface analysis techniques are particularly suited for the early recognition of degradation effects because irradiation intensity is highest at the surface and oxygen availability is not limited by diffusion. Irradiation can take place either in air with subsequent transfer of the sample into the vacuum of the spectrometer or through a UV transparent sapphire window directly in the vacuum chamber of the analytical apparatus. If the sample is irradiated under vacuum, the atoms and molecules desorbed from the surface can be detected with a mass spectrometer. It is thus possible to differentiate between radiation induced primary steps and oxidative secondary reactions.

But surface analysis methods can only characterize the unprotected material. In order to evaluate e.g. the effect of UV absorbers, EPR is more suitable. Radical processes are key reactions in the photodegradation of polymers. The ultrashort time weathering method developed at Bayer AG measures the concentration of radicals generated in a bulk polymeric sample as a function of irradiation time. In less than three hours quantification of the number of radicals formed in a polymeric sample when exposed to a specific spectrum of light provides an assessment of the light stability of a resin.

Polymers do not only degrade at their surface. The interface polymer/pigment has to be considered as well, since especially TiO_2 is known to degrade polymers by specific photocatalytic processes. In order to minimize these effects TiO_2 pigments undergo a special surface treatment. Although these treatments can be visualized by electron microscopy they are controlled routinely by surface analysis.

SPECTROSCOPIC METHODS

The interaction of light with matter has intrigued scientists since the day that Sir Isaac Newton first separated white light into its component colors by passing it through a prism. To understand how light, or more generally, electromagnetic radiation, interacts with matter requires a deep understanding of mathematics, chemistry, and physics. However, such depth of understanding is not necessary to treat spectroscopy on a practical level.

Infrared Spectroscopy

Infrared spectroscopy is perhaps the most useful of all analytical methods for the characterization of coatings. Although it is beyond the scope of this discussion to present a detailed theory, a brief outline is useful to more thoroughly understand and appreciate the information which can be obtained by this method.

Infrared spectroscopy falls under the heading of vibrational spectroscopy. Vibrational spectroscopy relies on the interaction of light with vibrating molecules. In simple terms, molecules can be thought of as balls connected by springs. These balls and springs are never at rest, but vibrate with characteristic frequencies which depend on the type of balls (atoms) and springs (chemical bonds). Figure 1 is an example of three possible vibrations which could occur among two hydrogen atoms bonded to a central carbon atom.

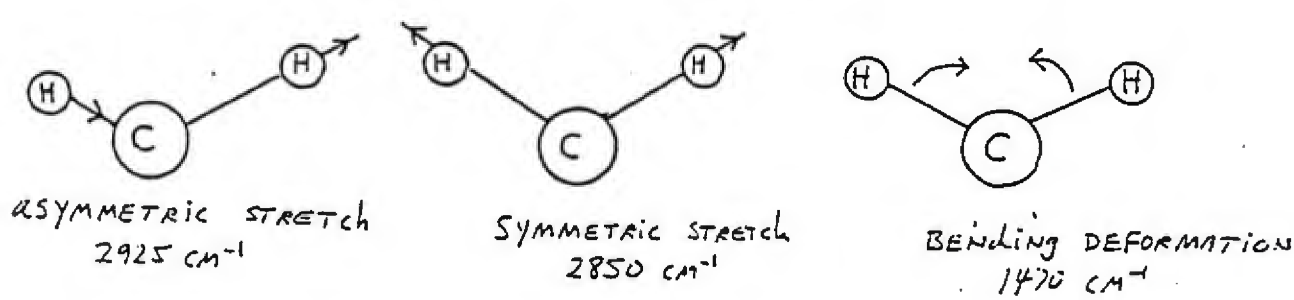

Figure 1 - Examples of stretching and bending vibrations of a CH_2 group.

Figure 1 is useful, in that it depicts how vibrations can occur as either stretching vibrations, or bending vibrations. These vibrations occur at various definite frequencies, given in units of wave numbers, or cm^{-1}. Other units of frequency can also be used, but cm^{-1} is the most convenient one for infrared spectroscopists.

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