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Technical Note

PERFORMANCE PREDICTION FOR COATINGS

Proceedings of a Workshop at the Naval Civil Engineering Laboratory, 15 September 1986

ABSTRACT A workshop was held on emerging technologies that might be applied to rapid performance prediction for coatings. Presentations were made by 14 invited participants, and abstracts of the presentations are included in this report. Prior NCEL research and plans for continued NCEL research were discussed.

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INTRODUCTION

A workshop on Performance Prediction for Coatings was held at the Naval Civil Engineering Laboratory (NCEL) on 15 September 1986. The workshop was held in conjunction with a task entitled Accelerated Testing of Paints, the objective of which is to develop test methods for assuring that the proper coatings, meeting specification and performance criteria, are procured and properly applied at Naval shore facilities.

NCEL is investigating rapid methods for predicting coating performance with the intent of developing tests that will indicate in a period of weeks, or preferably days, how well coatings will perform in the environments of Naval shore facilities. The initial consideration is coatings for steel, with emphasis on protection of structures in a seashore atmospheric environment. Later, performance tests of coatings for masonry or concrete, and also of coatings for wood, will be considered. NCEL is also investigating field tests for determining the quality of available coatings and of coated surfaces.

The chief objective of the workshop was to discover emerging technologies related to performance prediction of coatings that might be applied to rapid laboratory evaluations and to rapid field tests for coatings. Secondary objectives were to promote discussions and interactions among investigators with common problems and goals, and to use new information gained for improving the planned research at NCEL.

The workshop was attended by 14 invited participants (including 7 from universities, 4 from government laboratories, and 3 from industrial laboratories) who were asked to discuss their research that related to the prediction of the performance of coatings. It was also attended by personnel from NCEL and from the Naval Facilities Engineering Command.

The workshop was opened by Captain J. B. Caughman, Jr., Commanding Officer of NCEL, with a welcome to the participants and with a discussion of the magnitude of the problem at hand. The Navy spends 150 million dollars a year on painting operations. Therefore techniques for insuring the proper application of high quality coatings would have a large economic impact on the protection of Naval shore facilities.

The workshop was moderated by Dr. Peter J. Hearst, a research chemist at NCEL.

PRESENTATIONS

Presentations by invited participants were made in the order shown below. Each participant was invited to submit an abstract for publication in these proceedings. The titles of these abstracts and their page location in the Appendix are listed below after the name and affiliation of each speaker. A short summary of each presentation is given.

Key words: Organic coatings, Zinc Coatings, Weathering.

Dr. Carl J. Knauss, Kent State University, "Ultrasonic Detection of Diffusion and Adhesion Loss" (A-3)

Summary: A pulse echo technique is used to study the impedance of a coating film that may be deposited on a quartz bar. The elasticity and the viscosity affect this impedance. The attenuation of the echoes changes as the coating film dries or undergoes other changes.

Dr. Marek Urban, North Dakota State University, "Photoacoustic Fourier Transform Infrared Spectroscopy - An Early Detection Technique for Coatings Degradation" (A-11)

Summary: Several new FTIR techniques are sensitive to the nature of the surface being studied. The photoacoustic technique overcomes some of these limitations. By changing the modulation frequency, spectra that may indicate chemical changes can be obtained at various depths in the coating film or at the coating-substrate interface.

Dr. Tinh Nguyen, National Bureau of Standards, "Degradation of Protective Coatings on Steel in Corrosive Environments" (A-19)

Summary: Thin clear organic coatings on steel were investigated by reflection/absorption FTIR (FTIR-RA). Chemical changes in the coatings and at the metal/polymer interfaces were observed during aging of the coatings under different environmental conditions.

Thomas K. Rehfeldt, Sherwin-Williams Company, "Prediction of Degradation of Polymeric Coating Materials" (A-29)

Summary: Attempts were made to correlate various physical test results and effects of accelerated exposure with the performance in atmospheric exposure. The most applicable mathematical concept for treatment of the data appeared to be the Box-Jenkins analysis, which is an autoregressive integrated moving average model.

Dr. Jonathan Martin, National Bureau of Standards, "A Reliability-Based Program for Predicting the Service Life of Organic Coating Systems" (A-35)

Summary: The reliability-based program uses very accelerated aging, in this case at temperatures of up to 80 °C, together with extensive mathematical treatment of the results that may vary greatly among replicate panels, for the prediction of coating performance. Deterioration evaluation by thermographic imaging and other related work at NBS were also discussed.

Dr. Philip Taylor, Case Western Reserve University, "Predicting the Durability of Adhesives and Coatings by Remote Detection of Hidden Defects and Coating-Thickness Irregularities - A Theoretical and Numerical Study" (A-41)

Summary: Analysis of thermal waves produced by irradiation with modulated infrared laser sources can provide information about impurities at the substrate and about coating defects. Typical results and interpretations were discussed.

Dr. George Loeb, David Taylor Naval Ship Research and Development Center, "Electrical Detection of Coating Deterioration" (A-47)

Summary: Electrical impedance measurements of epoxy-coated steel panels were made at 95% relative humidity with a two-electrode system. The effects of defects at varying frequencies are discussed.

Dr. Martin Kendig, Rockwell Science Center, "Electrochemical Evaluation of the Long Term Corrosion Resistance of Polymer Coated Steel" (A-51)

Summary: An electrochemical impedance spectroscopy (EIS) apparatus, that is computer controlled, rapidly determines coating impedance at different frequencies. These measurements, and also potentiostatic cathodic disbonding (PCD), are affected by defects and deterioration.

Dr. Florian Mansfeld, University of Southern California, "An Electrochemical Impedance Spectroscopy Study of Reactions at the Metal/Coating Interface" (A-57)

Summary: A segmented two-electrode system, using coated substrates made of a series of strips of metal insulated from each other, was studied by EIS. The system was used for monitoring coating performance.

Dr. John Scully, David Taylor Naval Ship Research and Development Center, "Evaluation of Organic Coating Deterioration and Substrate Corrosion in Seawater Using Electrochemical Impedance Measurements" (A-59)

Summary: Coatings immersed in seawater were studied by EIS. Theoretical considerations and practical results were discussed.

Dr. Denny A. Jones, University of Nevada--Reno, "Alternate Immersion Accelerated Testing of Coating Systems for Naval Shoreline Facilities" (A-65)

Summary: Samples of the coating systems prepared for NCEL performance prediction studies were tested by alternate immersion in salt water. The results with different immersion conditions were reported.

Dr. James Stoffer, University of Missouri--Rolla, "Zinc Filled Coatings" (A-71)

Summary: The performance of different types of zinc rich coatings was discussed. The performance of these coatings cannot be followed by the same electrochemical methods used with organic coatings.

Dr. Bernard Appleman, Steel Structures Painting Council, "Reduced Time Frame for Predicting Coatings Performance" (A-81)

Summary: There are several approaches to obtaining performance data including natural and artificial environments and macroscopic and microscopic examinations. The time to reach selected damage levels or failure can be charted. The statistical approach of survival analysis was used to rank generic types of coatings.

John A. Gordon, Eastern Michigan University

Summary: Mr. Gordon was available in Southern California to represent his university. He did not have a prepared presentation and instead discussed some of his experiences with coating problems. He emphasized the importance of good coating application for good coating performance.

OTHER RESEARCH

We were fortunate that so many participants could attend the workshop and present the results of their research. Other research related to performance prediction for coatings has been conducted by investigators that could not attend the workshop. The following are examples:

Dr. David Bauer, Ford Motor Company, has studied free radical formation in coatings, which is related to coatings deterioration.

Dr. Loren Hill, Monsanto Company, using dynamic mechanical analysis, has found that gloss changes in irradiated coatings are also reflected in changes in mechanical properties.

Dr. John Simms, DuPont Company, has found that, for 25 coatings exposed in a DuPont weathering machine and in Florida, the acceleration shift factor varied from 2 to 60, and it was test and material dependent. Thus, the relative effect of artificial weathering for different coatings varied by a factor of 30, and the accelerated test results had to be carefully used in making any performance predictions.

Prior NCEL Research

NCEL research related to performance prediction for coatings was initiated more than 20 years ago (Ref 1 through 3). It has included the investigation of the products of irradiation of free coating films in quartz cells with mercury and xenon arcs, and irradiation in atmospheric exposure with sunlight (Ref 4 through 7). Volatile degradation products were identified by infrared spectroscopy through the Irtran windows of the cells. Changes in the coating films were followed by attenuated total reflection (ATR) spectroscopy; the identifiable changes were primarily related to increases in carbonyl groups. More modern Fourrier transform infrared (FTIR) instrumentation with multiple reflection ATR and other infrared techniques should give much greater information. The degradation results were affected by the type of irradiation used. This type of degradation is more closely related to changes in appearance than to the protective quality of the coating.

Accelerated weathering in the presence of salt was studied with a dew cycle Weather-O-Meter (Ref 8). The use of salt in this instrument is not recommended because of the corrosive effects on the instrument. The Weather-O-Meter was modified so that scribed panels, backed by a cotton cloth, could be sprayed from the back with refrigerated water during the dark cycle to cool the panels and induce condensation on the front surface. During the light cycle, this condensation evaporated again. Once a day, the lower of the two scribed areas on each panel was briefly immersed in salt water. With thin coating films, long filliforms formed at the scribe mark. With thick coating films, more typical undercutting was produced close to the scribe. The operation of the instrument was labor intensive and no attempt was made to correlate the results with the results of field exposures.

Changes in electrical properties of coatings immersed in seawater were studied for 13 coating systems for which performance data had been established at the NCEL atmospheric marine exposure sites on Kwajalein Island, in Hawaii, and at Port Hueneme (Ref 9). DC resistance, AC resistance, capacitance, and dissipation factor were investigated. Similar measurements over a wider range of frequencies could now be made much more rapidly by electrochemical impedance spectroscopy. Although coating systems that performed well showed less changes in electrical properties in short-term (10 da) or long-term (400-da) exposure, the correlation was not sufficiently good to use these changes for performance prediction.

The prediction of paint performance from a combination of accelerated laboratory tests, including changes in electrical properties, permeability data, and results of a wet-and-dry-cycle test, was also investigated (Ref 10). Linear regression analysis of the results from these experiments showed promise for predicting the performance of coatings within a generic type. The best predictors for vinyl coatings appeared to differ from the best predictors for epoxy coatings. But much more research would be required to provide valid performance predictions.

In addition to investigating laboratory tests for performance prediction, NCEL has also developed a field test kit for determining the quality of oil and latex coatings prior to application. The 14 test methods of the kit include a new method for measuring gloss by determining the maximum angle at which clear reflections can be seen. A method using a calibrated gray scale and a nomograph was devised to measure contrast ratio, and another simple method uses a spatula to determine sagging. More practical methods were developed for scrub resistance, washability, and leveling. Established methods for determining drying time, water resistance, hydrocarbon resistance, adhesion, and flexibility were included with modifications. This prototype test kit was prepared for the Army's Construction Engineering Research Laboratory (CERL), which made minor changes in the kit (Ref 11). CERL has distributed the test kit to about 200 field activities and is receiving positive responses. The kit is commercially available.

NCEL has also developed a prototype field test kit for mildewcides in coatings, which uses the baker's yeast that is available in markets and sterile Petri dishes with agar that are supplied in the kit. The effectiveness of the mildewcide is indicated by the distance from a centrally applied coating sample where the yeast growth is inhibited over a 72-hour period.

PLANNED NCEL RESEARCH

Current NCEL Plans

Dr. Hearst presented current NCEL plans for work related to performance prediction for coatings.

Present involvement of NCEL in the procurement of coatings is the development of recommendations for coatings for different uses by test and evaluation. Field requirements, environmental requirements, and manufacturers' proposed new coatings suggest potential coating applications. The results of field exposures of several years duration at aggressive marine sites, which show expected operational performance, and the results of laboratory analyses for critical properties, are used to develop recommendations for coating procurement. These recommendations are incorporated in federal and military specifications for coatings, in guides for construction specifications, and in guides for painting operations.

The objective of NCEL research is to develop new test methods for coatings that are short-term predictors of long-term performance. The work consists of three interrelated phases. Phase I is the development of techniques for artificially weathering coating systems on various substrates and the development of methods for early detection of coating failure to predict long-term field performance. Suitable methods would be used in procurement specifications and for acceptance tests. Phase II is the development of simple test kits to determine, in the field, the quality of coatings before application. Phase III is the development of tests for coated surfaces to verify proper application and to assess the condition of the coating during its service life.

Our steps in the development of a laboratory test method, under Phase I, began with obtaining a new weathering device. This is a KTA Envirotest, which combines simulated atmospheric weathering with a cycle that includes exposure to salt water. We are now determining the effects of changes in exposure cycles, including air temperature and immersion time, on the type and rate of deterioration. We will compare the results with those historically obtained in atmospheric exposure for selection of the best method. Concurrently, we have identified some of the techniques we plan to use for deterioration measurements. These include electrochemical impedance spectroscopy, for which we have obtained the necessary equipment, and infrared thermography, for which we are in the process of obtaining the necessary equipment and software. Laboratory weathering results with coated steel panels will be correlated with the results of field exposure to determine the validity of the accelerated test method.

Our emphasis will be on better methods for detection of initial deterioration, rather than on acceleration of coating deterioration. Thus we need better methods for detecting rusting, blistering, film deterioration at the surface and in the body of the coating, and loss of adhesion. The problem is complicated by the many processes that contribute to coating deterioration. These include photodegradation and oxidation that produce film breakdown, diffusion of water and oxygen that allow rusting, differential expansion and contraction between coating and substrate, freezing and thawing, abrasion, mildew formation, moisture migration in nonmetallic substrates, and deterioration of substrates.

For the development of methods for predicting the performance of coatings, it is important to compare laboratory results with the performance under natural conditions. Current plans are to expose eight coating systems of different generic types to laboratory tests and to atmospheric exposure at our tropical test site on Kwajalein Island. The laboratory exposures will include the Envirotest, the QUV apparatus (which provides alternate ultraviolet radiation and fresh water condensation), and the salt spray test. The deterioration will be evaluated by visual ratings for rusting and blistering, by electrochemical impedance spectroscopy, by infrared thermography, and possibly by other methods. The early laboratory deterioration results will be compared to the deterioration at Kwajalein.

The eight coating systems on steel panels that have been prepared for exposure include a 6-mil wash primer, zinc chromate primer, silicone alkyd; a 7-mil latex primer and topcoat; an 11-mil epoxy-polyamide primer, intermediate, and topcoat; an 11-mil epoxy-polyamide primer and intermediate, and urethane topcoat; a 14-mil inorganic zinc primer, epoxy-polyamide intermediate, and urethane topcoat; an 11-mil zinc-rich epoxy primer, epoxy-polyamide intermediate, and urethane topcoat; a 19-mil coal tar epoxy, two-coat; and an 8-mil vinyl primer, intermediate, and topcoat system.

It would be desirable to expand the above exposures by adding two sets of five coating systems each within the same generic type; for example, five alkyds, preferably of different performance, and five epoxies, or epoxies covered by urethanes. These ten coating systems would be applied at a dry film thickness of 8 mils on 1/16 by 6 by 12-inch steel panels for field exposure, on 1/16 by 3 by 6-inch panels for laboratory weathering, and on 1/32 by 3 by 6-inch panels for infrared spectral changes in laboratory weathering. They would also be prepared as free films for measurement of permeability and other physical properties. Application of some of the same systems at dry film thicknesses of 5 mils and 3 mils would allow the determination of whether the presumably more rapid deterioration of these thinner systems and the earlier obtainable data would give equally reliable prediction information.

The initial Phase I investigations of laboratory performance test methods will be on coatings for steel. Coatings for concrete and masonry and coatings for wood will be the subject of later studies.

The Phase II investigations of field tests for the quality of formulated coatings will seek to supplement the test kit for oil and latex coatings by a kit that can be used for high performance coatings. Additional properties to be determined may include pot life, solvent resistance, abrasion resistance, impact resistance, and hardness.

Phase III is the development of tests for coated surfaces to verify proper application and to assess the condition of the coating during its service life. Very few test methods are currently available and some of these are destructive tests.

Discussion of Methodology

To enhance the value of NCEL research and to provide better standardization and correlation of results among investigators, problems related to methodology were discussed. Responses to specific questions raised by Hearst are listed below:

How many replicate panels are required for laboratory and field exposures? -- Appleman uses six panels for atmospheric exposure and four panels for saltfog exposure. Martin had used 15 replicates in his stress tests.

What are possible problems in accelerating deterioration by using thinner coating systems? -- The coating application would have to be well controlled to avoid pinholes. The primer and topcoat should be applied in at least two coats each, if sprayed. An alternative is to use dip coating. No one believed that there was a critical minimum thickness. Appleman thought that there might be a greater change in effectiveness at about 5 mils. Some thought the minimum effective thickness for a primer might be about 2.5 mils, but this would depend on the surface roughness of the steel.

Should coated steel panels exposed to laboratory or field environments be scribed or unscribed? -- Recent NCEL procedure has been to put scribes on the lower third of the panels. Kendig thought that the scribes would become anodic and might protect the unscribed areas of the panels.* The consensus was that some of the exposed panels should be scribed to detect early deterioration at damaged areas, but that the majority of the panels should be unscribed.

Is there a standard method of scribing panels? -- Although the method of scribing can affect the performance, no one was aware of any standard method, and it was agreed that such a method would be desirable.

In exposures to salt water, should artificial seawater be used or is 5 percent aqueous sodium chloride preferable? -- Most felt that standardization on artificial seawater would be preferable. (The salt spray test and previous experiments with the Envirotest have used sodium chloride solution.)

Because coatings of the same designation are not always exactly the same, and because applications vary, it was suggested that coated panels be stockpiled to enable different investigators to perform experiments with replicate panels.

Much of the deterioration of coatings occurs at defects. Thus, we may study what happens because of improper application. Also, results with properly applied coating films may less readily correlate with the performance of coatings improperly applied in the field.

For testing the quality of applied coatings on steel surfaces, Kendig suggested investigating the possible use of an AC Impedance Tester advertised by the Tokyo Gas Company. This instrument is a simplification of laboratory electrochemical impedance spectroscopy equipment. It operates at several frequencies and costs several thousand dollars.

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*In NCEL experiments underway during the workshop and evaluated later, scribed panels exposed in the Envirotest did show less visual blistering at the unscribed portions of the panels than was observed on unscribed panels. This effect was noted in seven of ten sets of panels that were coated with relatively unprotective latex coatings.

WORKSHOP RESULTS

The participants discussed many interesting and potentially useful methods for detecting defects and deterioration of coatings. Six of the papers covered electrochemical methods and related topics for coatings on steel substrates, six covered spectroscopic and other methods for more general use, and one covered approaches to performance prediction.

The methods that were presented were used to investigate properties of coatings and changes of such properties as the coatings deteriorated in natural or accelerated environments. Some of the methods may, in the future, be useful for following changes in exposed coatings that can in turn be used for the prediction of coating performance. However, for all the methods (including those that were studied as possible performance predictors, such as EIS or reliability studies at elevated temperature) the predictions based on laboratory results will need to be correlated with actual coating performance under typical use to determine their practical applicability.

NCEL became involved in this field more than two decades ago. The workshop demonstrated that since, new techniques have been developed that allow much better detection of defects and changes in coating as they deteriorate. Although the instrumentation has been greatly improved and coating deterioration can be followed better, our ability to predict coating performance has not changed as dramatically. Accelerated tests currently employed in the coatings industry may be useful in indicating the direction for development and formulation of new coatings, but may be misleading in the prediction of the relative performance of individual coatings.

The discussions at the workshop focused chiefly on laboratory tests for coating performance, or on the equivalent of Phase I of the NCEL program. Laboratory methods, using more expensive and complex instrumentation but providing useful performance prediction information, will have to be developed before it is possible to develop the simpler instrumentation that will be required for use by field personnel for predicting the performance of available formulated coatings, or for determining the quality of applied coatings. It is thus important to continue research on laboratory methods for performance prediction to provide more ideas for field tests, under Phases II and III of the NCEL program. Such ideas will be the subject of future workshops.

The workshop was very stimulating and produced much personal interaction among the participants. Discussions of practical and useful experimental details were included. The discussions continued after the adjournment of the workshop and at a later informal dinner.

In retrospect, it would have been desirable to have a 2-day meeting to allow fuller discussion. There was no time to discuss augmentation of NCEL research with other research that would be particularly desirable.

There was a consensus that it would be desirable to hold similar workshops on a regular basis, perhaps annually, or at least biannually. Such workshops could be held separately or in conjunction with semiannual meetings of the Division of Polymeric Materials: Science and Engineering of the American Chemical Society or annual meetings of the Federation of Societies for Coatings Technology.

CONCLUSIONS

1. Considerable further experimentation, over several years, is required before the test methods and approaches discussed at the workshop can be used for performance prediction for coatings.

2. For using laboratory performance results to predict the performance of coatings on steel, electrochemical impedance spectroscopy (EIS) appears to be the most promising current method.

3. For early detection and for instrumental rating of rusting and blistering on steel panels, infrared thermography appears promising.

4. The development of better laboratory methods for performance prediction should aid in the development, or may be necessary for the development, of ideas for field test for predicting the performance of coatings prior to application (Phase II) or for testing in the field the quality of applied coatings (Phase III).

RECOMMENDATIONS

1. Workshops on performance prediction for coatings should be biannually. They should be 2 days long, announced at least 9 months in advance, and preferably held in conjunction with a national scientific meeting related to coatings (such as the American Chemical Society or the Federation of Societies for Coatings Technology).

2. The development of laboratory methods for performance prediction should be encouraged and supported to provide a better basis for the development of the field test methods that would be most useful for the Navy, the Government, and the construction industry.

ACKNOWLEDGMENTS

The donation by the participants of their time for the workshop presentations and for the preparation of the abstracts is gratefully appreciated.

The assistance of Dr. Richard W. Drisko of NCEL in the recording of the workshop proceedings is also appreciated.

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Appendix

Abstracts of Presentations

For Workshop on Performance Prediction for Coatings
Naval Civil Engineering Laboratory,
Port Hueneme, CA

Ultrasonic Detection of Diffusion and Adhesion Loss

Carl J. Knauss
Kent State University
Chemistry Department
Rheology and Coatings Laboratory
Kent, Ohio 44242

Abstract

Three techniques are described which can monitor the performance of coatings for prediction of early failure. The two techniques, ultrasonic impedometry and the strip delay line method, can measure the rate of diffusion of water and solvents and detect when materials begin to loose adhesion to metals and begin to corrode. The third method uses Lamb waves to detect incipient adhesion loss of a coating to metal sheets. These instruments in conjunction with additional accelerated test methods can aid in coating performance predictions.

Introduction

Our laboratory has for several decades been engaged in the development of new and novel methods as well as employing commercial techniques to monitor the rheology of films, coatings and adhesives in the initial state and monitor the viscosity and rigidity of formulated systems as they proceed from a liquid-to-solid. These rheological changes must be monitored as the material properties move towards a cured coating due to solvent loss, crosslinking, coalescence, oxidative polymerization, ultraviolet cure, and similar chemical and physical treatments that transform the liquid system to a solid coating.

Briefly described below are three devices all of which use a non-destructive pulse-echo technique to monitor changes in the viscoelasticity of coating systems as they cure or change due to diffusion of water or other solvents.

These methods are employed to monitor the diffusion of moisture through the coating towards the interphase and detect the loss of adhesion. Coatings that allow for diffusion of moisture, and ions through them to the interface will not perform well, lose adhesion, and allow for corrosion to begin on a metal substrate. Therefore, one of the main concerns is to keep one of the major corrosion ingredients from the interface. Without water, ions, and oxygen the corrosion process can not proceed. This transport of materials is not the only consideration to evaluate performance of coating for extended life value but is an important step which should be taken in conjunction with ultraviolet and salt spray and related tests.

Pulse-echo Method

The three types of measurements described below can all be done using the same electronic equipment whose operation is described here.

The pulse-echo technique is really a miniature sonar device whereby a ultrasonic pulse of four microsecond duration in the megahertz frequency region is sent to a PZT or quartz transducer affixed to the test device. The transducer converts the electrical energy to a mechanical pulse which produces a shear wave because of the crystal cut of the transducer. The shear pulses are reflected back and forth in the test device and each time an echo strikes the transducer, the pulse is converted from mechanical energy to electrical energy and is observed by a detection device. These echoes travel back and forth and decay exponentially until the signal is lost after which another pulse is introduced. The repetition rate of the initial pulse is 120 per second.

A block diagram of the necessary components are presented in Figure 1. The r.f. pulser whose frequency can be varied emits a signal as described above; our tests were usually run at 15 megahertz. The echoes reflected from the test device, in Figure 1 a delay line, are sent to a calibrated attenuator which is employed as a means of measuring the decibels of attenuation of the echoes caused by the sample on the line. The exponential decay of the successive echoes can be observed by an oscilloscope or can be noted by integrating the signal area under the detected r.f. echoes.

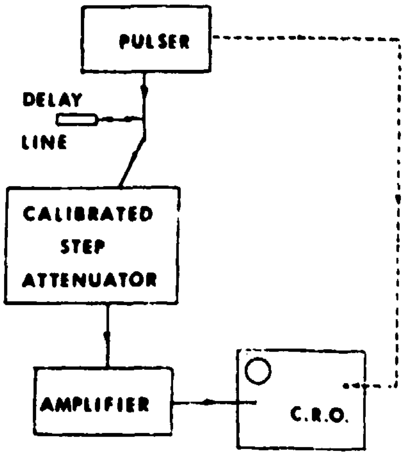

Figure 1

Using the above pulse-echo technique, one can use various devices to monitor changes of signal as the test samples undergo transformations.

Three methods have been used in our laboratory to measure diffusion and corrosion or loss of adhesion at the metal-coating interface. The three devices used are: (1) impedometer, (2) strip delay line, and (3) Lamb wave proporgation.

1. Impedometer

The impedometer is used to measure a coating as it changes from a liquid upon application to solid after cure. The shear mechanical energy is transmitted through a fused quartz bar to the coating-bar interface as shown in Figure 2.

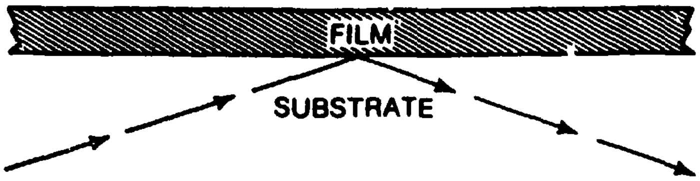

Figure 2

The sample for the pulse-echo impedometer is placed on top of a fused quartz bar is spread uniformly over the top surface; see Figure 3. The Y-cut transducer which produces a shear wave has a resonant frequency of 5 megahertz and can operate at the odd harmonics of that frequency. Our laboratory usually can work with this transducer up to 45 megahertz. If one wants to obtain higher frequencies, a higher natural resonant transducer must be used which can operate at higher harmonic frequencies. In order to work with thin films, higher frequencies must be employed since the shear wave must be partly dissipated in the coating and reflected back without traveling to the air-film interface.

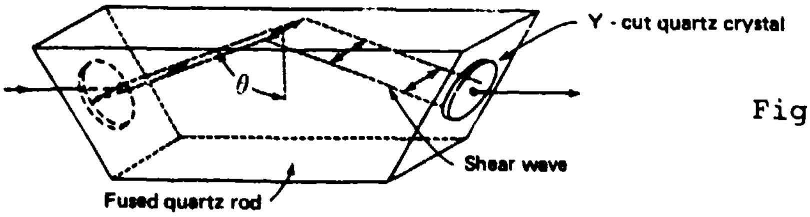

Figure 3

The technique that has proven to be of value for coatings is to measure the overall mechanical impedance, Z, which is produced by the film to the ultrasonic shear wave impinging from the substrate. The mechanical shear wave is polarized in a direction transverse to the propagation direction and parallel with the interface as noted in Figure 3. The Z is calculated from the geometry of the system and the known impedance of the substrate. Quartz is used because Z is well-known and it propagates the ultrasonic shear wave with little dispersion. Aluminum can also be used as a substrate but shows greater attenuation of the wave. Normal iron or steel samples give a much greater dispersion of the wave but control results sometimes are possible.

Measuring only the Z does not permit η' or G' to be isolated and calculated. If one obtains a limited amount of rigidity during the early stages of drying, G' can be calculated without knowing the phase shift as is noted by Knauss.[1] The apparatus was first described by Mason, Baker, McSkimin and Heiss[2] and also was applied to the study of lubricating oils by Barlow and Lamb[3].

The r.f. signal produced by the echoes is shown in part A of Figure 4; the detected echoes are shown in part B of Figure 4. After a coating is cured on the bar, it can be attacked by water of other solvents to determine if diffusion is taking place or perhaps follow the rate of diffusion to determine the performance of the coating to solvent environments. The echoes would rise towards the level they originally achieved prior to placement of the coating.

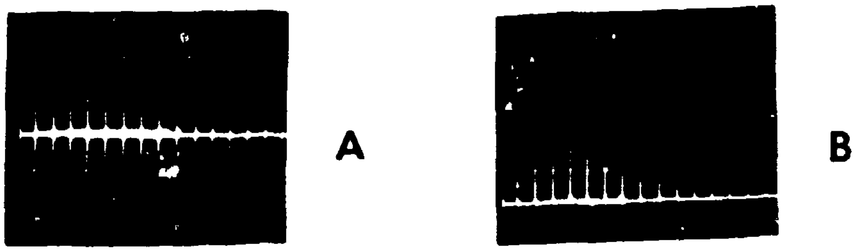

Figure 4

2. Strip Delay Line

A strip delay line consists of a rectangular plate with a piezoelectric shear transducer mounted on one end as in Figure 5. The transducer propagates a shear wave along the positive Y direction with the displacement in the +X direction. The x, y, and z directions represent the cut of the transducer on the end of the strip. Strip delay lines can have various types of wave motions propagated in them[4]. The thickness and frequency of the line determines the type of wave generated; our work was done using a symmetric shear SS (0) mode. The lines used operate in a frequency range of 1 MHz to 20 MHz; however, data reported by us is for 2.1 MHz.

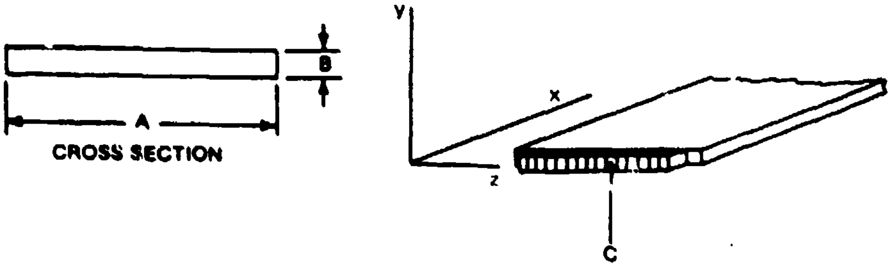

Figure 5

When a sample is placed in contact with the line the wave is attenuated and the propagation velocity or phase velocity decreases slightly. The attenuation is expressed in decibels per echo using the pulse-echo technique[5] and the decrease in delay time caused by the sample is expressed in degree of phase shift per echo. Both values are used for calculation of the shear modulus of the material.

The impedometer is not sensitive enough to measure the properties of low viscosity liquids and can not be used to dip into a container of material to be investigated. The strip delay line because of its extreme sensitive can not be covered by the sample to any great depth if one would want to follow the liquid-to-solid cure of a coating. After the coating is cured on the plate, the device can be immersed into a solvent to detect diffusion through the coating.

3. Lamb Wave Adhesion Detection

The same pulse generator described before can be used to excite a transducer immersed in an oil which can be moved to produce an angle of incidence of 0° to 90° between the probe, Figure 6, and a coated plate. The plate can be coated and cured under various conditions and checked to determine if corrosion products are developing at the coating-metal interface and/or the coating is loosing adhesion.

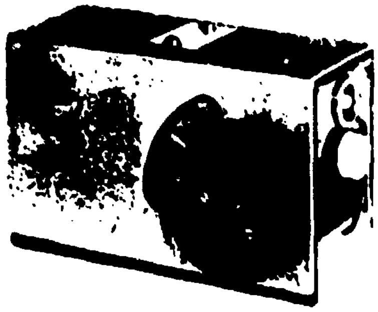

Figure 6

The probe shown in Figure 6 must be coupled to the test sample with glycerol and a similar probe must be placed at a set distance from the first so one can send the Lamb wave and the second receive the wave. The change in received signal indicates the changes in adhesion.

The transducer's angle of incidence must be changed so various modes of Lamb waves can be generated which depends on the frequency of the r.f. signal and the thickness of the test sample.

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PHOTOACOUSTIC FOURIER TRANSFORM INFRARED SPECTROSCOPY
AN EARLY DETECTION TECHNIQUE FOR COATINGS DEGRADATION

Marek W. Urban
North Dakota State University
Department of Polymers and Coatings
Fargo, ND 58105

ABSTRACT

A new spectroscopic tool, photoacoustic Fourier transform infrared spectroscopy as a method to characterize coatings and interfaces is described. It is a novel technique that allows to characterize surfaces at various depths and provides information on molecular level. Because of nondestructive nature it can be used as an early detection method of detection of weathering processes, kinetics of UV curing and to determine substrate-coating interactions. Major advantages and applications of this technique are described.

INTRODUCTION

With the advent of FT-IR spectroscopy, several surface sensitive techniques have been developed among which attenuated total reflectance (ATR), reflection-absorption (RA) and diffuse reflectance (DRIFT) spectroscopy play a key role. These and other surface techniques were developed as a need arose to study specific surface problems. Therefore, each surface technique is not a versatile method and the choice of which technique to use depends on the surface morphology and its optical properties. For example, a poor contact between the sample and the ATR plate limits application of the ATR method to study preferentially soft surfaces such as polymer films or rubber.[1,2] The reflection-absorption method, on the other hand, has been successfully applied to study polymer coatings on highly reflective surfaces of silver, gold or chromium.[3,4] Powders and fibers can be affectively analyzed using DRIFT technique.[5,6,7]

Thus, each surface technique has limited applications and, moreover, usually require sample preparation that can affect the morphology of the surface. The ideal technique would be one which produces infrared spectrum that retain the characteristics of a transmission spectrum while being subjected to minimal or no sample preparation and would provide no restrictions on a color or a shape of the surface. The relatively recent application of a 19th century concept, the photoacoustic technique, shows a great potential in overcoming the limitations imposed by other surface FT-IR techniques.

PHOTOACOUSTIC EFFECT IN THE INFRARED REGION

Figure 1 depicts the schematics of the experimental setup.

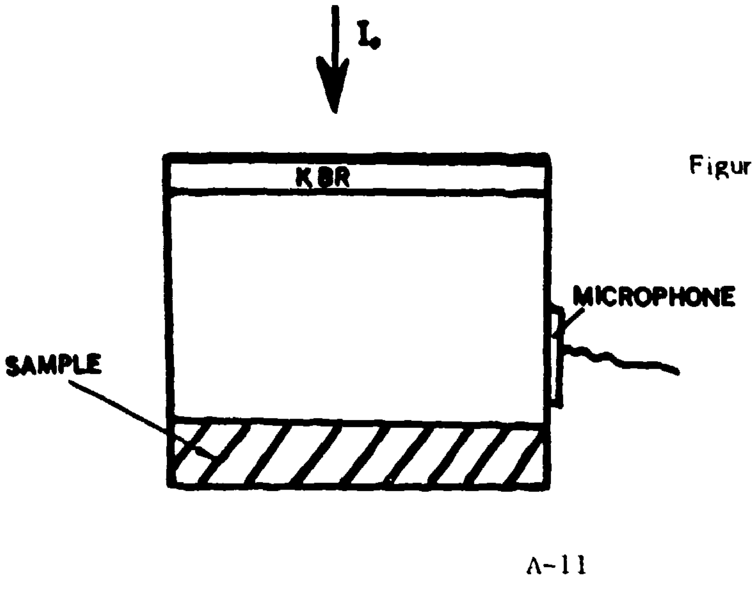

Figure 1. Schematic Diagram of the Photoacoustic Attachment.

The infrared spectrum is obtained by measuring the heat generated from the sample surface due to absorption processes. When modulated infrared radiation irradiates the surface the sample absorbs only photons with energy that correspond to allowed vibrational states within the molecular or crystal moiety. A release of the absorbed energy occurs usually in a form of heat generated from the surface. The heat released from the surface causes temperature fluctuations at the sample surface which, in turn, causes a small boundary layer of gas to expand and contract. This gas layer acts as an acoustic piston on the remaining volume of gas which carries the pressure changes to a sensitive microphone. The microphone detects the pressure changes and the generated electrical signal is Fourier transformed and recorded in the form of an infrared spectrum.

As stated above, there are two processes involved in the generation of photoacoustic signal: absorption of light and a heat release. This is schematically depicted in Figure 2.

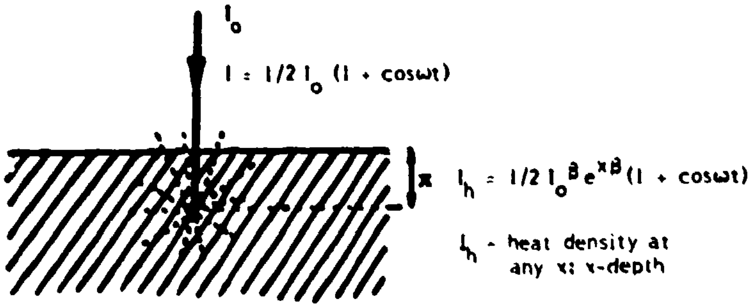

Figure 2. Generation of Signal in The Photoacoustic Effect.

$\mu_{op} = \frac{1}{\beta(\nu)}$ $\beta(\nu)$ - abs. coefficient

μ_{th} $\left[\frac{2\alpha}{\omega}\right]^{\frac{1}{2}}$ $\alpha = \frac{k}{\varphi C}$ - thermal diffusivity

k - thermal conductivity
φ - density
C- specific heat

μ_{op} - optical absorption length

μ_{th} - thermal diffusion length

Thus, the intensity of the photoacoustic signal generated from the surface is a function of optical and thermal properties of the sample. Rosencwaig has classified samples as optically transparent or opaque and thermally thin or thick (good or poor heat conductors) depending on the relationship between the absorption coefficient and thermal diffusion length.[14] Hence, photoacoustics in general, can be considered not only as a spectroscopic method; it is a calorimetric method to measure how much of the electromagnetic radiation absorbed by a sample is converted to heat. Therefore, it can be used to measure an absorption spectrum on the one hand, and the thermal properties of the surface on the other. With these spectroscopic and nonspectroscopic capabilities photoacoustics should find many important applications in the coatings industry.

SURFACE DEPTH PROFILING STUDIES

The classification of materials as optically opaque or transparent and thermally thick or thin as given by Rosencwaig has very important implications.[14] Here, we give only a short outline of the Rosencwaig-Gersho results. A magnitude of the photoacoustic signal generated from the surface depends on the modulation frequency of the incident light. For thermally thick and optically transparent materials, this relationship is given by equation 1:

$$PA \propto \omega^{-3/2} \quad (1)$$

where: PA - photoacoustic signal,

ω - modulation frequency.

According to the theory, a heat that is able to reach the surface is generated within the first thermal diffusion length from the surface and is related to the thermal properties of studied materials as well as the modulation frequency. Thermal diffusion length, μ_{th}, is related to modulation frequency, ω, through the following equation:

$$\mu_{th} = [2\alpha/\omega]^{1/2} \quad (2)$$

where: μ_{th} - thermal diffusion length

α - thermal diffusivity; $\alpha = k/\rho C$(k-thermal conductivity;

ρ - density; C - specific heat).

According to equation (2), a decrease in modulation frequency causes an increase of the thermal diffusion length and therefore, the photoacoustic signal that reaches the surface comes from greater depths. This is the basis for surface depth profiling studies. Thus, infrared spectra at various depths can be obtained. In modern FT-IR instruments the modulation frequency can be easily adjusted by changing the mirror speed of the interferometer.

Urban et al.[15] have studied a double layer film of PVF_2-on-PET, such as that shown in Figure 3.

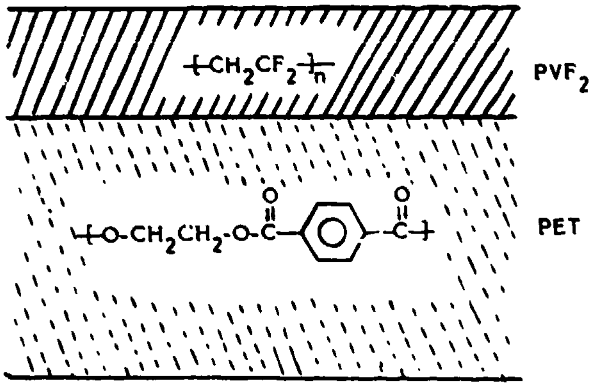

Figure 3. Double Layer PVF_2-on PET Films.

The bottom film, PET, has a characteristic band at 1738 cm^{-1} which is due to C=O vibration of PET. By monitoring the intensity of this band as a function of mirror velocity, one should be able to determine the penetration depth of infrared light into the surface. Figure 4 shows a series of the PA FT-IR spectra obtained with various mirror velocities.

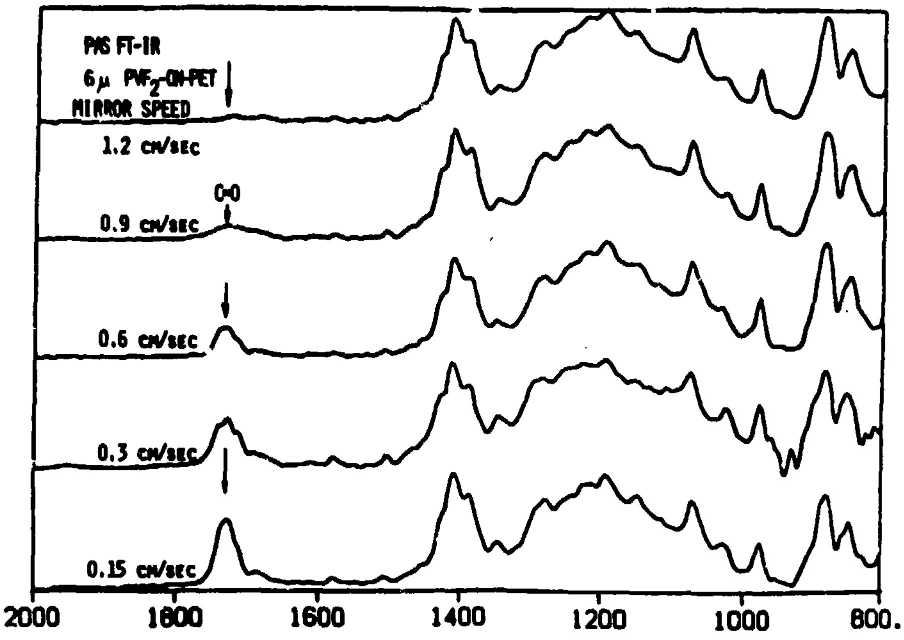

Figure 4. Photoacoustic Spectra of 6μ Thick PVF$_2$ Layer on PET Obtained with various Mirror Velocities. (Reproduced by Permission From Ref. 15).

It is seen that, as the mirror speed decreases, the intensity of the carbonyl band increases. Thus, the slower mirror velocity (lower modulation frequency) leads to a deeper penetration depth of light into the surface. According to the theory for optically transparent and thermally thick films, such as PVF$_2$ and PET films, a log-log plot of the integrated intensity of the carbonyl band as a function of modulation frequency (which is proportional to the mirror velocity of Michelson interferometer, V; ($\omega = 4\pi V\nu$) leads to a slope of -3/2. Figure 5 depicts this relationship and obtained slopes for 6 and 9μ thick PVF$_2$ layers on PET are in agreement with the theory.

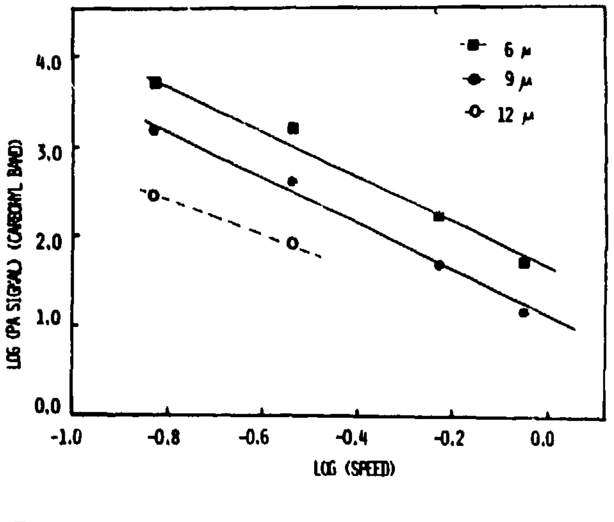

Figure 5. Log-Log Plot of Integrated Intensity of the Carbonyl Band as a Function of the Mirror Velocity: A - 6μ PVF$_2$ Film; B - 9μ PVF$_2$ Film; C - 12μ PFV$_2$ Film. (Reproduced by Permission from Ref. 15).

Thus, this model system can be translated to more practical applications, in particular, to study interfaces between coatings and substrates or an early detection of corrosion processes at the interface.

COATING-SUBSTRATE INTERFACE

The structure, environmental stability and composition of coatings are intimately related to the properties of many materials in their end uses. The surface treatment is particularly important to improve hydrothermal resistance of interfaces in composite materials. In order to improve this resistance and to increase the bonding between glass fibers and a polymer matrix, the fibers are treated with coupling agents, usually oligomers.

Unlike monomeric species adsorbed on the surface, trifunctional oligomers such as γ-metacryloxypropyltriethoxysilane (γ-MPS), may form multilayers that interact with each other as well as with the substrate.[16] Figure 6 shows PA FT-IR spectra of SiO_2 and γ-Al_2O_3 treated with hydrolyzed γ-MPS solution.

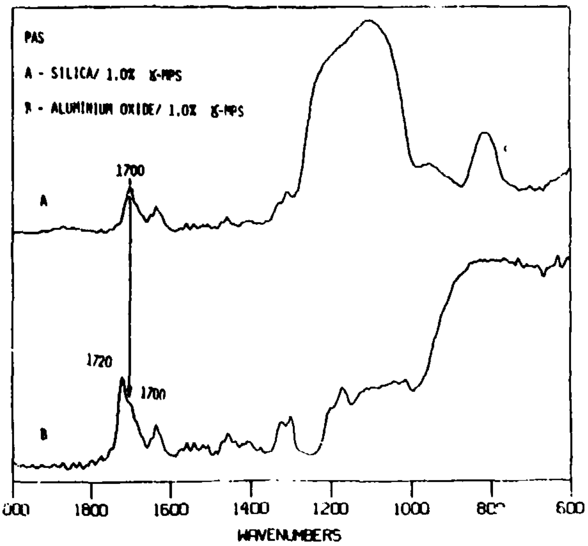

Figure 6.
PA FT-IR Spectra of Silica and Alumina Treated with 1% γ-MPS Solution.
(Reproduced by Permission from Ref. 16).

Although both spectra show similar features due to the coupling agent, the relative intensities of the carbonyl bands are different. Each spectrum shows two carbonyl bands: the band at 1700 cm^{-1} is due to the hydrogen-bonded carbonyl groups whereas the 1720 cm^{-1} band is due to free C=O (nonbonded) species. It is apparent to note that the relative intensities of these bands are different. The 1720 cm^{-1} band is stronger when γ-MPS is deposited on γ-Al_2O_3. The same band, however, becomes weaker when g-MPS is deposited on SiO_2. The opposite behavior shows the band at 1700 cm^{-1} (hydrogen-bonded carbonyls). This observation is consistent with the fact that the alumina surface has less hydroxyl groups present on the surface. The above example clearly demonstrates that PA FT-IR spectroscopy can be applied to monitor bonding between coatings and metal oxide surfaces. Moreover, it can be used to quantitatively determine surface functionality and reactivity. A quantitative analysis of both bands as a function of γ-MPS concentration on γ-Al_2O_3 surface is shown in Figure 7.

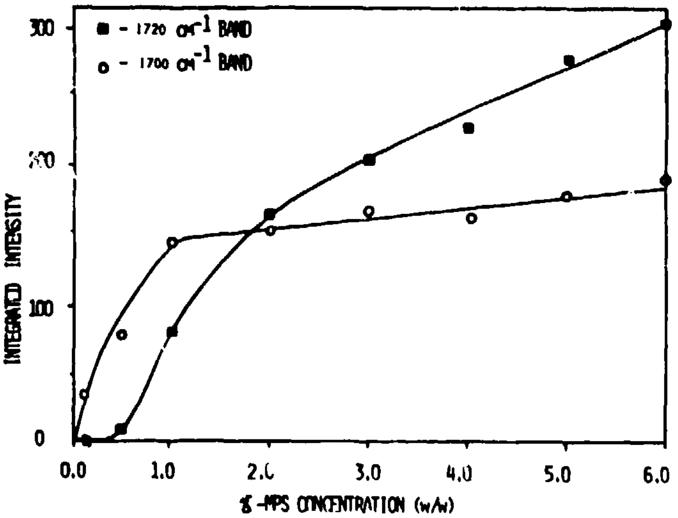

Figure 7.
Integrated Intensity of the Carbonyl Band as a Function of the γ-MPS Coupling Agent.
(Reproduced by Permission from Ref. 16).

In the 0-1% concentration range, the hydrogen-bonded carbonyl band at 1700 cm^{-1} increases rapidly whereas the free C=O intensity at 1720 cm^{-1} is very low. Above 1% concentration the former flattens and the latter increases. This behavior indicates that at 1% Y-MPS concentration all surface hydroxyl groups have reacted with the coupling agent and the excess forms non-hydrogen bonded Y-MPS surface layers. Thus, using PA FT-IR spectroscopy it is possible to detect and quantitatively analyze bonding between the substrate moiety and the oligomer, in this case, the Y-MPS coupling agent and $Y-Al_2O_3$.

POTENTIAL OF PA FT-IR SPECTROSCOPY

PA FT-IR can be applied to study the surface protection of polymeric materials, wood, paper, fibers and composite materials. The versatility of this technique in answering a broad spectrum of questions such as coating composition at various depths, surface functionality of substrates, coating-substrate bonding mechanisms is still in an initial stage. This is because no more than a few years ago the technique was in development stage. Relatively low signal-to-noise ratio made application of this technique rather impractical. Today, with additional improvements, we are in a position that photoacoustic infrared spectrum can be obtained in a few minutes. Thus, PA FT-IR creates great opportunity for coatings industry to answer a number of important questions and offers advantages summarized below:

1. The studied sample is in its native state (no sample preparation).
2. It allows to perform surface depth profiling studies.
3. It is possible to monitor the orientation of the surface.
4. It has relatively good sensitivity (few monolayers coverage).

With these advantages it can be applied to in-situ studies of weathering and degradation processes of coatings, corrosion, kinetics of UV cured coatings and as an early detection method in detrimental effects of sunlight. Until the development of photoacoustic spectroscopy, many natural or synthetic materials could not be studied by conventional spectroscopic techniques. Usually these materials occur in the form of gels, oils, suspensions of fibers, textiles, or paints, coatings and so on. With photoacoustic spectroscopy, optical absorption spectra of virtually any material can be obtained. Although the formative stages of photoacoustics have passed, its potential both as a research and as an analytical tool appears unexplored. This is particularly true in the field of coatings where there is a need for such a technique.

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Degradation of Protective Coatings on Steel in Corrosive Environments

T. Nguyen, E. Byrd and D. Bentz

Protective organic coatings, although highly polymeric, are frequently susceptible, in service environments, to degradation that reduces their effectiveness. Electrochemical and surface analytical literature (1,2) indicate that degradation at the steel/coating interface is primarily responsible for the failure of coatings to protect metal substrates from corrosion. Degradation at the interface can lead, for example, to delamination of the coating and corrosion of the substrate beneath a protective coating. If the effectiveness of protective coatings is to be increased through development of improved coatings and coating systems, it is essential to have a better understanding of the mechanisms by which interfacial degradation occurs.

Current surface techniques such as x-ray photoelectron and Auger electron spectroscopies and ellipsometry have been useful in understanding the mechanisms of delamination of coatings on metals. However, the two former techniques, though capable of providing chemical information, are destructive methods and the latter only provides physical and geometrical properties; none are suitable for in-situ metal/polymer interfacial studies. We have employed reflection/absorption FTIR (FTIR-RA), which has shown great promise as a nondestructive tool for chemically characterizing surface and metal/polymer interfaces (3), to study the interfacial interactions and degradation of protective coatings on steel in corrosive environments. We have analyzed in depth the FTIR-RA spectra of organic coatings on steel substrates and have applied this technique for quantitative studies of thick coatings on steel substrates (4,5).

The degradation in the bulk and at the metal/coating interfaces of three coatings, epoxy, polyurethane and polybutadiene, on steel substrates exposed to corrosive environments was investigated using the FTIR-RA technique (6-10). Coatings of various thicknesses on polished cold-rolled steel substrates were exposed to aerated 80% RH (saturated salt solutions) at 40° and 75°C for up to 8 months, and FTIR-RA spectra and optical micrographs were taken at different time intervals. To differentiate the thermal oxidative effect from the corrosion process effect, samples were also exposed to a 0% RH and 75°C environment. The results obtained (e.g., figure 1) have shown that amine-cured epoxy degrades in the corrosive environment but not in the thermal oxidative environment, suggesting that the highly alkaline corrosion products are probably responsible for the coating degradation. FTIR-RA results indicated that, in a corrosive environment, amine-cured epoxy on steel undergoes considerable weakening and dissociation of the hydrogen bonds, and dehydration reactions (e.g., figure 2 and reaction 1) which subsequently results in allyl-nitrogen bond scission and loss of aromatic structure in the main chain (reaction 2).

Our work on thin films (< 500 nm) has indicated that there is no strong chemical interaction between the amine-cured epoxy and steel substrate, and our thermodynamic calculations have shown that the epoxy/steel bond is not stable in water and even less stable in aqueous corrosion solutions. Both of these results may explain the premature delamination of this coating system in corrosive environments as observed in our laboratory and also reported by the industry. Based on this work, we suggest that for this coating system to be used in corrosive environments, the steel surface must be chemically modified to increase mechanical adhesion and metal/coating bond stability in aqueous environments.

In contrast, polybutadiene coating shows considerable interaction with steel substrate. This is consistent with the observation that in corrosive environments, polybutadiene debonds cohesively, not adhesively as in the case of amine-cured epoxy. In corrosive environments, polybutadiene undergoes not only hydrogen bond weakening (figure 3) but also extensive degradation in the chain. This latter degradation results in the formation of various highly - oxidized products such as acid and ester and loss of unsaturation (figure 3b). Most of the unsaturation loss in the early corrosive degradation occurred at the vinyl end.

Although we have not analyzed the degradation of polyurethane coatings due to corrosive exposures in detail, our preliminary results (figure 4) indicate that polyurethanes undergo extensive crosslinking, which results in brittleness and crazing in the coating, and degradation which results in a decrease of amide I, amide II and NH groups and formation of nonassociated NH.

The characterization of fairly complex organic molecules by FTIR-RA formed during degradation offers a powerful means for studying the degradation processes, both in the bulk and at the interface of protective coatings on steel subjected to corrosive environments. The information obtained has been very valuable in understanding the mechanisms by which a protective coating degrades during service.

Parallel to our works on degradation mechanisms of protective coatings on steel, we are also searching for new and/or improved methods to nondestructively detect early corrosion on steel beneath opaque coatings. Current methods to detect early corrosion (micrometer size spots) on bare metals involve the use of scanning electron and light microscopies which provide only qualitative assessments of the corrosion. For metals protected by thick clear and opaque organic coatings, prior research at our laboratory has led to development of a laboratory method, based upon infrared thermography, to quantitatively assess corrosion on a millimeter scale (11). Our subsequent research using thermal-wave imaging in conjunction with computer image analysis, has led to quantification of micrometer-size corrosion spots on metals, with or without thin protective organic coatings layers (12-15). The research has been supported by the Office of Nondestructive Evaluation of the National Bureau of Standards.

Thermal-wave microscopy is a new nondestructive technique which can detect and image surface and subsurface defects such as cracks, voids, delaminations, and dopant regions, at a higher resolution than the conventional optical, x-ray or acoustic probe methods. The technique employs heat flow to detect spatial variations in the thermal properties of a material; it is very sensitive to minor disruptions in the lattice structure, e.g., due to the addition, by diffusion or implantation, of foreign ions at concentrations less than 1 in 10^3.

The resolution and penetration depth of thermal-wave microscopy depend upon the beam spot size and modulation frequency, and the thermal properties of the materials investigated. The resolution varies from 200 to 0.2 μm in thermal conductors, and from 20 to 0.02 μm in thermal insulators, depending on the frequency.

Thermal-wave electron microscopy has been successfully applied in our lab to, 1) imaging corrosion products of approximately 5 μm in size on the surfaces of both bare steel and steel protected by clear or opaque organic coatings, 2) imaging the microstructure of steel both in and outside corroded areas, as well as under a thin organic film, 3) estimating thicknesses of corrosion product layers, and 4) determining, through use of computer image analysis procedures, the shape and area, and percent of the total area which has corroded. Examples of these studies are illustrated in figures 5 and 6. The method has potential impact as a technique for rapidly screening the effectiveness of corrosion inhibitors and protective coatings, and for developing data on fundamental degradation processes which are needed in the development of test procedures to aid service life prediction of protective coatings.

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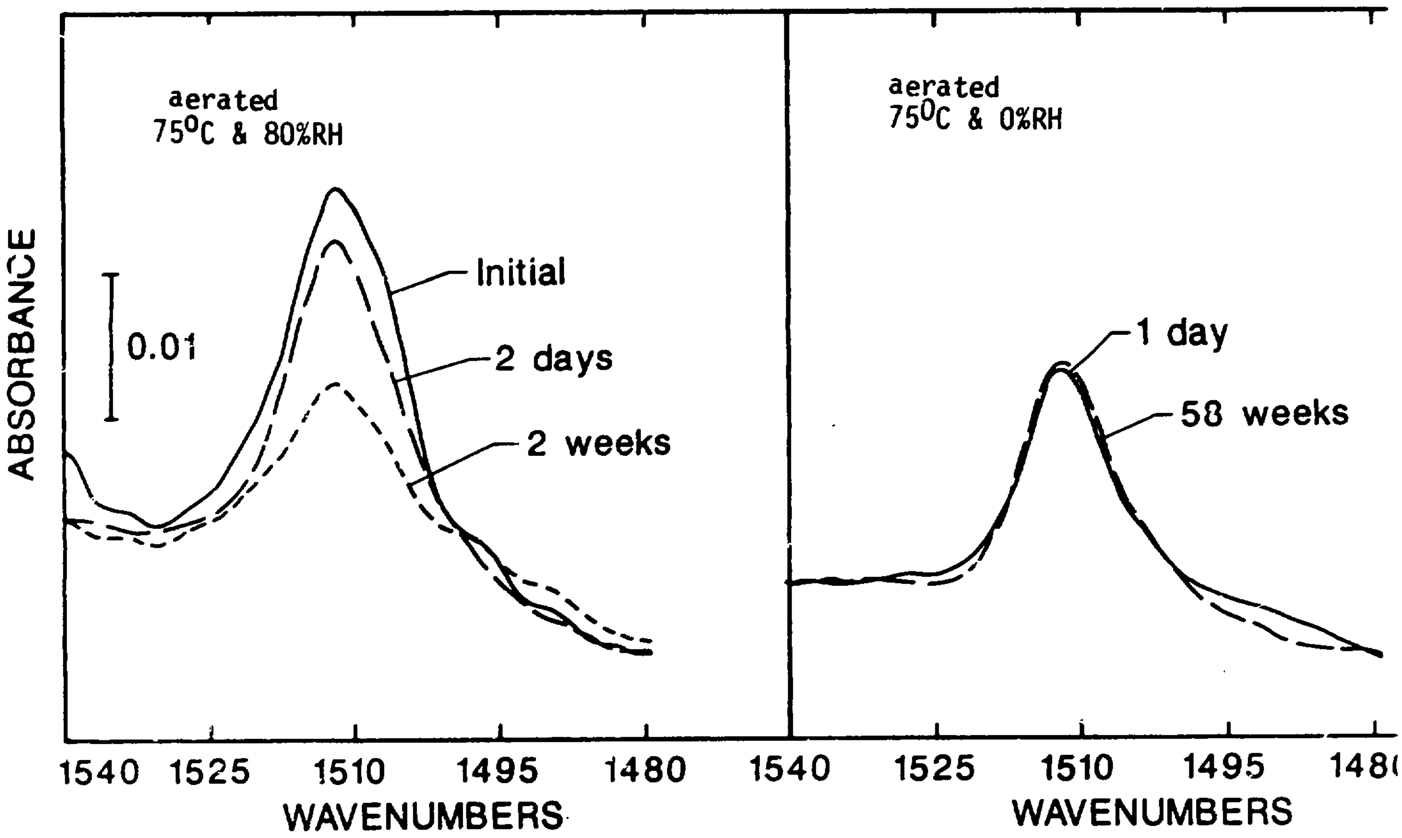


Figure 1. FTIR-RA of the 1513 cm^{-1} band of a 49 nm amine-cured epoxy coating on steel aged in corrosive and oxidative environments, showing the degradation occurs in the former but not in the latter.

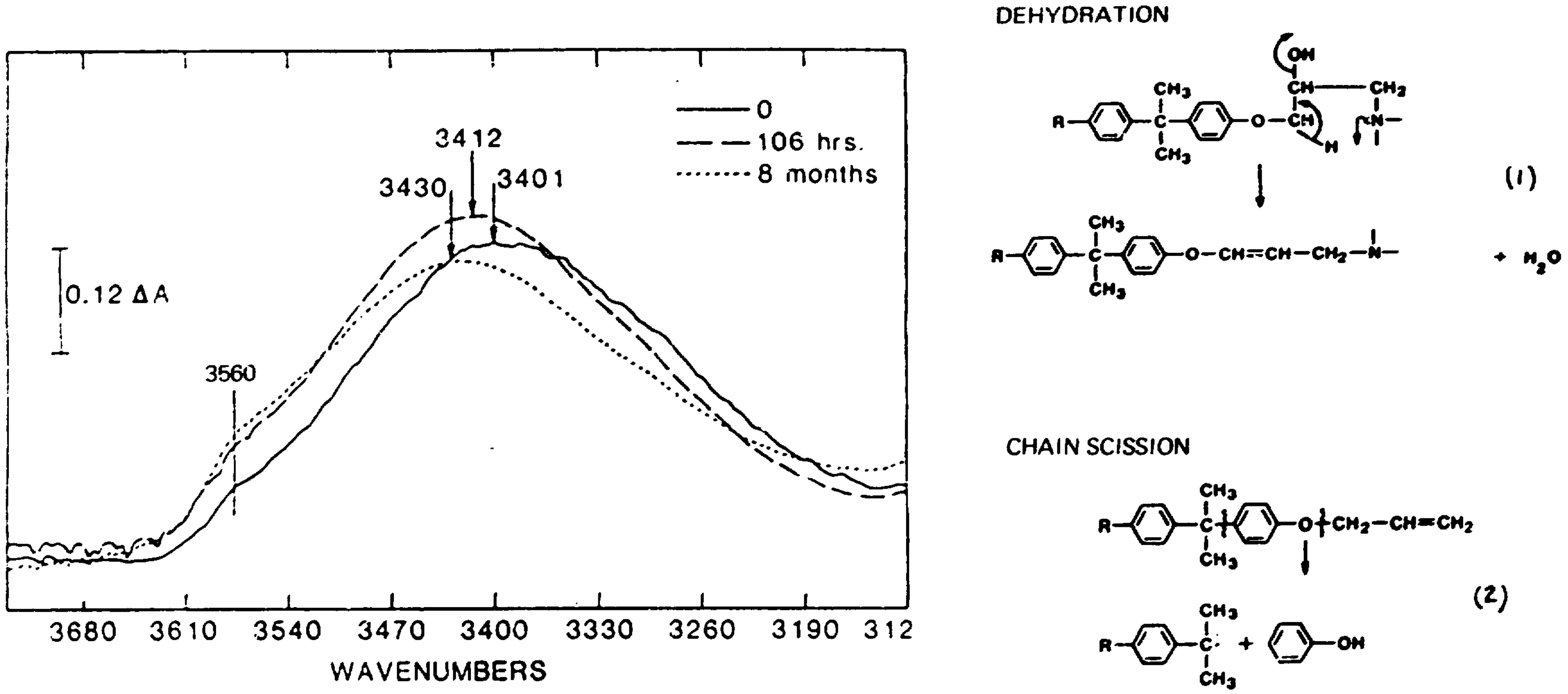


Figure 2. FTIR-RA of the H-bonded OH stretching vibration of an amine-cured epoxy coating on steel aged in 40°C and 80% RH environment, showing the weakening (shift to higher frequency) and dissociation (intensity increase of the nonassociated OH stretch at 3560 cm^{-1}) and dehydration reactions.

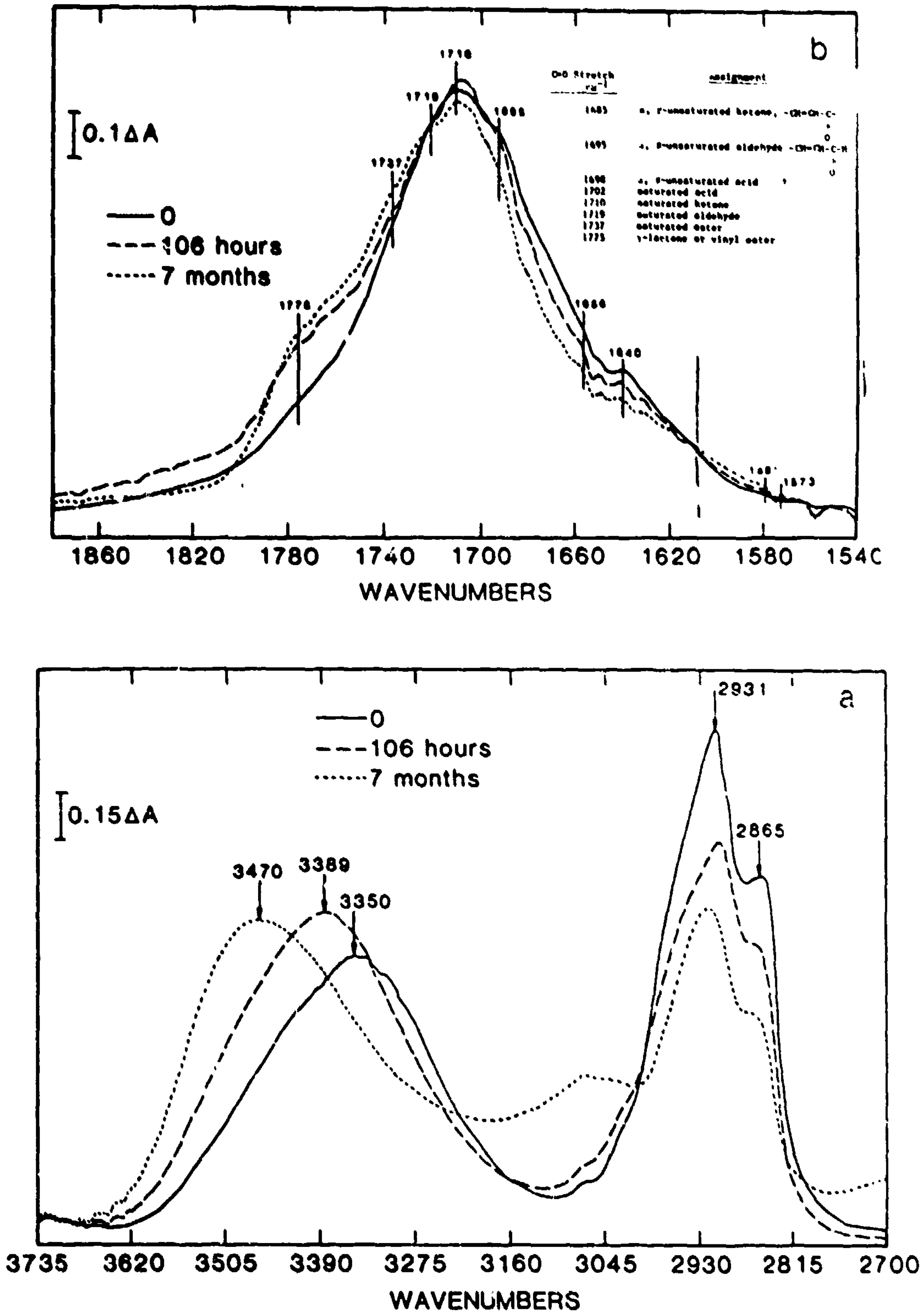


Figure 3. FTIR-RA of the H-bonded OH and CH stretching vibrations of a polybutadiene coating on steel aged in a 40°C and 80% RH environment, showing the H-bonds weakening and degradation of main chain (a), and formation of highly oxidative products (b).

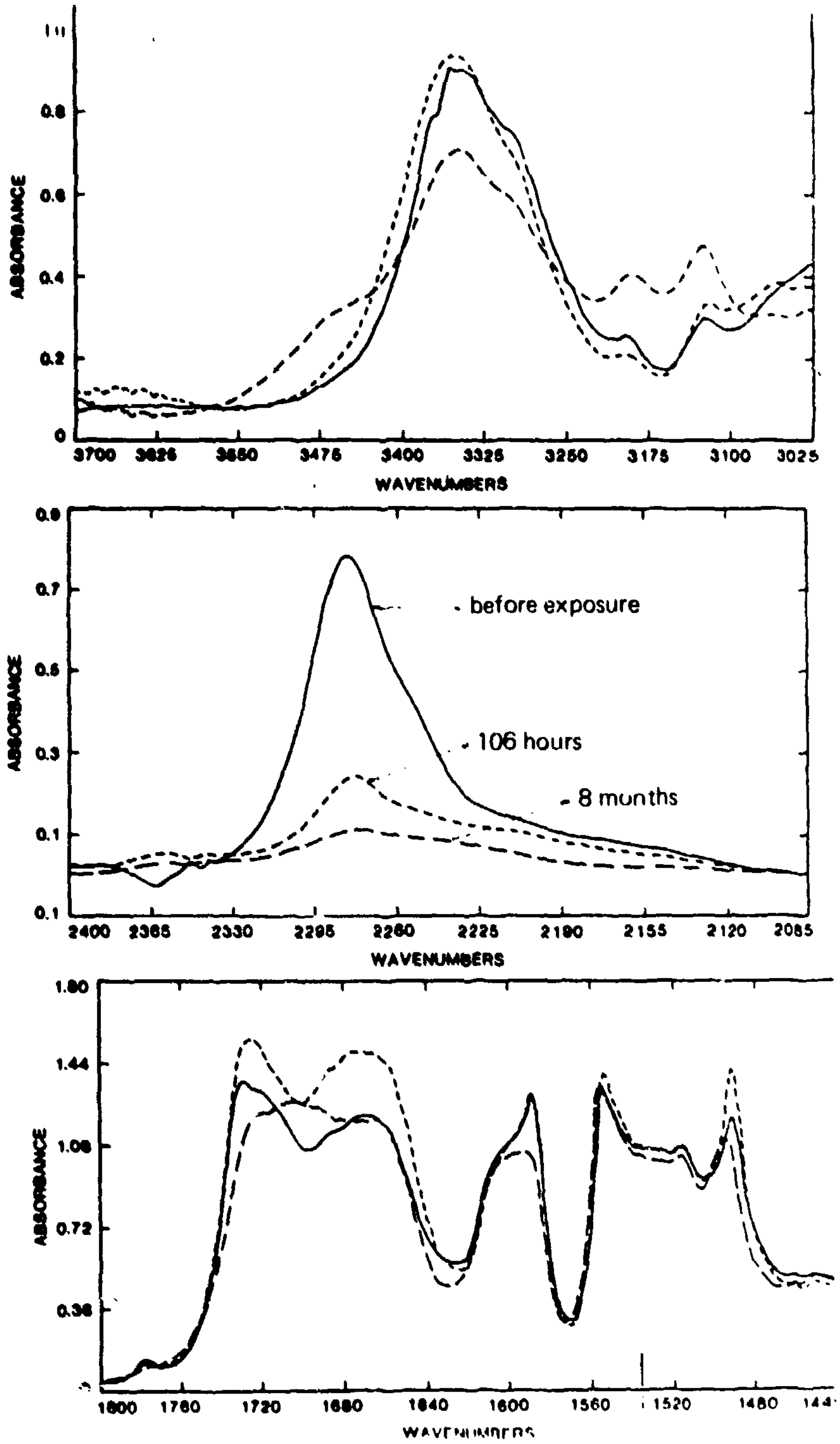


Figure 4. FTIR-RA of a polyurethane coating on steel aged in a 40°C and 80% RH environment, showing degradation at various functional groups (NH at 3200 - 3500 cm^{-1}; amide I, 1650 - 1740 cm^{-1}; amide II, 1450 - 1520 cm^{-1}; and amide III, 1220 - 1320 cm^{-1}; and continuing crosslinking, decrease of NCO group at 2280 cm^{-1}).

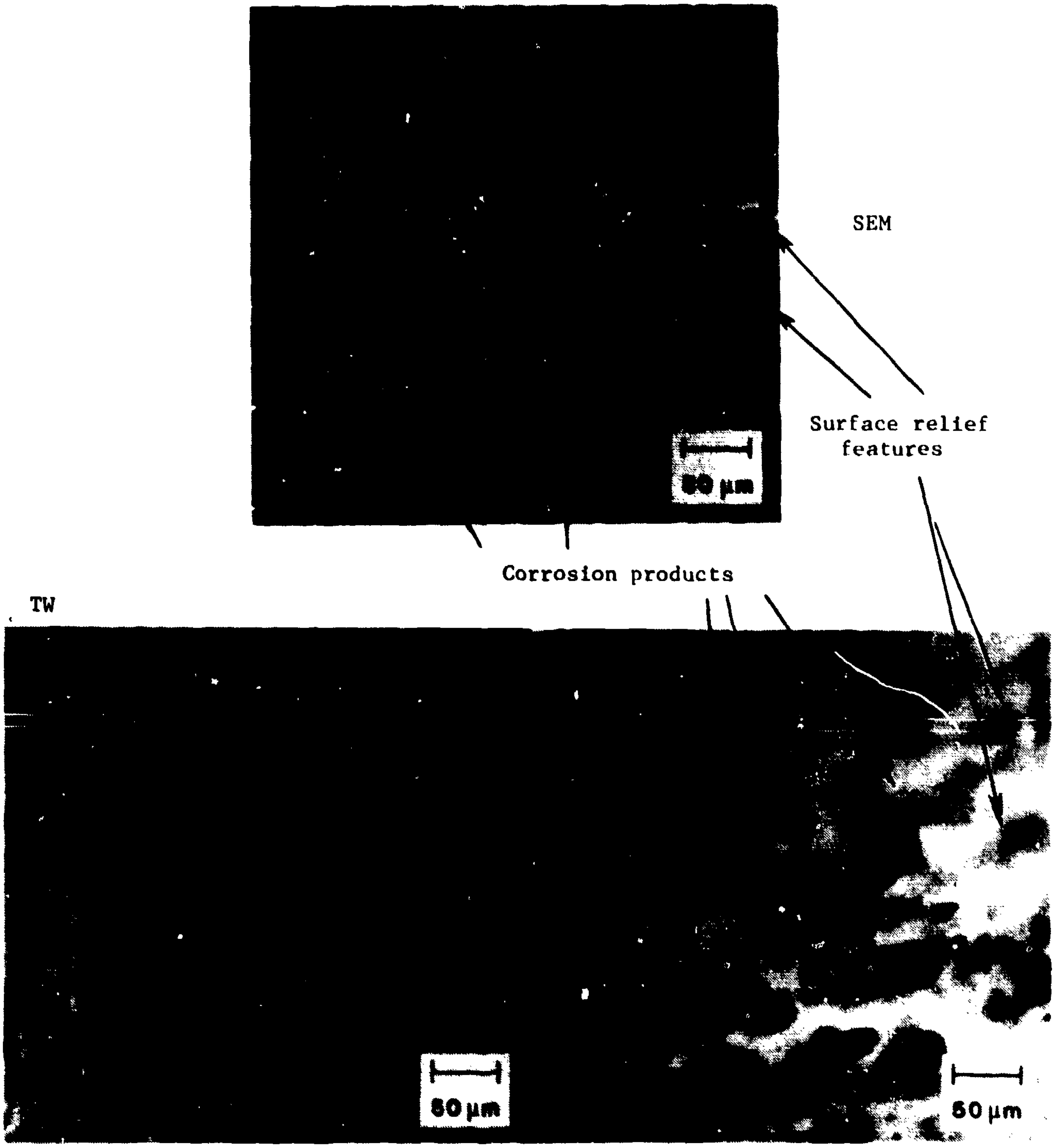


Figure 5. Thermal wave and SEM images of corrosion on an unprotected, rough steel sample, showing the sharper contrast by TWI than SEM which allows quantification of corrosion on steel by image analysis; the small corrosion spots are about 6µm.

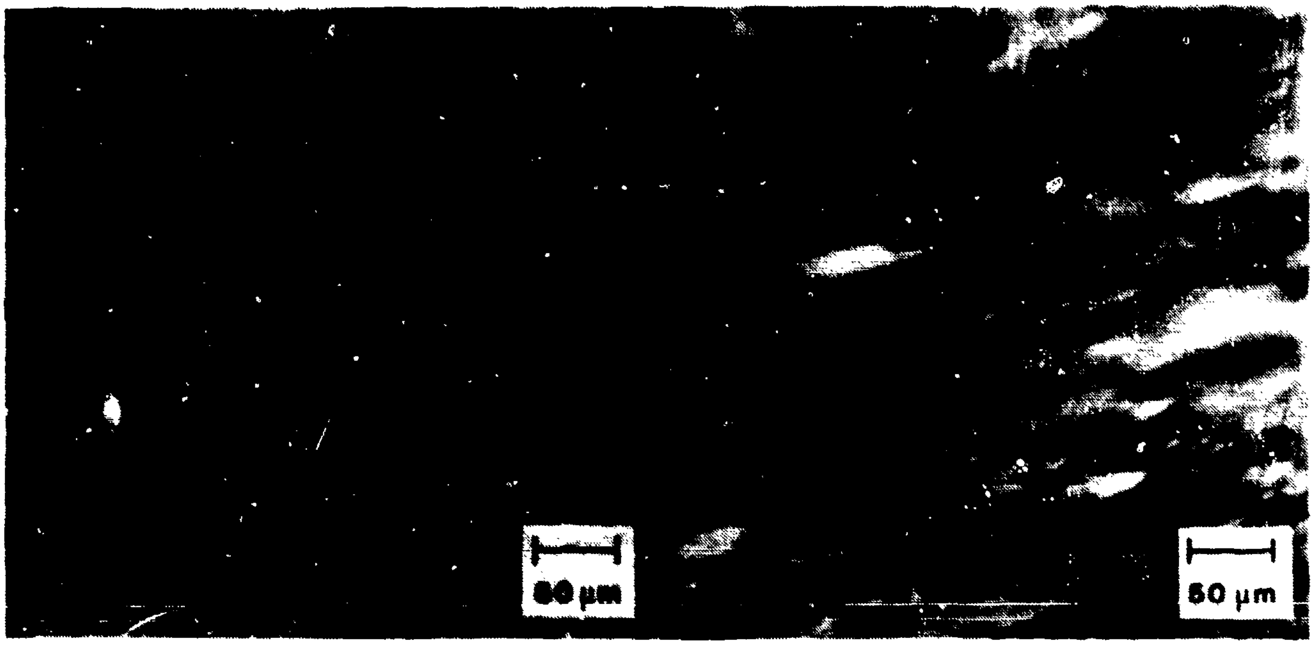


Figure 6. Thermal wave and SEM images of corrosion on a steel sample protected by a 3μm orange slkyd coating, showing the corrosion under opaque coating.

PREDICTION OF DEGRADATION OF POLYMERIC COATING MATERIALS

T. K. Rehfeldt

Sherwin-Williams Co. Central Research Center
10909 S. Cottage Grove Avenue
Chicago, Illinois 50628

A major concern in the coating industry is the longevity of paints and coatings. Repainting is often very expensive of money and/or time, therefore, knowledge of the useful service life of coatings is valuable. Spurred by the desire to provide durable coatings with known lifetimes and aided by Air Force Contract F33615-81-C-5091, we undertook a program to develop methods to characterize coating degradation during service, and to find means to predict lifetimes of current systems.

The early work was supported by the Wright Aeronautical Laboratory at Wright Patterson A.F.B. and is described in report number AFWAL-TR-84-4174. Because of this support most of the coatings studied were urethane based aircraft coatings meeting MIL-C-83286 specification, and we are primarily concerned with photooxidation of the coating.

Current coating tests do not provide much information about the changes to the coating which eventually lead to coating failure during exposure to atmospheric conditions. It was felt that there are methods of characterization of coatings which would relate to changes in performance during exposure and, hence, could provide information which could be used to extend the service life.

A large number of coating samples were prepared for accelerated and real time exterior exposure. Standard physical paint tests were made on all coatings. An objective of this investigation was to try to use these tests as a measure of coating degradation and to find tests which would be representative of the changes in the polymer and which would correlate with standard paint tests.

The physical tests investigated included pencil hardness, gloss, pendulum hardness, reverse impact, cross hatch adhesion, and contact angle of water.

The measurements necessary for predictive characterization of degradation of many coatings are those which measure surface chemistry or physics. Measurements of bulk properties do not change appreciably until coating failure is imminent. Thus, these measures are of little value for evaluation of current state or prediction of remaining lifetime.

Photooxidation and related degradation measurements begin at the surface of the coating and proceed into the coating. Therefore, measurements of chemical and physical changes occurring at or near the surface provide information on the state of the coating and on the likelihood of failure within a specified time.

Techniques such as Fourier transform infra red spectroscopy in the photoacoustic mode, contact angle, electron spin resonance, scanning Auger spectrometry, and X-ray photo-electron spectroscopy are most suitable for the required analysis of the coating surfaces.

Hardness, impact resistance, dynamic mechanical analysis, and other bulk property measurements do not provide useful information about the state or progress of coating degradation unless the system is near failure.

Conventional techniques of data analysis are not sufficient to allow reasonable inferences to be made from the data about the condition of the coating. Standard regression and other statistical calculations can be used to eliminate totally random data but for inferences more sophisticated techniques such as Box-Jenkins Time Series Analysis, Reliability Theory, Weibull Statistics, Bayesian Statistics, etc. must be used.

The technique which was investigated most fully here is time series analysis. Time series analysis refers to attempts to make inferences from data which is a sequence of measurements taken on a variable or process over time. One approach to this analysis is to apply ordinary least squares regression techniques to the data by using time as one of the independent variables. However, measurements of the same thing at different times are not independent measurements and, therefore, the primary requirement of regression and correlation analysis is violated, ipso facto.

There are generally four components of a time series, viz. 1) Long term trend, 2) Cyclical effect (which is not predictable), 3) Seasonal effect (which is predictable), and 4) Random variation. Random variation is always present; the others may be present.

When the random variation is large relative to the other effects, the most efficient estimator of the response in period t+1 is t and the confidence interval is calculated from the variance about the mean of all previous responses. In general, the confidence interval will increase with the square root of the time horizon and the precision predictions decreases with the square root of the time horizon. This is a 'random walk' model and is illustrated by events such as the Dow Jones Averages.

With this model very early values have a contribution to the precision of the forecast which is equal to the contribution of very recent values. This tends to provide a good forecast of long term trend but does not follow cyclical and seasonal variations. One way around this is to use moving average models, such that only the most recent k values are used to calculate the variance about the predicted value. Moving average methods can be simple averages of the last k values or some sort of weighted averages. Commonly, for series with a curvilinear trend exponentially weighted moving averages are used. An example here is population predictions.

In cases where there is a strong trend and/or strong seasonal behaviour there is a high correlation between values in the series; i.e. when period t is high period t+1 is likily to be high. Or if June is high December may be low. This calls for an autoregressive model. The applicability of this type model can be checked by determining the autocorrelation functions of the series. In the easiest case of a first order autoregressive model, which is indicated by a high correlation of the value in period t with the value of t-1 and little correlation of the values with t-2,3...n, effects of variations in the past are contained and accounted for in the most immediate value and hence this value becomes an independent variable in generalized least squares regression analysis. A common application of this type of analysis is sales vs. marketing data where advertising, for example, in this month produce sales next month, etc.

The approach developed by G. E. P. Box and G. M. Jenkins combines these various methods into an analysis which allows choice of the most appropriate model, provides checks of precision, and allows 'what if' types of interpretation. The Box-Jenkins analysis is an autoregressive integrated moving average model (ARIMA).

The Box-Jenkins analysis first evaluates the partial autocorrelation function and determines the order of the appropriate moving average. At this point we can determine the autoregression, any seasonality or cyclical behaviour, and the need for a weighted average. When the appropriate model has been chosen a generalized least squares fit of the data is constructed followed by a careful analysis of the residuals. Indicated changes or modifications to the Box-Jenkins parameters are made and the fit is checked again. If the analysis has been properly derived the function is then tested for accuracy of prediction into future periods.

There are three adjustable parameters in a Box-Jenkins analysis, one for the autoregressive term, one for the differencing or lag term, and one for the moving average term. In addition corrections to each of these for cyclical behaviour may be added as three optional terms.

The approach is very flexible, and provides a great deal of information. There are few requirements for application of the Box-Jenkins approach, chiefly that the underlying probability distribution for the variations must not, itself, change with time.

Displays 1 through 4 illustrate how the Box-Jenkins approach was applied to analyze the change of gloss of an urethane coating during QUV exposure.

Display 1 shows the autocorrelation function of the gloss data, which is used to determine the order of the autoregression terms and to indicate the need for differencing of the data.

Display 2 shows the partial autocorrelation function. The partial autocorrelation function is the autocorrelation function of successive differences of the data, i.e. the first value is the correlation of the value at time t with the value at time t-1. This is used to determine the order of the differencing and moving average terms.

Examination of Displays 1 and 2 led to the choice of 0 for the autoregression term, the use of 2nd differences, and 2nd order moving averages. The data was then fit using these coefficients.

Display 3 is a plot of residuals vs actual values of gloss indicating the random nature of the residuals.

Display 4 is a plot of the fitted and actual plot of gloss vs. time, and indicates a good fit particularly in the middle ranges which are of the most interest.

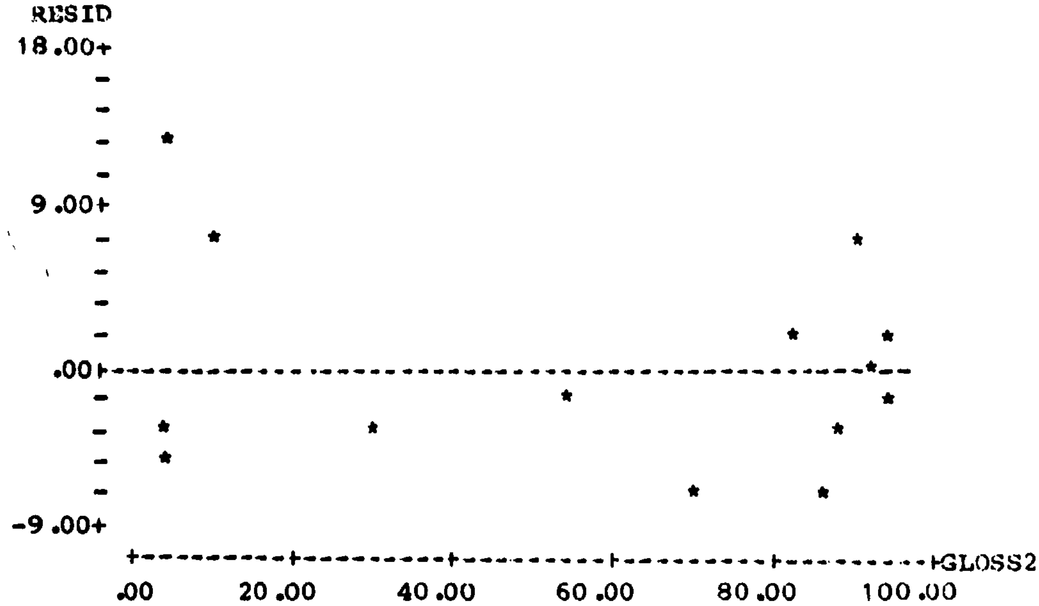
Display 1. Autocorrelation Function of the Gloss Time Series

```
 R          -1.0 -.8  -.6  -.4  -.2   .0   .2   .4   .6   .8   1.0
              +----+----+----+----+----+----+----+----+----+----+
 1    .860                             XXXXXXXXXXXXXXXXXXXXXX
 2    .667                             XXXXXXXXXXXXXXXXXX
 3    .436                             XXXXXXXXXXXX
 4    .199                             XXXXXX
 5    .002                             X
 6   -.133                          XXXX
 7   -.233                       XXXXXXX
 8   -.297                      XXXXXXXX
 9   -.352                    XXXXXXXXXX
10   -.377                    XXXXXXXXXX
11   -.384                   XXXXXXXXXXX
12   -.343                    XXXXXXXXXX
13   -.269                      XXXXXXXX
14   -.184                        XXXXXX
```

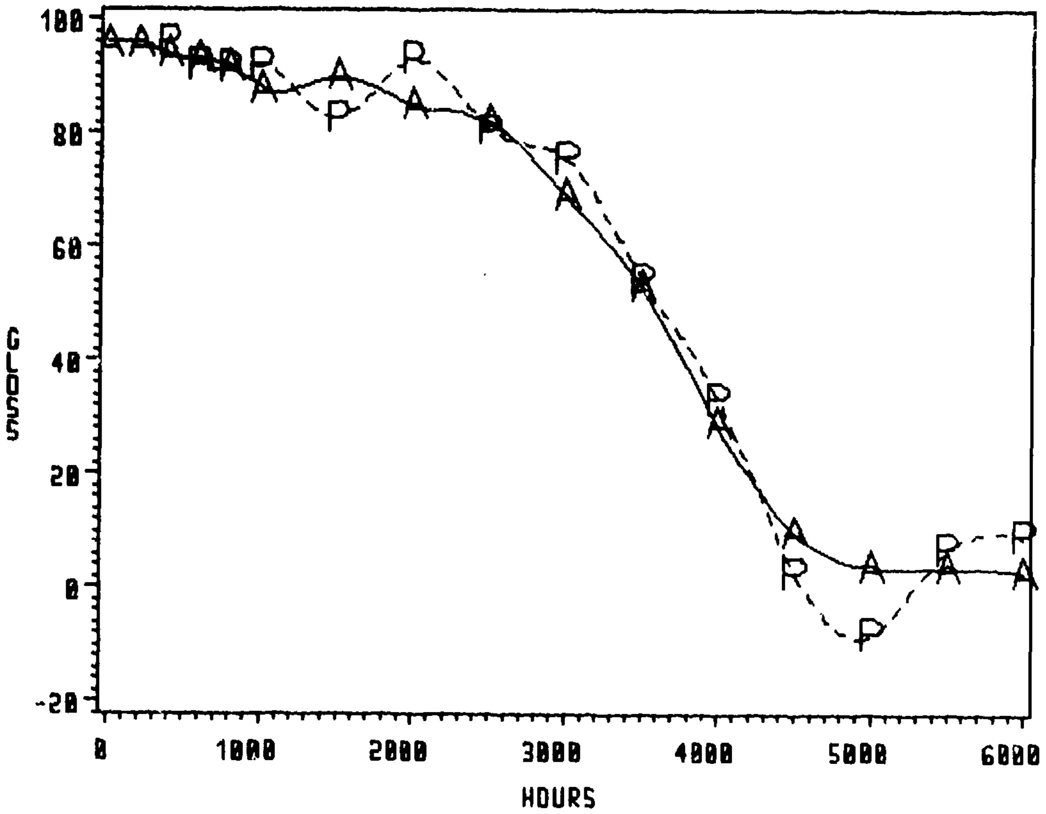
Display 2. Partial Autocorrelation Function of Gloss Time Series

```
          R -1.0 -.8  -.6  -.4  -.2   .0   .2   .4   .6   .8   1.0
              +----+----+----+----+----+----+----+----+----+----+
 1    .860                             XXXXXXXXXXXXXXXXXXXXXX
 2   -.278                      XXXXXXXX
 3   -.241                       XXXXXXX
 4   -.153                         XXXXX
 5   -.014                             X
 6    .046                             XX
 7   -.112                          XXXX
 8   -.085                           XXX
 9   -.164                         XXXXX
10   -.009                             X
11   -.052                            XX
12    .078                             XXX
13    .013                             X
14   -.061                           XXX
```

Display 3. Scatter Plot of Residuals vs Actual Values



Display 4. Actual and Predicted Times Series for Gloss Data



A RELIABILITY-BASED PROGRAM FOR PREDICTING THE SERVICE LIFE OF ORGANIC COATING SYSTEMS

Jonathan W. Martin
Mary E. McKnight
and
Tinh Nguyen
Center for Building Technology
National Bureau of Standards
Gaithersburg, MD 20899

Over the last two decades, significant changes have occurred in the coatings industry resulting from the enactment and enforcement of air quality and hazardous chemical legislation. This legislation is forcing the industry to abandon traditional coating systems, such as red-lead alkyds, for new, low volatile organic content, non-lead and chromate based systems [1]. Criteria for the effective selection, use, and maintenance of these new systems require a reliable base of data on their performance and service life. But for many of these new systems, only limited performance data is available. An urgent need exists, therefore, for generating a reliable base of data in the shortest possible time.

Performance data (service life data) can be generated from either accelerated laboratory or outdoor aging tests. Accelerated laboratory experiments are preferred to outdoor aging tests, since the acquisition of service life data resulting from accelerated laboratory tests is almost always faster than outdoor aging tests and since it should be, at least theoretically, possible to design accelerated laboratory tests which are capable of accurately predicting a coating system's service life for a wide-variety of outdoor exposure environments. Unfortunately, results from current accelerated aging tests seldom provide a basis for reliably predicting a coating system's outdoor performance and for this reason, it has been generally concluded by the coatings community that little credence can be given to accelerated aging test results or, for that matter, accelerated aging tests.

This conclusion may be premature, however, in that much of the blame assigned to accelerated aging tests may be more appropriately assigned elsewhere; for example, to 1) the lack of forethought or effective problem definition in the design and utilization of accelerated aging tests, 2) our lack of knowledge of critical coating system performance variables, 3) our ineffective measurement of changes in these variables with exposure time, 4) our inaccurate or nonexistent characterization of outdoor environments, particularly at the micro-environmental level, and 5) the rudimentary mathematical procedures (correlation analysis) utilized in generating service life estimates from laboratory and outdoor exposure tests. As a case in point, the experiences in the coatings' community can be contrasted with those of the electronics community. Specifically, in a 1979 report on the ability of reliability-based approach (predicting long-term performance from short-term laboratory based tests) to predict the service life of electronic components, it was concluded that "whilst inaccuracies of reliability prediction are recognized, an investigation into the field of mean times between failures of over 130 diverse electronic, electro-pneumatic, and mechanical equipment and systems found that 63% were within a factor of 2 of the predicted value; whilst 93% were within a factor of 4" [2]. The report goes on to conclude that a large portion of these estimation errors can be attributed to the poor records supplied from the field. This success record is not unique to the electronics industry, since similar testimonials can be found for the effectiveness of reliability-based procedures in the mechanical, aerospace, and medical industries. Since these results are, in general, much better than those experienced by the coatings community, it seems worthwhile to explore the merits of a reliability-based procedure for predicting the service life of coating systems.

The main objective of the reliability-based program at the National Bureau of Standards (NBS) is to quantitatively predict the service life of an organic coating system which is subjected to its intended operating and service environment [3-8]. Service life is defined in terms of the probability that a coating system will perform its intended function (protection, aesthetics, or both). Service lives are given in probabilistic terms to account for the extremely high variability observed in the times-to-failure of nominally identical panels exposed to the same environment [8]. Reliability theory also provides techniques which can be used to help identify the causes of a coating failure (called reliability physics [9]) and even to improve the service life of a coating system (called reliability growth [9,10]). Many case studies testifying to the success of these procedures have been published.

Reliability analysis techniques, however, do not diminish the efforts of the coating specialist. Instead, they provide the coating specialist with mathematical tools which can be used to better direct his efforts. To demonstrate this, a flow chart of our reliability-based program for coatings is presented in Fig. 1. This flow chart can be broken down into four main parts: 1) coating material property measurements, 2) environmental variable measurements, 3) laboratory or field experiments and evaluation, and 4) mathematical analysis. These four parts are similar to current practice, except for the heavy emphasis on mathematical analysis in a reliability-based program. This emphasis is important, because reliability theory demands specific information from the other segments of the research program, which would not necessarily be recognized. For example, if the objective of the research is to quantitatively predict the service life of a coating system, then the evaluation procedures must be quantitative. The need for developing improved quantitative evaluation methods has led to NBS research in non-destructive evaluation methods using thermographic imaging and computer image processing [11,12]. If the objective is to gain a better understanding of the relative importance of different environmental factors on the degradation of a coating system, then experiments must be designed to provide this information; hence, NBS's use of partial factorial experimental designs and multivariate discriminatory analysis. Finally, if the objective of the research is to gain a better understanding of the chemical and physical processes governing degradation, then fundamental measurements of the coating system properties must be made including measurements of the film properties, the film/substrate interface properties, the substrate, and the coating system as a whole; hence, NBS's work in studying the chemical degradation at the coating/substrate interface using FTIR [13,14] and thermal-wave microscopy [15] and in measuring other essential properties such as surface roughness [16], internal stress, and building condition assessment [17].

The research into a reliability-based program is really just beginning, however. Although inroads have been made to account for the high spatial and temporal variability in the time-to-failure data for coating systems [8] and into quantifying the engineering performance of a coating system, much work needs to be done in improving accelerated aging tests, measuring critical coating system properties, making improved outdoor environmental measurements, and developing mathematical and statistical procedures to isolate the most critical material and environmental factors. Work is on-going at NBS and other laboratories to meet these objectives.

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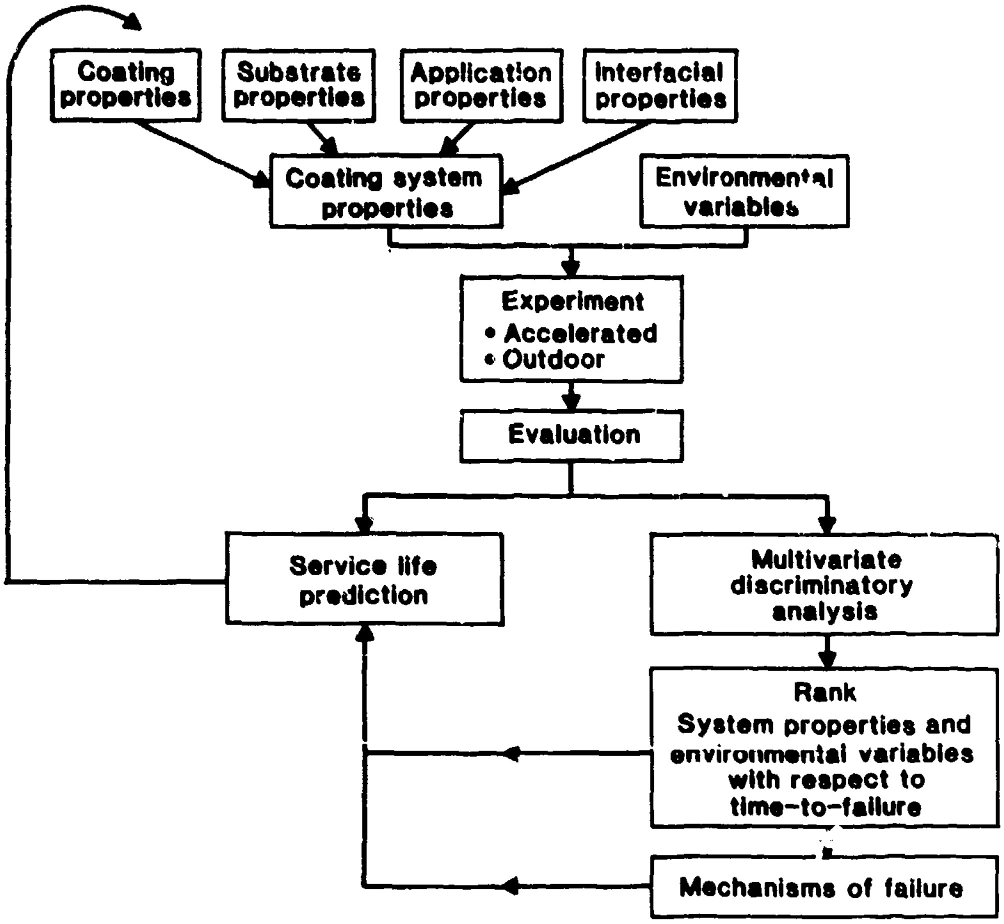
RELIABILITY AND LIFE TESTING APPROACH TO SERVICE LIFE PREDICTION



PREDICTING THE DURABILITY OF ADHESIVES AND COATINGS BY REMOTE DETECTION OF HIDDEN DEFECTS AND COATING-THICKNESS IRREGULARITIES -- A THEORETICAL AND NUMERICAL STUDY

V. K. Pinus and Philip L. Taylor
Department of Physics
Case Western Reserve University
Cleveland OH 44106

Methods have recently been developed to detect delaminations and other hidden flaws lying beneath the surface of polymeric materials by means of thermal-wave imaging. We describe a theoretical basis for expanding the usefulness of this non-destructive means of evaluating the quality of coating coverage and bonding.

There is currently great interest in the use of infrared laser radiation as a means of remote detection of flaws in bonds to surfaces and of uneven thickness in coating layers. The goal of our work has been to develop a thorough theoretical understanding of these techniques by examination of the heat-transfer mechanisms in materials and geometries of practical interest. In this way we hope to be able to optimize the parameters of the irradiating and detecting equipment and to develop numerical algorithms to display three-dimensional images of hidden defects.

Prediction of the durability of adhesives, sealants, and coatings in structural applications remains an important practical problem. Methods have long been sought to detect delamination, grease contamination, and other flaws when hidden by opaque layers of material. The recent introduction of thermal-wave imaging as an inexpensive means of remote non-destructive evaluation of polymer layers has given some hope that some of these problems can be solved. Current methods, however, are largely empirical, and can give contradictory results. A deeper theoretical understanding of the mechanisms is essential if the reproducibility, contrast, resolution, and sensitivity of these techniques are to be improved.

Much information regarding subsurface defects can be obtained by study of the pattern of heat flow that occurs after a sample is irradiated by light or by particle beams.[1-3] This technique of remote inspection of polymers by thermal-wave imaging has recently received attention as a means of detecting subsurface defects.[4-8] No special preparation of the sample is required and no physical contact is imposed. Some sample results reproduced from Ref. 5 are shown in Fig. 1.

In this scheme, a modulated source of energy, for instance an infared laser, is directed at a region of the sample and gives rise to thermal waves. These waves propagate from the absorption region into the sample and along the sample surface. They have a wavelength approximately proportional to the square root of the product of the thermal diffusion length and the modulation period, and decay exponentially as they propagate. The spatial and temporal dependence of the infrared radiation reemitted by the sample surface depend on both the geometric and thermo-optic properties of the sample and such characteristics of the incident laser beam as infrared frequency, modulation frequency, intensity and spatial distribution.

In principle it is possible to form a three-dimensional image of subsurface structure in an opaque material by means of an analysis of the amplitude and phase of emitted radiation, and some progress has been made in this direction.[4-7] The complex phenomena involved, however, require a greater level of sophistication in their theoretical treatment than they have so far been accorded. Existing treatments have led to contradictory conclusions concerning image contrast and resolution, and thickness limitations of samples.[4-8]

We propose to develop a more complete and powerful theoretical framework for the analysis of this effect by including the consequences of diffraction and scattering of subsurface thermal waves and also of the photoacoustic effect. The generation of sound pulses by the incident laser radiation can lead to heat production not accounted for in simpler theories, and which may thus give distorted thermal images. Very recently the first experimental evidence has been published[8] for the existence of the strong interaction between thermal waves and acoustic waves in imaging measurements.

The electronic structure of polymers must be expected to be an important factor in determining the absorption of infrared radiation, and can lead to irregularities in thermal-wave propagation. While ultraviolet light would avoid this problem, the method would cease to be nondestructive at large laser intensities[9-12], and some study of the maximum permissible intensity seems desirable.

Our goal is thus the production of a theory capable of giving both realistic reconstruction of defects from their thermal images and the establishment of the limiting values of laser wavelength and intensity and of sample thickness for which the method can be applied.

We have derived a basic set of equations that describe the development of the temperature field in both coating and substrate layers for any arbitrary given laser flux density as a function of time. By solving these equations one can determine the temperature fields for any given laser flux density. From this one may then determine the infrared radiation field. After that one can calculate such experimentally measured quantities dependent on the infrared radiation field as the spectral surface luminosity, the brightness temperature, the color temperature, and the emittance of the body. In this way it should be possible to determine which quantities are more sensitive and more appropriate for thermal-wave imaging. Such a calculational program will require considerable numerical computation. Finally, using the results of our numerical calculation, we will be able to give practical recommendations for appropriate choices of experimental arrangements in order to optimize the usefulness of the method.

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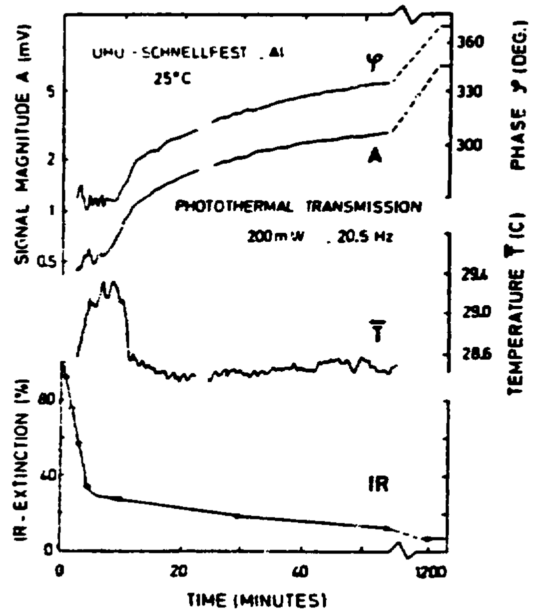
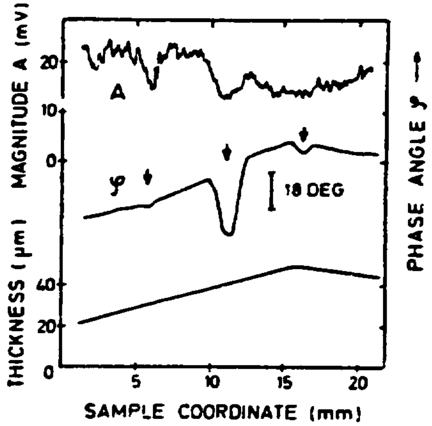
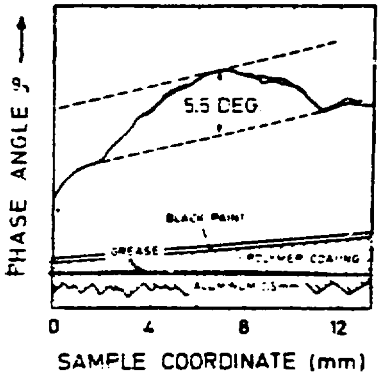


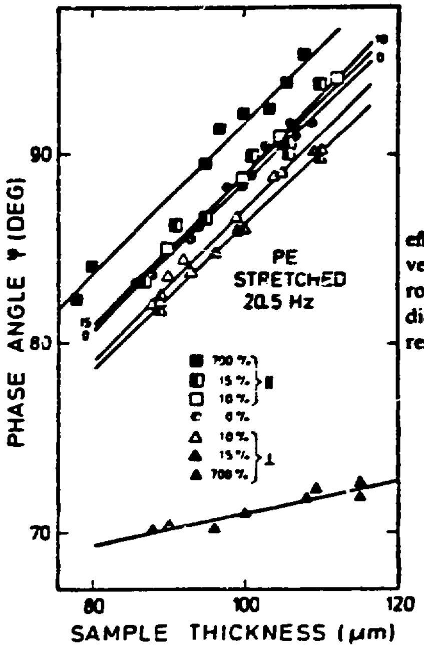
Curing process of epoxy resin between two 0.5-mm aluminum plates (curves A, φ, and $\overline{T}$). Bottom curve IR obtained with conventional infrared transmission spectroscopy on epoxy resin with no metal. Mixing of the components at zero on time scale.



Remote probing of coating thickness using magnitude A and phase angle φ of transmitted thermal wave. Arrows indicate surface defects. Bottom curve shows measured thickness of coating.



Coating delamination (simulated by a thin layer of grease under part of the polymer coating) detected by a phase change of transmitted thermal wave. Part of the curve has been recorded twice to demonstrate reproducibility. Modulation frequency 20.5 Hz.



Molecular orientation effect in black polyethylene revealed by thermal wave anisotropy. Squares and triangles indicate sample orientation with respect to stretch direction.

FIGURE 1. These sample results, reproduced from the work of Busse and Eyerer in Ref. 5, show the use of thermal imaging to study curing, delamination, coating thickness and molecular orientation.

ELECTRICAL DETECTION OF COATING DETERIORATION

G.Loeb and J. Mihm, Code 2841, DTNSRDC

Electrical impedance measurements of epoxy-coated steel panels at 95% relative humidity using two electrodes were performed for two reasons: to complement other studies performed when the panels are immersed in ASTM seawater using the 3-electrode method, and also to ascertain whether significant predictive capabilities were achievable with this method. The data obtained to date are still fragmentary, but an example will be shown of a matched pair of panels to illustrate the type of data obtained.

Steel Q-panels were degreased with toluene, and coated with epoxy MIL-24441 series coatings, or translucent coatings formulated with the same ingredients except for a substitution of finely divided quartz (Cabosil) for the normal pigments. A second translucent coating, formulated from the same materials but with no particulate material knowingly added, was also used.

The panels were dip-coated, as in ASTM Standard D823, to obtain uniform films on the small sample panels used. (Spray application was seen to be much less uniform, although more similar to actual practice.)

Measurements were made on freshly made (but completely cured) panels. They were then immersed in ASTM seawater. After the panels had been immersed for various periods of time, a set of immersed impedance measurements was made with the three-electrode technique. The panels were then removed from the ASTM seawater bath and allowed to equilibrate for 18 hrs. with air at 95% RH in a sealed vessel (over a saturated water solution of Na_2HPO_4).

Measurements were made in a Balsbaugh cell whose electrode spacing could be varied to accomodate the panels. One electrode was the steel itself; the other was a circle 3" in diameter, with the outer 1/4" a guard ring. The micrometer-driven electrode was brought into contact with the painted surface for measurements.

The impedance bridge (HP4274A) assumes a parallel circuit while measuring capacitance (C_p) and dissipation factor (D) at 11 values of the frequency (f) between 100 Hz and 100 Khz. The values at 100 and 120 Hz were noisy, and significant values could only be obtained by averaging many readings. Resistance (R_p) was estimated according to the relationship:

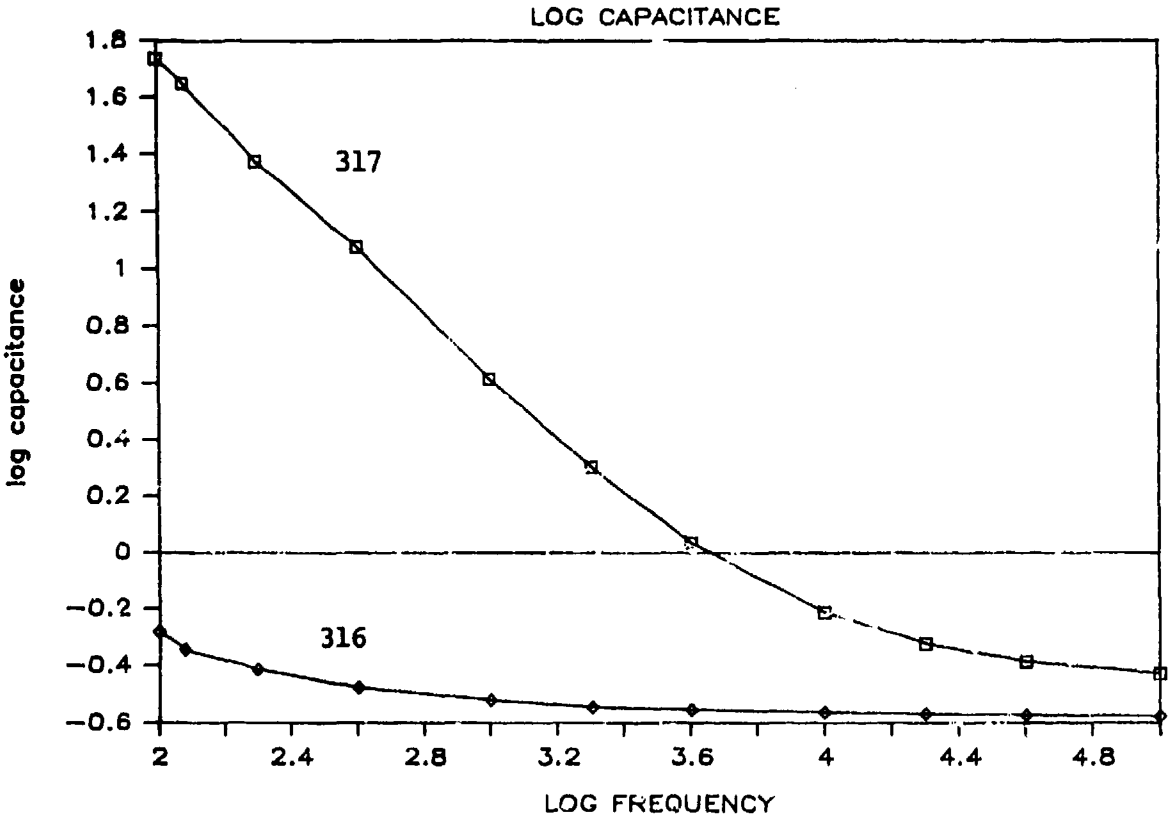
$$(R_p) = 1/D*2*Pi*f*(C_p)$$

Previous experience with this equipment at our laboratory indicates that the measurements are accurate to within 20%. Refinement of the calibration proceedure is expected to improve the accuracy of the already acquired data in the very near future, and additional data is to be obtained. At present, we can detect trends which are consistent with expected characteristics of anticorrosive coatings. As an example, the data in Figures 1, 2, and 3 are obtained for epoxy coatings aged for 211 days. Panel 316 was in very good condition, while panel 317, prepared in the same manner, was observed to have a very small blister. The apparent capacitance of panel 316 was in the range 0.2 - 0.5 nf, the dissipation factor amplitude was 0.02 at high frequency and increased to 3.0 at low frequency. (The apparent parallel resistance was too high for measurement with this equipment. Calculation on the basis of the equation yields values of 300 Kohm - 1300 Kohm). The apparent capacitances of Panel 317, in contrast, are 0.4 - 54 nf, a variation of two orders of magnitude over the frequency range covered; the dissipation factor was much higher at some frequencies, and the apparent parallel resistance was two orders of magnitude lower. The lower resistance values are to be expected for a less perfect barrier film. Higher capacitance is also expected, because water has a higher dielectric constant.

Changes in apparent capacitance and tan D over the frequency range can be expected for equivalent circuits containing components of constant value. However, they may also be indicative of processes occuring in the film which are frequencydependent, such as induced ion migration in a more permeable substance, which may be related to film structure. Computations relating both the immersed electrochemical properties and the humidity-equilibrated films described herein must await evaluation of the normalization parameters of the cell used, as mentioned above.

We are grateful to Mr. Earl Diamond of DTNSRDC Code 2713 for the use of, and instruction concerning, the bridge and cell in his care.

Figure 1



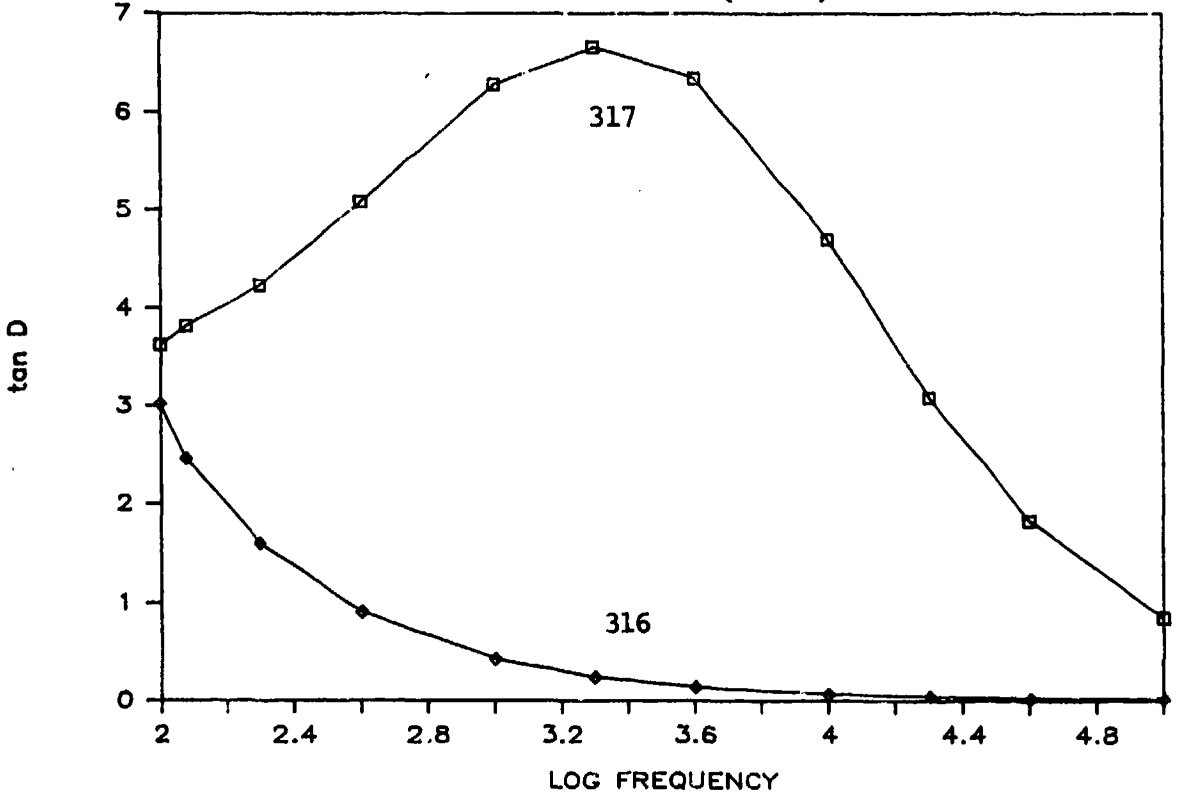


Figure 2

DISSIP. FACTOR (TAN D)

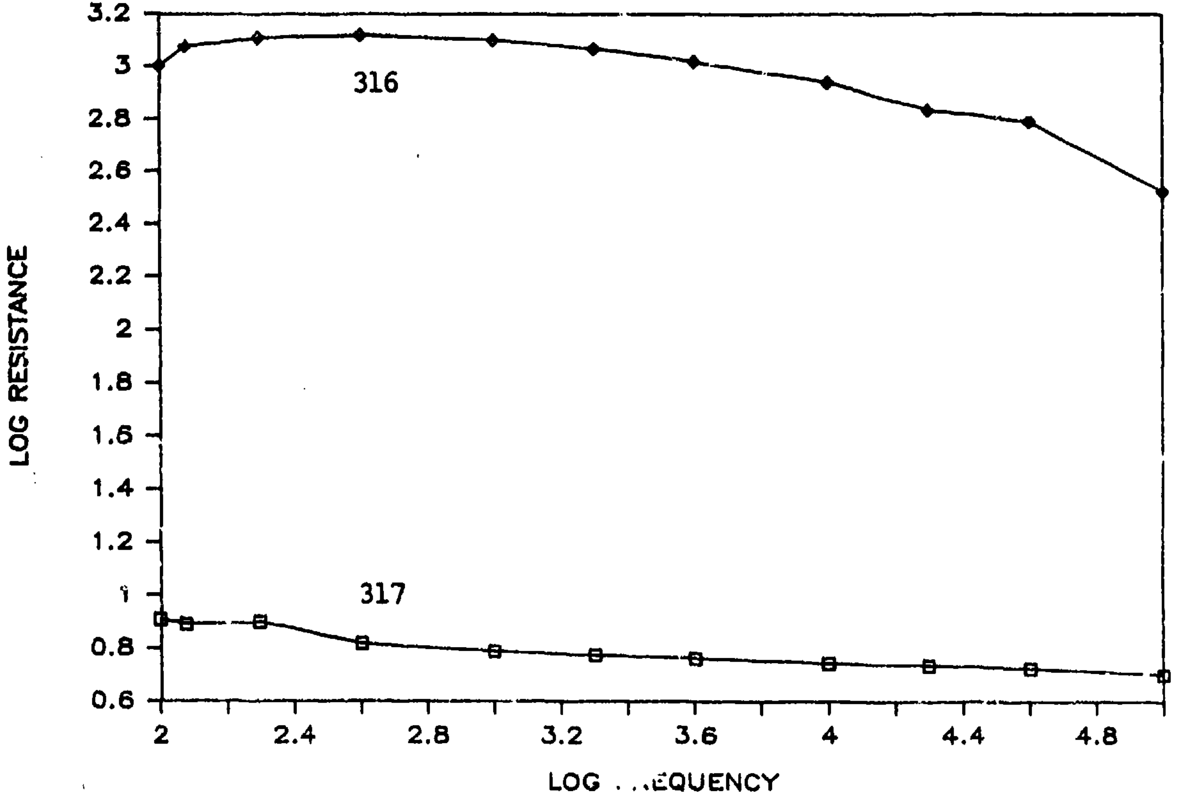


Figure 3

PANEL RESISTANCE

Electrochemical Evaluation of the Long Term Corrosion Resistance of Polymer Coated Steel

Martin W. Kendig
Rockwell International Science Center
1049 Camino dos Rios
Thousand Oaks, CA 91360

A combination of relatively rapid electrochemical test methods have been developed at the Science Center as part of a now completed program supported by The Office of Naval Research (1) which allows early prediction of the relative resistance of polymer coated steel to corrosion. The degradation of polymer coated steel is a very complex process and depends on a number of interrelated processes and initial conditions as shown in Fig. 1. Both adhesion of the coating to the substrate as well as the barrier nature of polymer determine the life of the coated steel in a given environment.

Once the coated steel is placed in a corrosive environment, corrosion follows the form shown in Fig. 2. Corrosion initiates at initially present defects where anodic dissolution occurs(Fig. 2-1). The anodic reaction at the defect drives the adjacent region cathodic where aqueous oxygen diffusing through the coating is reduced to form a highly alkaline environment at the coating/metal interface. The resulting alkaline environment enhances the disbonding of the coating from the interface, thereby propagating the coating failure. This process is often referred to as cathodic disbonding. Simultaneously, the anodic formation of a voluminous oxide enhances the defect as a result of mechanical stress. A combination of two electrochemical methods, electrochemical impedance spectroscopy (EIS) and potentiostatic cathodic disbonding (PCD) enable evaluation of the 1) extent of defect formation, 2) transport of water through the coating and 3) rate of cathodic disbonding.

The cathodic disbonding test is schematically shown in Fig. 3. This test entails polarizing a scribed coated steel surface for a given length of time followed by removal of the disbonded coating and analysis of the disbonded area. A cathodic disbonding efficiency may be calculated as the ratio of the area disbonded to the charge passed.

Fig. 4 shows the apparatus used to collect electrochemical impedance spectra. It includes a computer controlled potentiostat and a transfer function analyzer. Fig. 5 shows the circuit analog for a coated steel surface. The elements of the circuit analog include a capacitance C corresponding to the capacitance for the coating dielectric, R_{po}, a resistance due to the ionic transport across the coating through virtual pores or defects. A parallel combination of R_p the polarization or corrosion resistance, and C_d, the double layer capacitance of the metal surface is in series with R_{po}. In many cases, C_d and R_p cannot be resolved. However, the coating capacitance C and R_{po} are readily determined in most instances. The volume fraction of water uptake can be calculated from the increase in C resulting from uptake of the high dielectric aqueous medium. R_{po} provides a measure of the quantity of defects in the polymer coating. Impedance measurements, therefore, quantify non-destructively the rate of water transport through the coating and the formation of defects in the coating where anodic dissolution initiates. Fig. 6 shows an impedance spectrum for a phosphated and coated steel test panel plotted as the log of the impedance magnitude and phase angle vs the log of the angular frequency. A computer fit evaluated the impedance parameters inset in Fig. 6.

A number of painted phosphated-steel coupons of known salt spray behavior were evaluated using EIS and PCD which allowed evaluation of the water uptake, R_{po} and cathodic disbonding efficiency. A combined function of cathodic disbonding efficiency measured over a 72 h period, and water uptake measured after 24 h correlated well with 900 h salt spray tests. Hence, the electrochemical methods provide a rapid quantitative means for classifying coatings as to their corrosion resistance (2).

1. F. Mansfeld and M. Kendig, "Life Prediction of Corrosion of the Polymer Coating / Metal Interface", Final Report,

2. M. Kendig, "Rapid Evaluation of Polymer Coated Steel to Corrosion", unpublished Science Center Technical Report, SCTR-85-5 (1985).

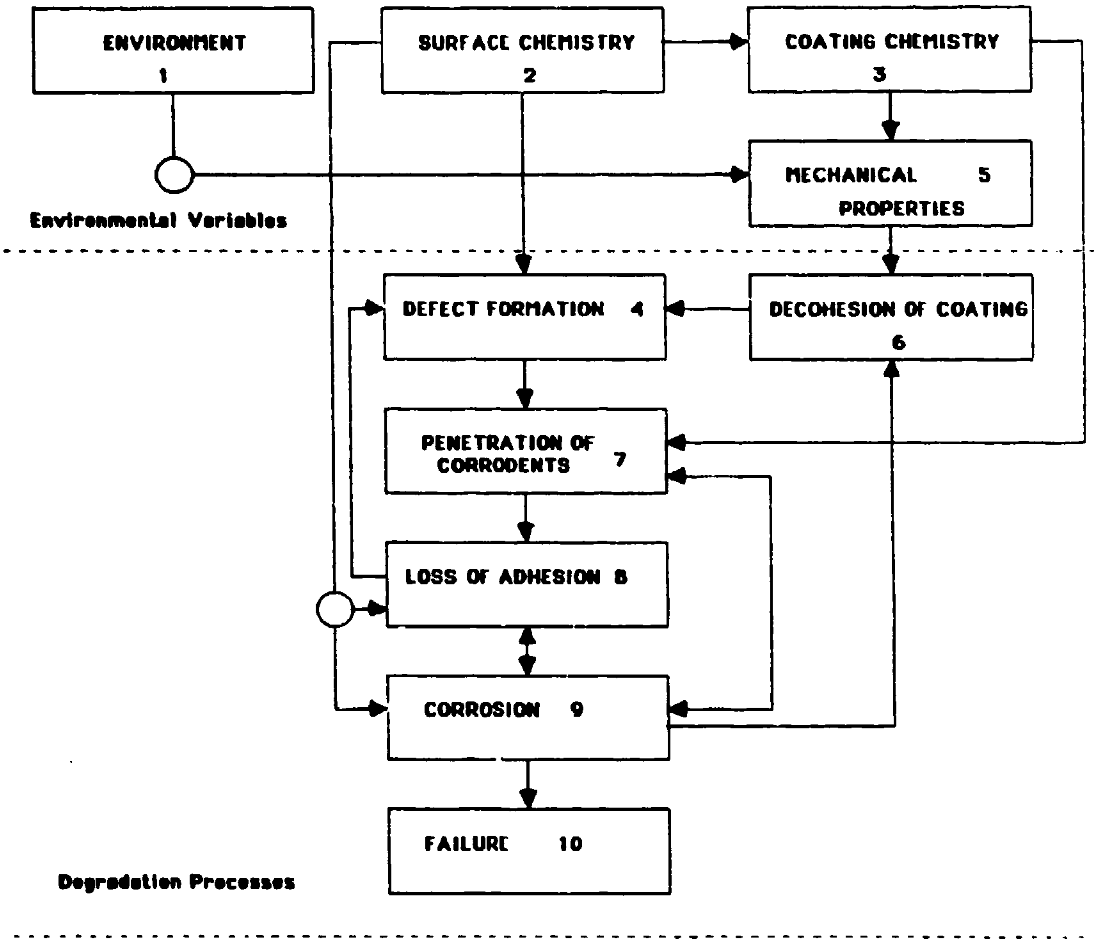


Fig. 1. Lifetime prediction model for polymer coated metal (1).

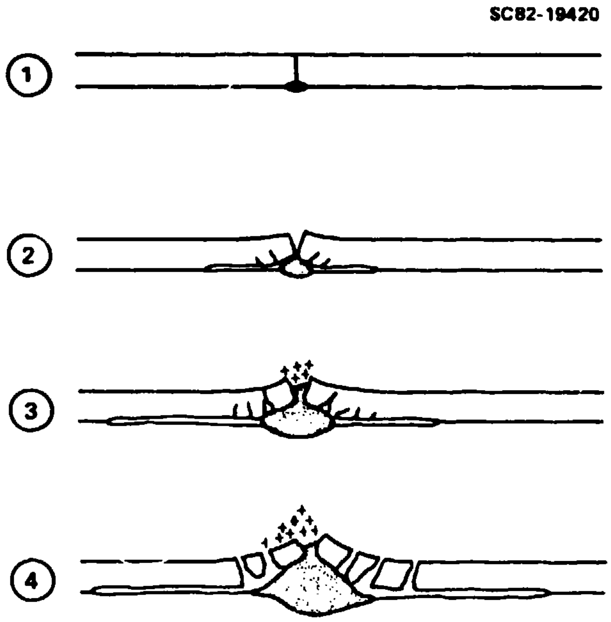


Fig. 2. Schematic of the mechanism of corrosion of polymer coated steel.

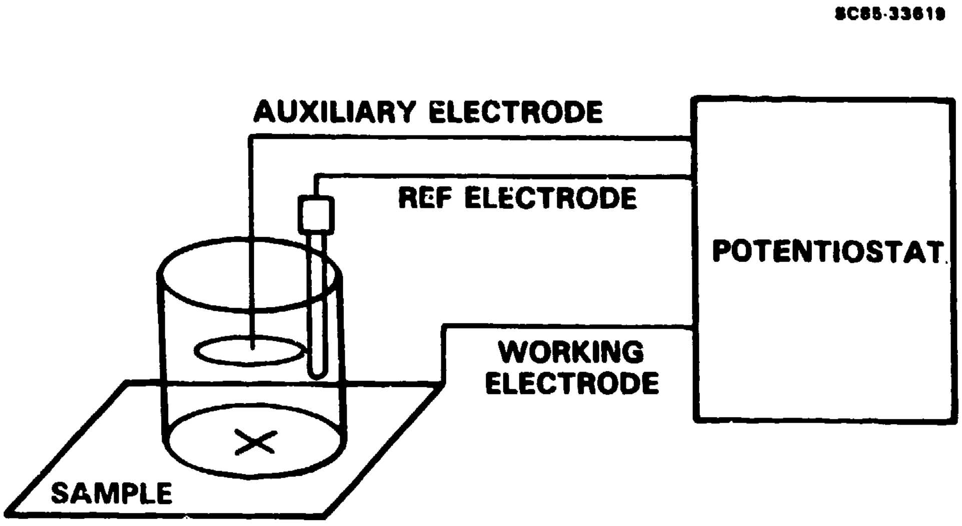


Fig. 3. Schematic for the cathodic disbonding test.

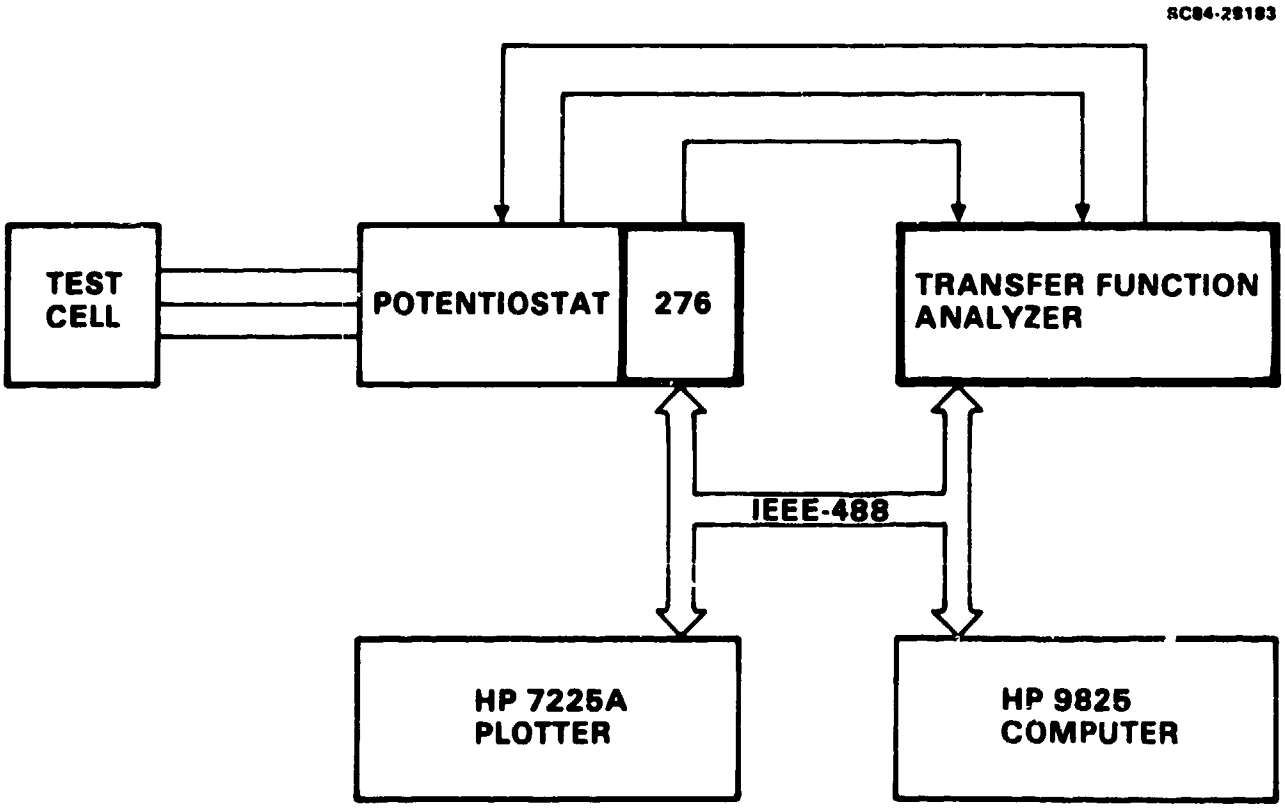


Fig. 4. Schematic for the apparatus used to measure electrochemical impedance.

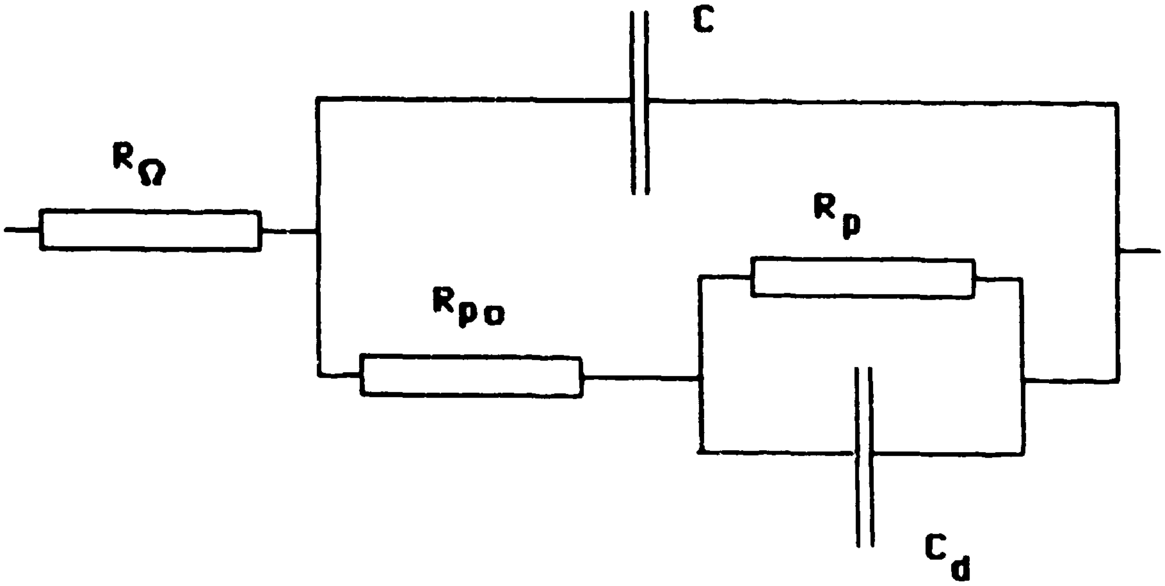


Fig. 5. Circuit analog for the electrical response of a polymer coated steel.

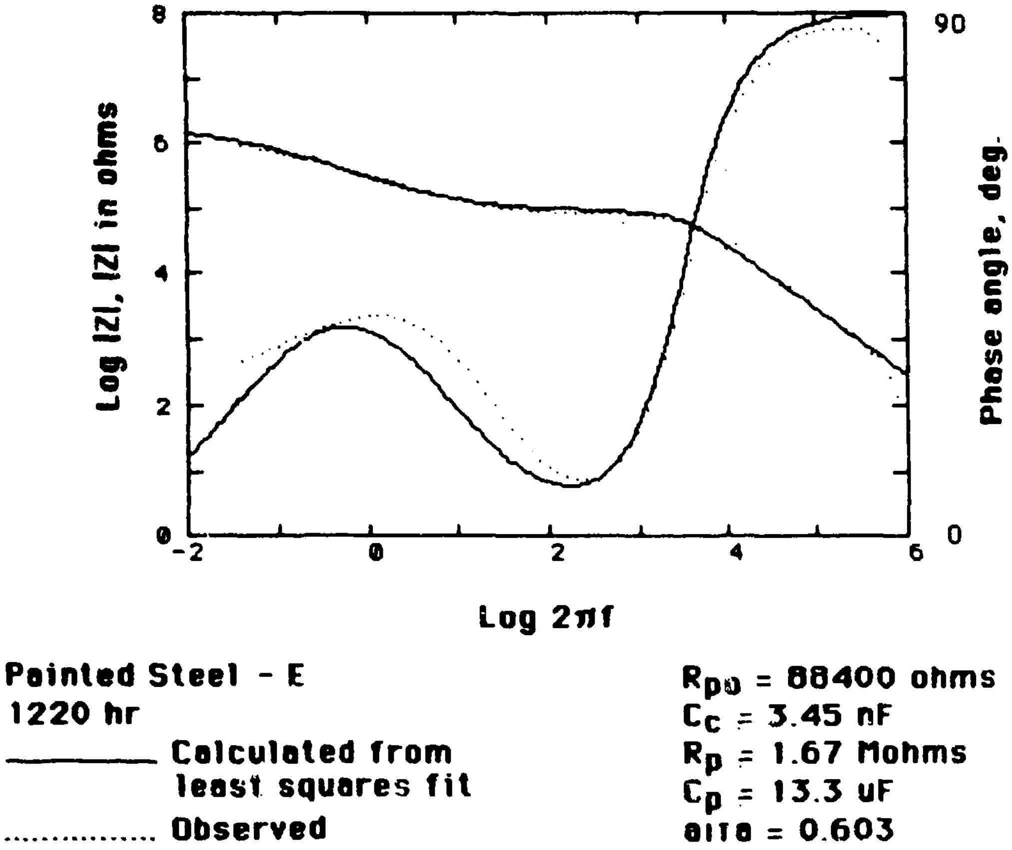


Fig. 6. Impedance spectrum for a painted phosphated steel.

AN ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY STUDY OF REACTIONS AT THE METAL/COATING INTERFACE

by

F. Mansfeld,* S. L. Jeanjaquet and M. W. Kendig

Rockwell International Science Center
Thousand Oaks, CA 91360

ABSTRACT

A segmented two-electrode system has been used to obtain impedance spectra under a polymer coating. These spectra have been compared with those obtained across the coating between the short-circuited steel electrodes and a counter electrode. Similar experiments have been carried out for Cu/steel and Zn/steel with a 20 μm epoxy coating. For these electrode systems the galvanic current between the two dissimilar metals has been recorded continuously as a function of exposure time to NaCl. A transmission line model has been used to obtain estimates for the delaminated volume and the polarization resistance of the steel electrodes.

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*Present Address:
Department of Materials Science
University of Southern California
Los Angeles, CA 90089-0241

EVALUATION OF ORGANIC COATING DETERIORATION AND SUBSTRATE CORROSION IN SEAWATER USING ELECTROCHEMICAL IMPEDANCE MEASUREMENTS

John R. Scully
David W. Taylor Naval Ship R & D Center
Marine Corrosion Branch, Bethesda, MD 20084

INTRODUCTION

The basis for using electrochemical techniques for evaluating organic coating deterioration on metals lies in the presence of ions in the coating and at the metal/coating interface. As the electrolyte permeates the coating, ionic transport occurs through the bulk of the coating and through the coating pores, resulting in a loss in coating electrical resistance and a rise in substrate corrosion. Therefore, electrochemical techniques such as impedance measurements have a definite use in monitoring corrosion performance.

One of the main advantages of the AC impedance technique over a more traditional DC technique is its ability to study corrosion reactions in low conductivity media or through poorly conducting films, where the high ohmic contribution in such films obscures the faradaic (corrosion) response of the metal substrate. Another advantage of this technique is its nondestructive nature, making it suitable for in-situ testing.

Frequently, electrochemical descriptions of coating/metal systems and corrosion processes are illustrated by equivalent electrical circuit models, as in Figure 1. The general equivalent circuit shown in Figure 1 consists of the following parameters: the solution resistance for the bulk solution and electrical leads, $R\Omega$; the coating capacitance for the dielectric coating, Cc; the "pore" resistance, Rp, which describes the coating penetration by the electrolyte; and the general impedance, Zi, corresponding to the electrochemical reactions occurring at the metal/coating interface.

For many systems, Zi can be described by a transfer resistance, Rt, in parallel with a double layer capacitance, Cd, as seen in Mode I of Figure 1. In other cases, Zi is best represented by Rt in series with a Warburg Impedance, W, (Mode II of Figure 1) where Rt describes the metal/electrolyte corrosion and W the diffusion related impedance of the rate limiting species.

The specific objective of this research was to demonstrate the feasibility of monitoring, evaluating, and quantifying the nature and degree of coating deterioration and subsequent underfilm corrosion of HY-80 steel in seawater, using electrochemical AC impedance techniques.

EXPERIMENTAL CONSIDERATIONS

Materials and Environments

HY-80 steel plates were studied with three different types of spray applied coatings. Two types of epoxy polyamides were used, as well as a vinyl tar coating. The coating thicknesses ranged from 2.5 to 4.5 mils, with the vinyl tar coating approximately 4 mils thick and the epoxy coatings between 2.5 and 4.0 mils.

The specimens were kept under controlled temperature, electrolyte concentration, and dissolved oxygen content. ASTM artificial seawater was used as the electrolyte, and air bubblers were used to maintain a fully aerated condition.

Two exposure conditions were applied to the specimens: in one case the samples were allowed to freely corrode; and in the second case cathodic polarization was maintained at -1.10 volts (SCE) under potentiostatic control.

Data Analysis

In evaluating the impedance spectrum, several cases occur. At very high frequencies, the impedance is frequency controlled by the coating capacitance, Cc, and a line with a slope of -1 is seen on the Bode plot (see Figure 1). At intermediate frequencies, a frequency independent portion of impedance is observed corresponding to RΩ +Rp. In addition, there may be another frequency independent region corresponding to RΩ +Rp +Rt. This type of behavior is also illustrated in Figure 2, which is an example of impedance changes with respect to frequency, and an example of the changes of this relationship over a 285 day exposure period.

At low frequencies, a more complex analysis is often required for the faradaic reactions. The Warburg parameter, W, is found from a plot of the real component of impedance versus the frequency raised to the -0.5 power. The capacitances, Cc and Cd, may be determined from the appropriate impedance versus frequency data. From the double layer capacitance, the active area of corrosion can be estimated.

It is recommended that the coating capacitance be determined from dielectric measurements as well, since for many systems the values of capacitance in two RC networks in the cell are similar enough to cause overlapping processes. This can hinder interpretation of the data.

Thus by collecting both an impedance spectrum and independent dielectric measurements, the performance of the coating, (including its resistive and capacitive components responsible for coating degredation) and substrate corrosion may be monitored.

RESULTS AND DISCUSSION

Coating Deterioration

The epoxy polyamide coatings under freely corroding conditions showed a decrease in pore resistance (Rp) from about 1.0 x 10^6 ohm-cm.sq. to about 0.1 x10^6 ohm-cm. sq. in all cases (see Figure 3). Vinyl tar coatings exhibited slightly lower values of pore resistance (.15 to .40 x 10^6 ohm-cm.sq.) despite the thicker coatings.

The samples which were cathodically polarized showed much greater decreases in pore resistance, with order of magnitude decreases in pore resistance observed in both the vinyl and epoxy coatings. Again, the vinyl tar coating seemed to show a greater amount of degradation than the epoxy.

Substrate Corrosion

An approximate value of the transfer resistance, Rt, was estimated from low frequency impedance data and monitored as a function of time. Freely corroding epoxy polyamide coatings showed order of magnitude increases in the parameter 1/Rt, indicating corrosion attack even in the absence of massive coating failure (Figure 3). This points out why evaluations of coating properties alone are inadequate. Vinyl tar coatings also suffered a similar increase in corrosion attack, with substantial increases observed in the region of holidays.

The cathodically polarized panels showed a rapid increase in 1/Rt at a much earlier stage than the freely corroding panels. However, the values tended to stabilize and even decrease somewhat in the case of the thicker tar. This effect may be caused by the formation of deposits which block coating pores and holidays.

Area Effects

In the case of freely corroding steel with epoxy coating, the capacitance measurements indicated that the actively corroding panel area increased from .05% to 55%. These results correspond well with visual observation of blistering and rust spots, and also are realistic in comparison to previous experience.

Mass Transport Effects

The extent of corrosion at the metal/coating interface is partially dependent on solution properties such as the specific diffusion and solubility of the ions in solution. A slope of -1/2 on a log-log plot would indicate a diffusion controlled film degredation process. This type of data was found for epoxy polyamide coatings. Thus, a correlation between mass transport rates of damaging species and coating deterioration rates may be feasible.

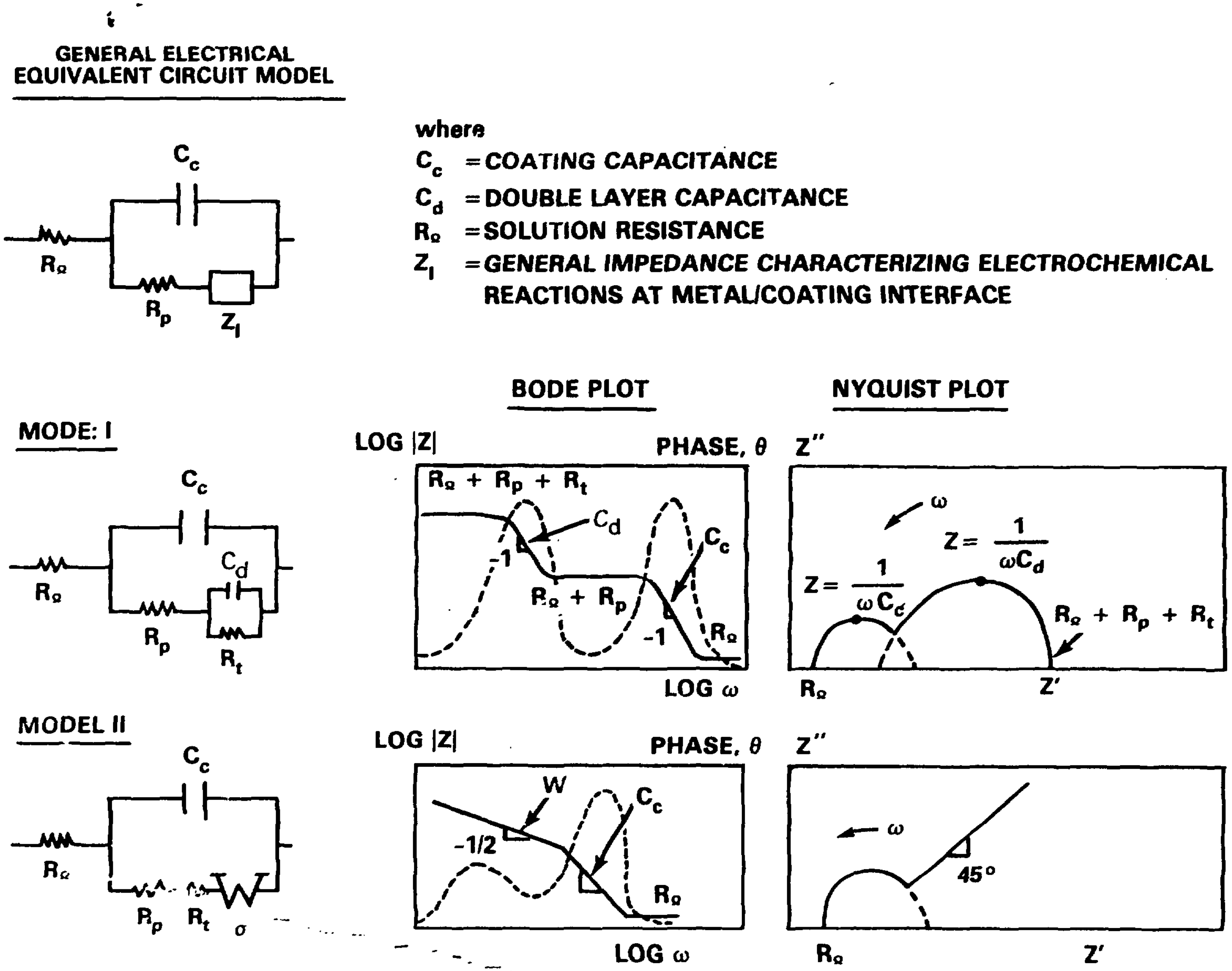


Figure 1. Equivalent circuit models for metal/coating/electrolyte systems.

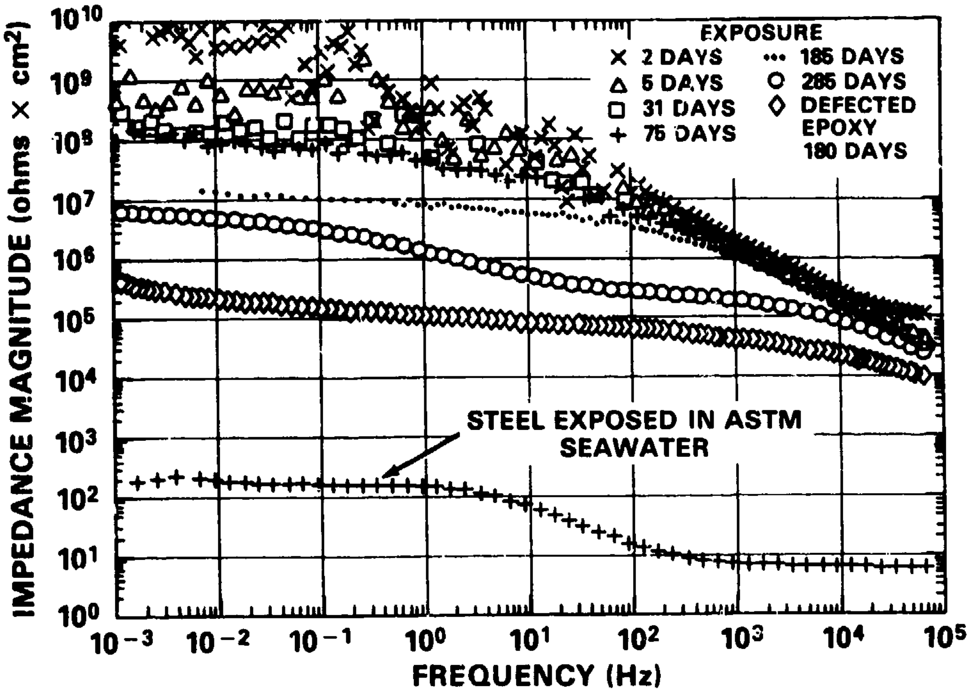


Figure 2. Bode plots for epoxy-polyamide coated steel in ASTM artificial ocean water from 2 to 285 days.

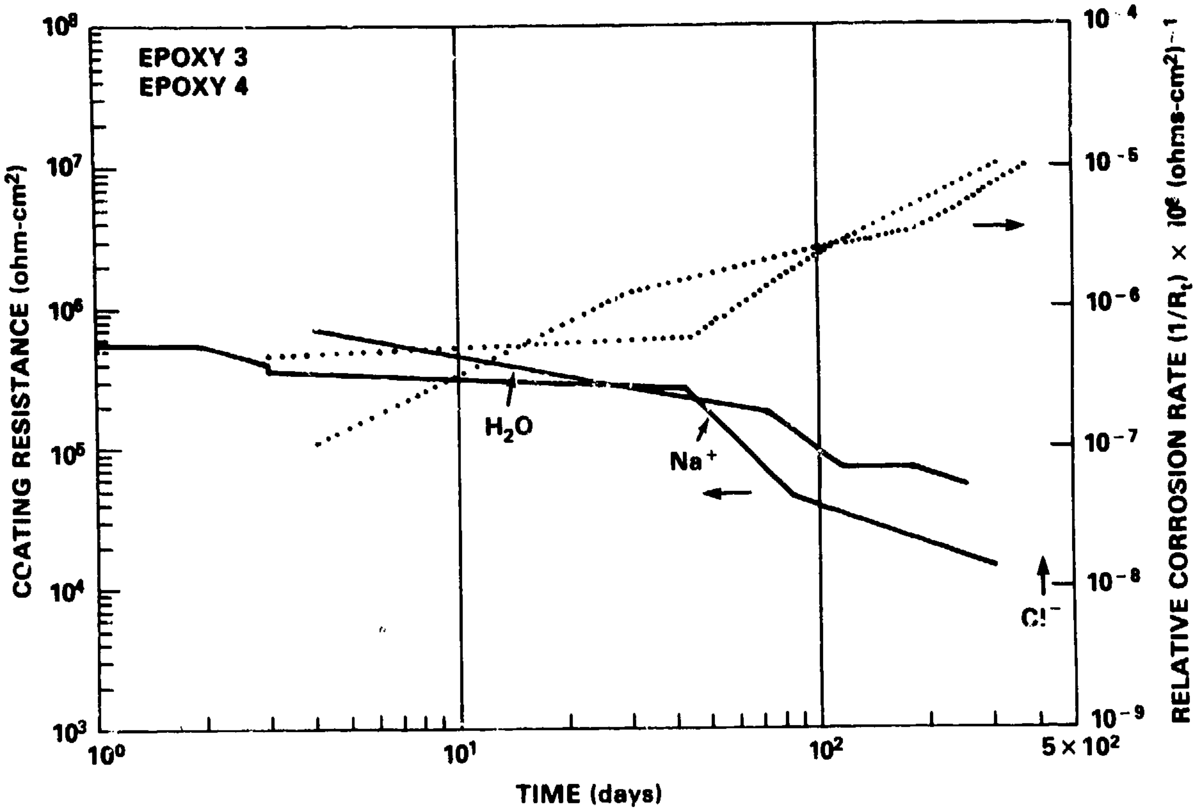


Figure 3. Change in epoxy-polyamide coating resistance under freely corroding conditions in ASTM artificial ocean water.

ALTERNATE IMMERSION ACCELERATED TESTING OF COATING SYSTEMS FOR NAVAL SHORELINE FACILITIES

Denny A. Jones, Professor and Chairman
Dept. of Chemical and Metallurgical Engineering
University of Nevada-Reno
Reno, NV. 89557

Presented at the Workshop on
Performance Prediction for Protective Coatings
Naval Civil Engineering Laboratory
Port Hueneme, California
September 15, 1986

In previous work (1) at the University of Nevada-Reno, it was found that alternate immersion exposures accelerated underfilm attack on coated automotive sheet steel. This presentation reported on similar preliminary work on coating systems for steel considered for use in various Naval shoreline facilities.

Experimental Materials and Procedures

Samples, 6 x 10-inch x 1/4-inch thick, of each of nine coating systems were supplied by NCEL. Specifications are reproduced from Hearst (2) in Table I.

Specimens of about 3/4-inch x 3/4-inch were cut from each coating system sample. The cut edges provided the necessary exposed steel surface to evaluate underfilm attack. The specimens were drilled and tapped on one of the coated faces to accept a threaded rod sheathed in thick-wall Teflon tubing. A compression nut at the opposite end of the rod produced a water-tight seal between the specimen face and the Teflon tubing. Figure 1 shows the assembly with the Teflon tubing pressed through a rubber stopper which fits into a glass bottle of about 300-cc capacity.

Alternate immersion was effected during an experimental run by pushing the Teflon tubing with the inner threaded rod through the stopper to position the specimen either above or below the solution level in the bottom of the bottle. A 24-hour alternate immersion cycle consisted of a 0.5 to 1-hour immersion period in the solution followed by the remaining time in the humid atmosphere above the solution. In changing from immersion to humid air exposure, the excess solution was evaporated from the specimen surface in a warm air stream to remove the incipient water film which had been found previously (1) to simulate lower corrosion in continuous immersion without alternate exposure to a humid atmosphere.

Results and Discussion

The primary variables in this study were composition of the immersion solution and temperature during the humid air period exposure. The various experimental conditions are listed in Table II along with the results of visual examinations after 10 alternate exposure cycles during a period of two weeks.

The results may be summarized, together with additional observations, as follows:

Continuous Immersion at room temperature caused no blistering, consistent with previous results (1), because only a colloidal corrosion product was formed which did not undercut the coating. The corrosion products produced only minor stains on the coated surfaces.

Alternate Immersion in 3% NaCl at room temperature produced blistering on latex and vinyl coatings. The vinyl coating was somewhat more resistant than the latex coatings. Heavy rust deposits formed on the exposed bare surfaces of the edges and on the coating surfaces, especially near the edges. Coating systems with a zinc bearing undercoating had reduced deposits at the edges and near the edges due apparently to sacrificial protection by the zinc.

Alternate Immersion at 50C in 3% NaCl generally accelerated the attack on the susceptible coatings in the same environment at room temperature. The coal tar epoxy coating system showed some blistering at 50C, but no other coatings were blistered which did not blister at room temperature.

Alternate Immersion in sulfate (same normality as 3% NaCl) at room temperature produced heavy deposits but was less aggressive in causing blistering.

Alternate Immersion at pH 5, 3% NaCl at room temperature, caused more extensive corrosion of the exposed edges, but caused less blistering of susceptible coatings.

References

1. D. A. Jones, R. K. Blitz, and I. Hodjati, "Alternate Immersion Testing of Coated Automotive Sheet Steel," Corrosion,

2. P. J. Hearst to D. A. Jones, Memorandum L52/PJH/39, December 16, 1985.

TABLE I.

DESCRIPTION OF COATED STEEL PANELS FOR TESTING BY NCEL, PORT HUENEME, CA

PANEL ID and QUANTITY			DFT	SPECIFICATION AND FORMULA NUMBER	MANUFACTURER	DATE APPLIE
A	30 EACH	1 COAT	0.5	MIL-P-15328 F-117 WASH PRIMER	GSA	6/13/85
		2 COAT	2.0	TT-P-645 F-84 ZINC CHROMATE PRIMER	GSA	6/13/85
		3 COAT	2.5	TT-E-490 SILICONE ALKYD COPOLYMER	GSA	6/14/85
BD	30 EACH	1 COAT	2.5	DEVFLEX MD-4979 (RED)	DEVOE	6/11/85
		2 COAT	2.5	DEVFLEX MD-2707 (WHITE)	DEVOE	6/12/85
BP	30 EACH	1 COAT	2.0	MIL-P-28577 PRIMER, LATEX	PROLINE	8/19/85
		2 COAT	3.0	MIL-P-28578 WATER REDUCIBLE SEMI-GLOSS	PROLINE	8/20/85
C	30 EACH	1 COAT	3.0	MIL-P-24441A F-150R66 (GREEN) EPOXY-POLYAMIDE	DEVOE	6/11/85
		2 COAT	3.0	MIL-P-24441A F-151R66 (Gray) EPOXY-POLYAMIDE	DEVOE	6/12/85
		3 COAT	3.5	MIL-P-24441A F-152R66 (WHITE) EPOXY-POLYAMIDE	DEVOE	6/13/85
D	30 EACH	1 COAT	3.0	MIL-P-24441A F-150R66 (GREEN) EPOXY-POLYAMIDE	DEVOE	6/13/85
		2 COAT	2.5	MIL-P-24441A F-151R66 (GRAY) EPOXY-POLYAMIDE	DEVOE	6/14/85
		3 COAT	3.5	MIL-P-81773 DEVTHANE F-239 MD4618/MD4619	DEVOE	6/17/85
E	30 EACH	1 COAT	3.5	MIL-P-23236 CATHA-COAT 304I TWO-COMPONENT SELF CURE INORGANIC ZINC	KOPPERS	6/18/85
		2 COAT	4.0	MIL-P-24441A F-150R66 (GREEN) EPOXY-POLYAMIDE	DEVOE	6/19/85
		3 COAT	3.5	MIL-P-81773 DEVTHANE F-239 MD4618.MD4619	DEVOE	6/20/85
F	30 EACH	1 COAT	2.5	MIL-P-46105 PRIMER, ZINC-RICH EPOXY	PROLINE	8/20/85
		2 COAT	4.0	MIL-P-24441A F-150R66 (GREEN) EPOXY-POLYAMIDE	DEVOE	8/21/85
		3 COAT	3.0	MIL-P-81773 DEVTHANE MD4618/MD4619 F-239	DEVOE	8/22/85
G	30 EACH	1 COAT	8.0	SSPC NO. 16 COAL TAR EPOXY (BITUMASTIC 300M)	KOPPERS	6/17/85
		2 COAT	8.0	SSPC NO. 16 COAL TAR EPOXY (BITUMASTIC 300M)	KOPPERS	6/18/85
H	30 EACH	1 COAT	2.0	BUREAU OF RECLAMATION VINYL VR-3 INERTOL PRIMER (TILE RED) 837A	KOPPERS	6/19/85
		2 COAT	2.0	BUREAU OF RECLAMATION VINYL VR-3 INERTOL INTERMEDIATE (GRAY) 849	KOPPERS	5/20/85
		3 COAT	2.0	BUREAU OF RECLAMATION VINYL VR-3 INERTOL TOP COAT (WHITE) 850	KOPPERS	6/20/85

TABLE 2.
RESULTS OF ALTERNATE IMMERSION TESTS

NB: no blistering
EB: edge blistering
UB: uniform mild blistering
HB: heavy blistering

ND: no deposits
ED: rust deposits near edges only
MD: moderate rust deposits
HD: heavy rust deposits

	Experimental Conditions, Immersion in 3% NaCl unless otherwise indicated				
Designation: Coating System	Continuous Immersion Room Temp.	Alternate Immersion Room Temp.	Alternate Immersion 50C	Alternate Immersion Sulfate, RT	Alternate Immersion pH5, RT
A: Alkyd	ND, NB	HD, NB	HD, NB	HD, NB	HD, NB
BD: Latex	ED, NB	MD, UB	HD, UB	HD, NB	HD, EB
BP: Latex	MD, NB	HD, HB	HD, UB	HD, UB	HD, UB
C: Epoxy-Polyamide	ND, NB	MD, NB	MD, NB	HD, NB	MD, NB
D: Epoxy-Polyamide/Urethane	ED, NB	MD, NB	MD, NB	MD, NB	ED, NB
E: Inorganic Zinc/Epoxy/Urethane	ND, NB	ND, NB	MD, NB	MD, NB	MD, NB
F: Organic Zinc/Epoxy/Urethane	ED, NB	MD, NB	MD, NB	MD, NB	MD, NB
G: Coal Tar Epoxy	ND, NB	MD, NB	MD, MB	ED, NB	ED, NB
H: Vinyl	ED, NB	ED, EB	HD, EB	MD, NB	MD, EB

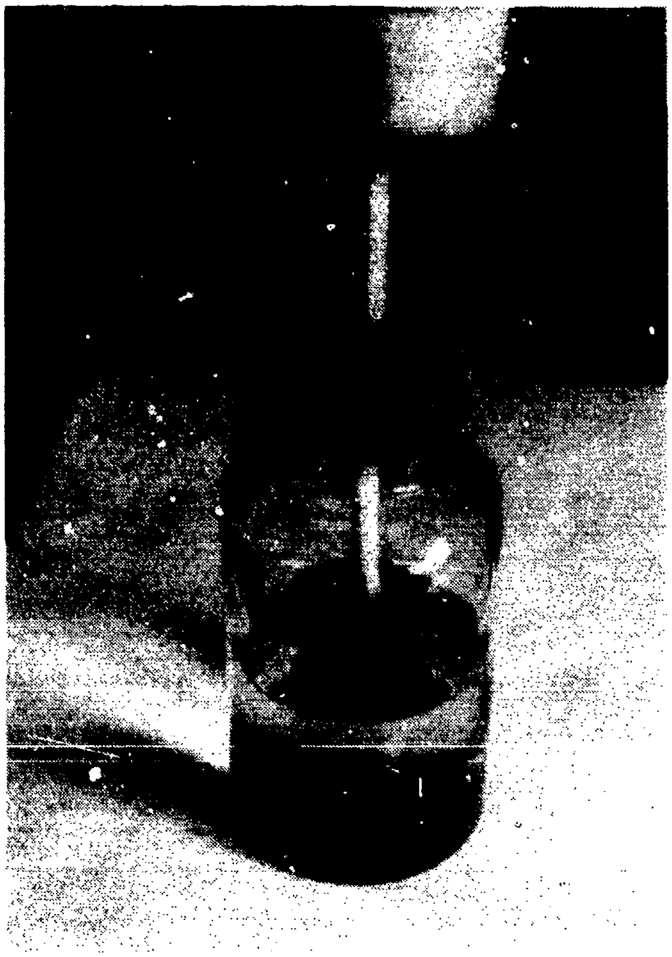


Figure 1. Cell for alternate immersion of coated steel specimens.

ZINC FILLED COATINGS

By

J. O. Stoffer
University of Missouri-Rolla
Rolla, Missouri

and

John Montle
Carboline Co.
1401 S. Hanley Rd.
St. Louis, MO 63144

Corrosion is the deterioration of a substance because of reaction with it and its environment. It is a natural occurring process just as water flowing down hill. The driving force that makes metals corrode is a consequence of their existence in their natural form. Iron oxide, hematite, when mixed with coke and lime undergoes a reaction to produce iron metal, CO and slag when energy is applied to it, (Slide No. 1). The reverse of this is corrosion and iron goes back to iron oxide which is rust.

The definition of an anode, cathode and electrolyte are critical to understanding the zinc rich coatings, (Slide No. 2.) An example of a galvanic battery is included, (Slide No. 3.) This depicts iron going to solution as iron ions and this releases electrons. The electrons flow toward the cathode. The respective reactions taking place are shown in Slide No. 4.

To summarize this, for corrosion to occur there must be formation of ions and release of electrons to the anionic surface where oxidation of the metal occurs. There must a simultaneous acceptance at the cathode surface of the electrons generated at the anodes. Corrosion occurs only at the anode.

Galvanic action refers to the changes in normal corrosion behavior that result from current generated when one metal has contact with a different metal. From the relative electrochemical potentials of the metals listed, (Slide No. 5), we see that magnesium is highest and gold is lowest. The electrical potential listed for magnesium is -2.3 volts, standard potential and varies to 1.68 for gold. The zinc/iron galvanic cell is shown as Slide No. 6. This is what happens when we electrically connect the zinc and iron through a cell that conducts current. We see that there will be electron flow from the zinc anode to the iron cathode and the iron will not corrode. Even if some iron ions should form momentarily they immediately react with the electrons, migrate to the cathode to from metallic iron. One would get the same effect if we impressed an electric current to the iron. As a matter of fact impressing current is a common practice for underground structures in power industries.

Why not use other metals? We find that magnesium sacrifices much faster than zinc. Aluminum forms a tight adhering oxide film which insulates it from further sacrifice so we're left with zinc in the middle of this EMF series. We say that zinc sacrifices at a reasonable rate and is the most practical to use. So what we do is prepare a coating that is zinc filled where we have intimate contact of zinc to zinc and the zinc metal with the iron surface so that we have the ability for the zinc to sacrifice itself. The method for preparing a zinc filled coating is that we have a conductive zinc filled coating that protects the metal by a galvanic cathodic protection. The zinc sacrifices itself and corrodes in preference to the iron. This method of protecting the steel will continue until the effective available zinc is used up. For the ideal condition we must keep the local zinc corrosion at an absolute minimum while the sacrificial reaction proceeds just fast enough to provide protection. The corrosion of zinc is uniquely fitted for the use as a sacrificial metal. In the atmosphere exposure zinc reacts with moisture and oxygen air to form zinc oxide and zinc hydroxide. These salts are fairly soluble and if this is the only reaction that occurred then the life of the zinc coating would be quite short. However, the second reaction takes place with carbon dioxide from the air to form an insoluble zinc carbonate.

This basic zinc carbonate is a tightly adhered semipermiable barrier that protects the zinc from corroding too rapidly and yet providing sufficient permiability to provide necessary electrical current to keep steel from corroding. The function of the zinc rich coating is to prevent corrosion of the substrate beneath the coated surface. Topcoats are applied over this in terms of zinc rich primers to lengthen the life of the system and prevent atmospheric corrosion of the zinc.

There are both organic and inorganic types of zinc rich coatings and there are several classifications of inorganic zinc rich systems as shown in Slide No. 7. There are certain requirements for the zinc coatings, (Slide No. 8). It has to have the ability to carry a high volume of zinc and maintain good film integrity. We have must have intimate zinc/zinc contact and zinc steel contact. The zinc must be free to sacrifice. It should have good alkali resistance of binder and the binder should hold the zinc particles together. It should be a porous material. I think this is extremely critical. The characteristics of the ethyl silicate zinc rich primers are listed in Slide No. 9. This is solvent based system. This is essentially what we call inorganic zincs and they are porous materials. They have to be porous materials to permit the sacrificial process to take place. In addition to being porous, they have to have good zinc to zinc and zinc to steel contact. A measure of this metal to metal contact is shown by a measure of the resistance Vs percent zinc as shown in Slide No. 10. For the zinc rich coating to perform well, it needs high zinc loading, above 70% for inorganic and above 80 or 90% for organic zincs.

This is where the problem arises, and one main goal of this conference,or meeting, is to look at ways to test early failure of coatings. One method presented is the electrochemical impedance measurements where failure is determined by a decrease in resistance. This would not be applicable for zinc rich coatings where the decrease in resistance indicates good metal/metal contact. Because of the porosity and resistance measurements, they may give rise to opposite types of readings than would be available for other types of coatings. Where most other coatings have a nonporous type film, the zinc rich coatings, the ethyl silicate based ones, have to have a porous film to function properly. Any of the tests that are mentioned subsequently in the papers here usually are based upon a nonporous coating as far as the testing process is concerned. Also, most of the testing processes were based on no ability to conduct current. The zinc rich coatings have to have intimate contact of zinc to zinc and zinc to iron. Therefore, if any metal were to be in contact with the measuring devices mentioned previously they would show a degradation of the coating itself whereas in reality it was still functioning properly. Caution should be excercised in evaluating the zinc rich coatings by methods discussed by previous speakers. We find that the zinc rich coatings are one of the best coatings for the protection of steel known today. They are sacrificial. They need to be coated with an organic topcoat to take some of the abusive wear. Slides 11, 12, and 13 show how the zinc rich coatings perform in salt spray testing.

SLIDES

1. Hematite (Fe_2O_3) + Coke (Carbon) + Lime (Impurity Remover) $\xrightarrow{\text{Energy}}$ Iron Metal (Fe) + CO_2 + Slag

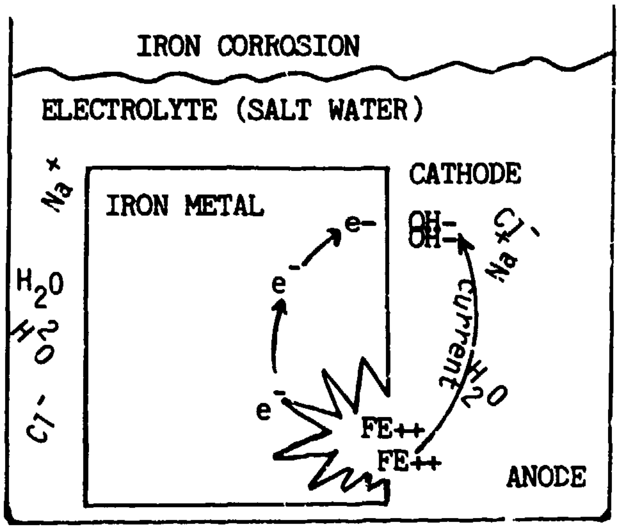
2. DEFINITIONS

ANODE-term used to describe that position of a metal surface that is corroded and from which current leaves the metal and enters solution.

CATHODE-term used to describe the metal surface from which the current leaves the solution and returns to the metal.

ELECTROLYTE-a solution with the ability to conduct electricity due to presence of ions.

3.



4. ANODE & CATHODE REACTIONS

ANODE: $4Fe \rightarrow 4Fe^{++} + 8e-$

CATHODE: $8e- + 4H_2O + 2O_2 \rightarrow 8OH^-$

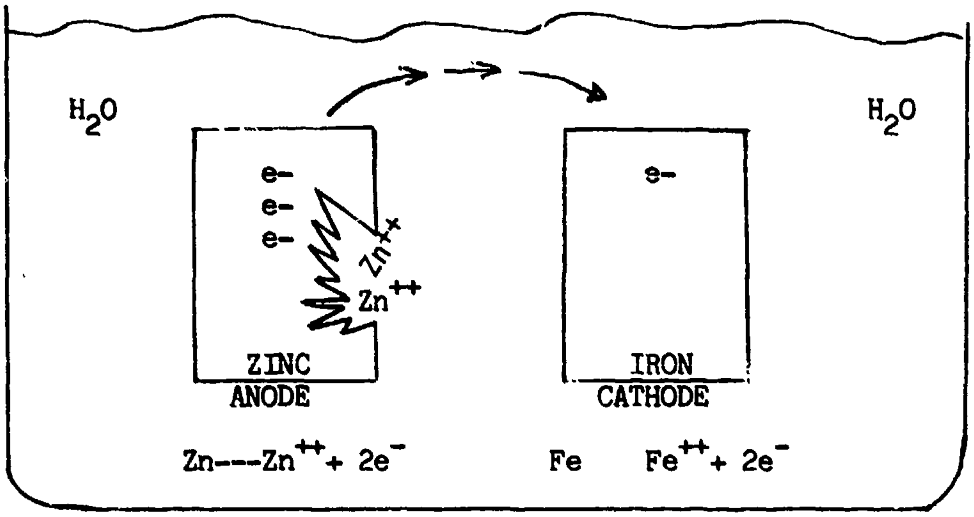
TOTAL REACTION: $4Fe + 2O_2 + 4H_2O \rightarrow 4Fe(OH)_2$

FURTHER REACTION: $4Fe(OH_2) + O_2 \rightarrow \underset{\text{(Rust)}}{2Fe_2O_3} + H_2O$

5. ## ELECTRICAL POTENTIALS

Magnesium	- 2.34	Std. Potential (Volts)
Aluminum	- 1.67	
Zinc	- .763	
Iron	- .44	
Hydrogen	- 0	
Copper	+ .345	
Platinum	+ 1.20	
Gold	+ 1.68	

6. ## ZINC/IRON GALVANIC CELL



7. ## TYPES OF INORGANIC ZINC COATINGS

1) Alkali silicates, post cured
2) Alkali silicates, self cured
3) Silicate complexes, solvent based & self cured (ethyl silicates)

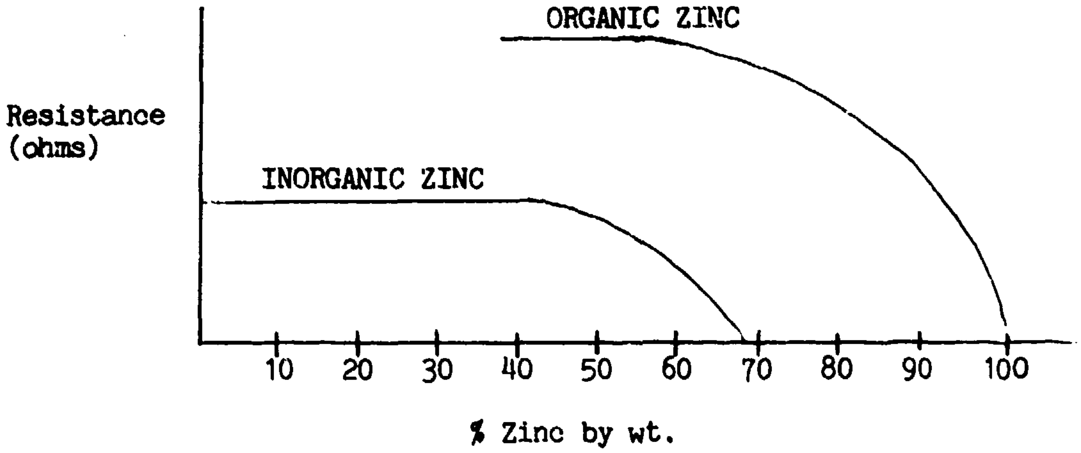
8. CHARACTERISTICS OF ETHYL SILICATE ZINC RICH PRIMERS

1) Solvent based
2) 1 or 2 package
3) Commercial blast generally acceptable
4) Excellent performance
5) Tendency to cause topcoat bubbling during application
6) Alcohol based
7) Can be applied below "freezing" temperatures
8) Cures best at high humidities
9) Better physical properties than water based silicates (impact resistance, mudcracking resistance, etc.)

9. PROPERTIES DESIRED FOR EFFECTIVE CATHODIC PROTECTION

1) Ability to carry a high volume of zinc.
2) Intimate zinc/zinc contact and zinc/steel contact.
3) Freedom to sacrifice.
4) Good alkali resistance of binder.
5) Binder that "glues" zinc particles.
6) Porosity

10.



Report by Keane, Weaver and Bruno 6/81

Table 5. SSPC Classification of Zinc--Rich Paints
(as per SSPC-Paint 20)

I. INORGANIC

- **I-A. Post-Curing**
- **I-B. Water-Reducible**
  - **I-B1. Sodium/Lithium Silicate**
  - **I-B2. Sodium/Potassium/Lithium Silicate**
  - **I-B3. Potassium Silicate**
- **I-C. Solvent-Reducible**
  - **I-C1. Ethyl Silicate**
  - **I-C2. Cellosolve Silicate**
  - **I-C3. Butyral Silicate**
  - **I-C4. Butyral Silicate (Modified)**

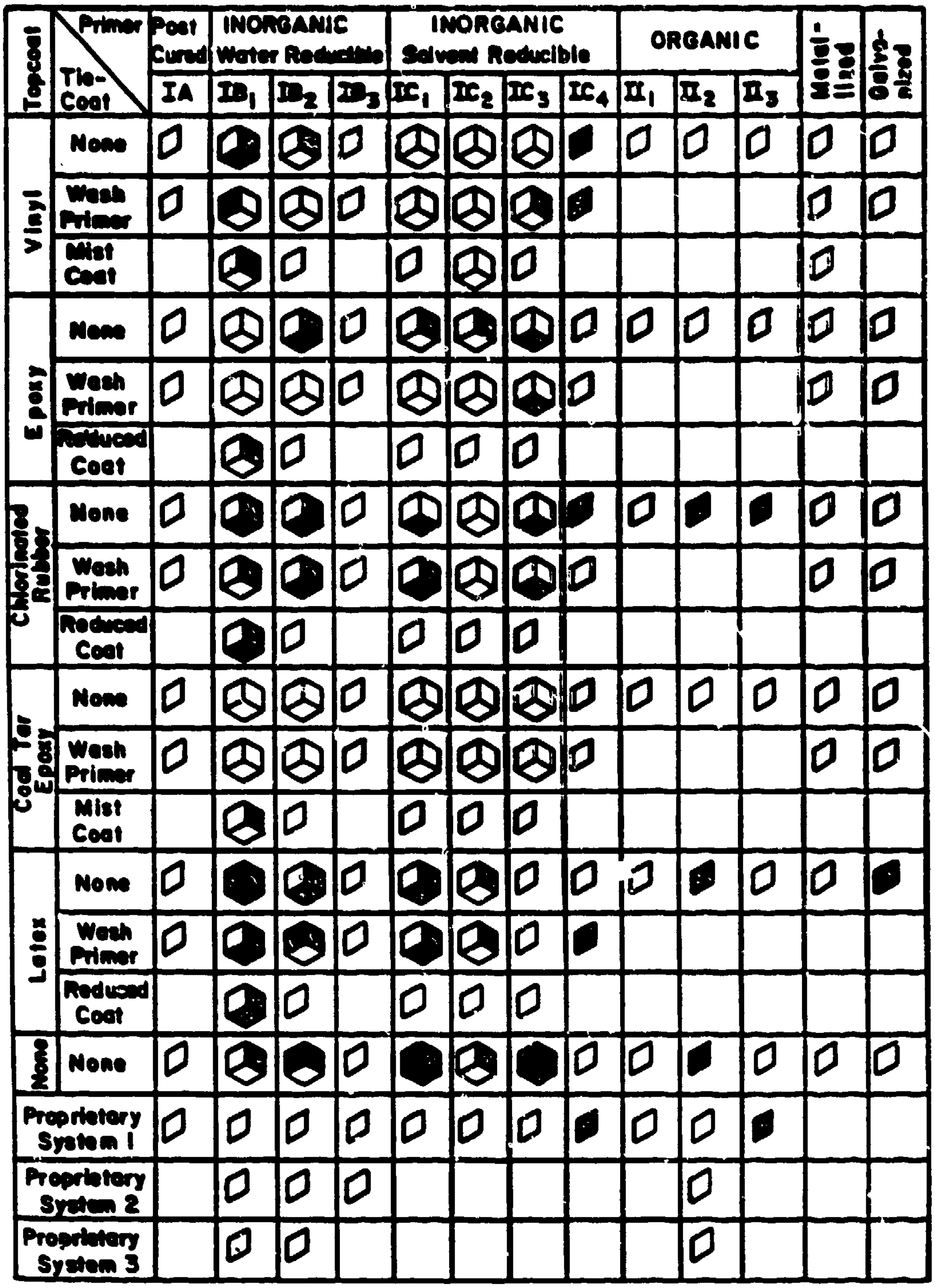
II. ORGANIC

- **II-1. Epoxy Polyamide**
- **II-2. Phenoxy**
- **II-3. Chlorinated Rubber**

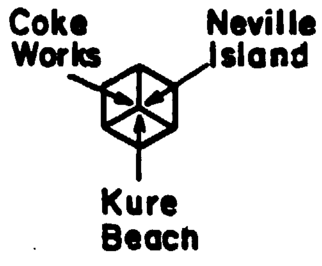
Table 6. Generic Topcoats Used in Zinc--Rich Topcoat Study

VINYL	**SSPC-Paint 9, "White (or Colored) Vinyl Paint"**
EPOXY	**SSPC-Paint XEP2X, "Epoxy Polyamide Topcoat"**
CHLORINATED RUBBER	**SSPC-Paint 19, "Chlorinated Rubber Topcoat Paint"**
COAL TAR EPOXY	**SSPC-Paint 16, "Coal Tar Epoxy-Polyamide Black (or Dark Red) Paint"**
LATEX	**SSPC-Paint XWB2X, "Latex, Semi-Gloss Exterior Topcoat"**

Table 10. Qualitative Summary of Rust Performance
(5 - Year atmospheric exposure)



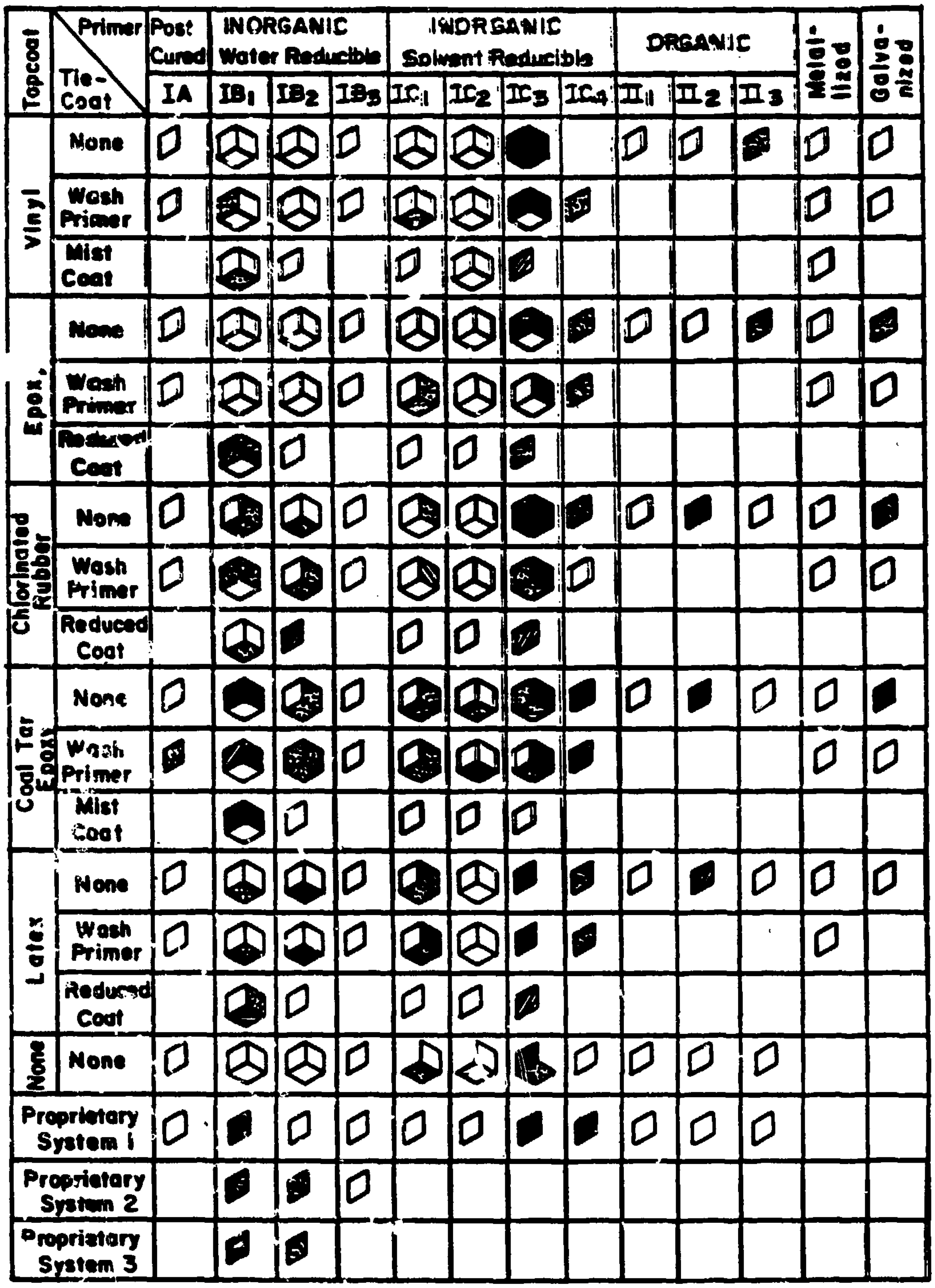
Topcoat	Tie-Coat \ Primer	Post Cured	INORGANIC Water Reducible			INORGANIC Solvent Reducible				ORGANIC			Metal-lized	Galva-nized
		IA	IB₁	IB₂	IB₃	IC₁	IC₂	IC₃	IC₄	II₁	II₂	II₃		
Vinyl	None	▱	◐	◐	▱	⬡	⬡	⬡	▰	▱	▱	▱	▱	▱
	Wash Primer	▱	◐	⬡	▱	⬡	⬡	◐	▰				▱	▱
	Mist Coat		◐	▱		▱	⬡	▱					▱	
Epoxy	None	▱	⬡	◐	▱	◐	◐	◐	▱	▱	▱	▱	▱	▱
	Wash Primer	▱	⬡	⬡	▱	⬡	⬡	◐	▱				▱	▱
	Reduced Coat		◐	▱		▱	▱	▱						
Chlorinated Rubber	None	▱	◐	◐	▱	◐	⬡	◐	▰	▱	▰	▰	▱	▱
	Wash Primer	▱	◐	◐	▱	◐	⬡	◐	▱				▱	▱
	Reduced Coat		◐	▱		▱	▱	▱						
Coal Tar Epoxy	None	▱	⬡	⬡	▱	⬡	⬡	⬡	▱	▱	▱	▱	▱	▱
	Wash Primer	▱	⬡	⬡	▱	⬡	⬡	⬡	▱				▱	▱
	Mist Coat		◐	▱		▱	▱	▱						
Latex	None	▱	⬢	◐	▱	◐	◐	▱	▱	▱	▰	▱	▱	▰
	Wash Primer	▱	◐	◐	▱	◐	◐	▱	▰					
	Reduced Coat		◐	▱		▱	▱	▱						
None	None	▱	◐	◐	▱	⬢	◐	⬢	▱	▱	▰	▱	▱	▱
Proprietary System 1		▱	▱	▱	▱	▱	▱	▱	▰	▱	▱	▰		
Proprietary System 2			▱	▱	▱						▱			
Proprietary System 3			▱	▱							▱			



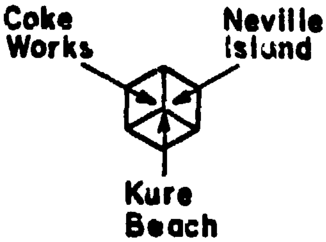
VIS-2 Rust Rating

□	10	Good
▨	9, 8	Fair
■	≤ 7	Poor

Table 11. Qualitative Summary of Scribe Performance
(5 - Year atmospheric exposure)



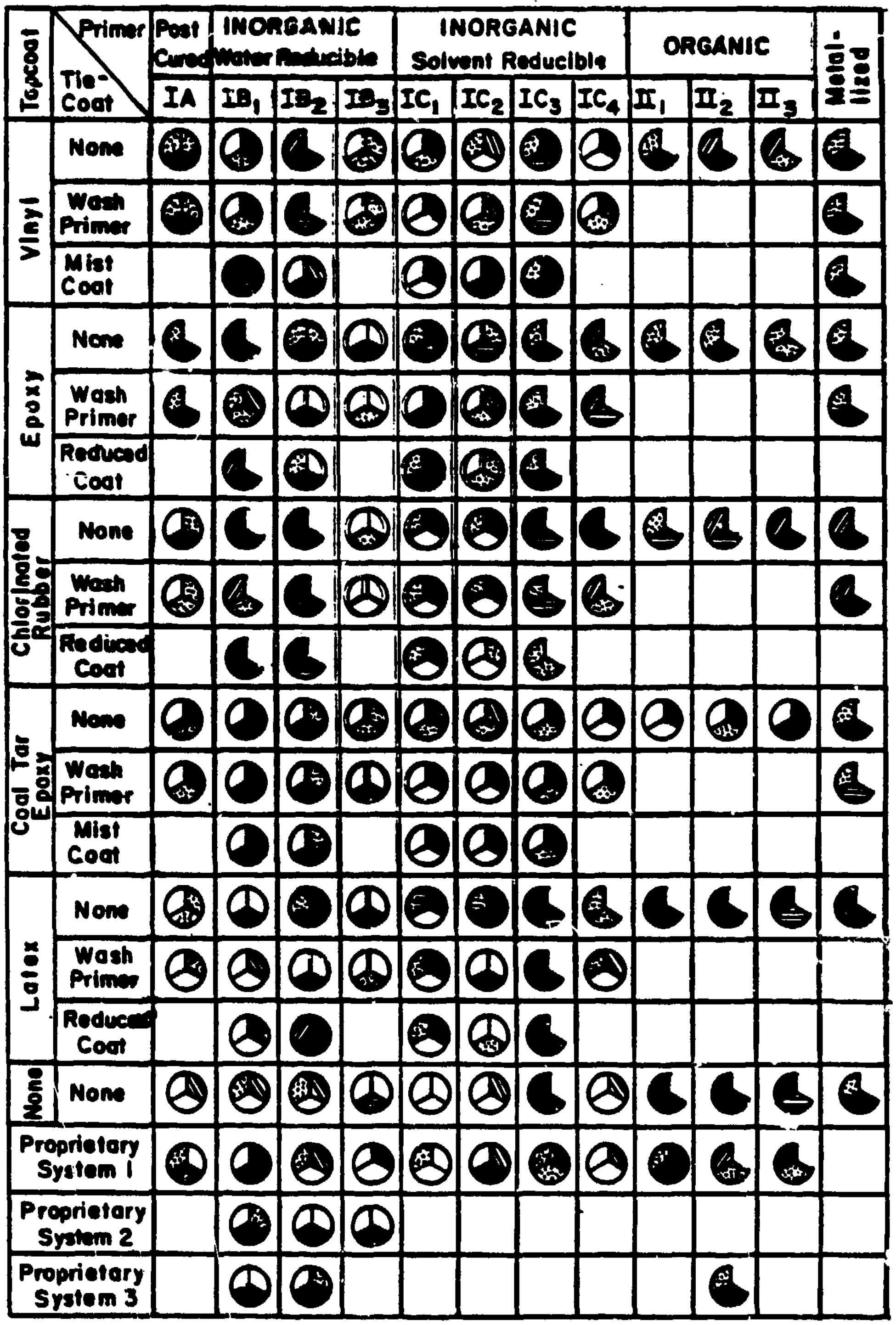
Topcoat	Primer / Tie-Coat	Post Cured	INORGANIC Water Reducible			INORGANIC Solvent Reducible				ORGANIC			Metal-lized	Galva-nized
		IA	IB1	IB2	IB3	IC1	IC2	IC3	IC4	II1	II2	II3		
Vinyl	None	▱	⬡	⬡	▱	⬡	⬡	⬢		▱	▱	▰	▱	▱
	Wash Primer	▱	⬡	⬡	▱	⬡	⬡	⬢	▰				▱	▱
	Mist Coat		⬡	▱		▱	⬡	▰					▱	
Epoxy	None	▱	⬡	⬡	▱	⬡	⬡	⬢	▰	▱	▱	▰	▱	▰
	Wash Primer	▱	⬡	⬡	▱	⬡	⬡	⬡	▰				▱	▱
	Reduced Coat		⬢	▱		▱	▱	▰						
Chlorinated Rubber	None	▱	⬡	⬡	▱	⬡	⬡	⬢	▰	▱	▰	▱	▱	▰
	Wash Primer	▱	⬢	⬡	▱	⬡	⬡	⬢	▱				▱	▱
	Reduced Coat		⬡	▰		▱	▱	▰						
Coal Tar Epoxy	None	▱	⬢	⬡	▱	⬡	⬡	⬢	▰	▱	▰	▱	▱	▰
	Wash Primer	▰	⬡	⬢	▱	⬡	⬡	⬡	▰				▱	▱
	Mist Coat		⬢	▱		▱	▱	▱						
Latex	None	▱	⬡	⬡	▱	⬡	⬡	▰	▰	▱	▰	▱	▱	▱
	Wash Primer	▱	⬡	⬡	▱	⬡	⬡	▰	▰				▱	
	Reduced Coat		⬡	▱		▱	▱	▰						
None	None	▱	⬡	⬡	▱	⬡	⬡	⬡	▱	▱	▱	▱		
Proprietary System 1		▱	▰	▱	▱	▱	▱	▰	▰	▱	▱	▱		
Proprietary System 2			▰	▰	▱									
Proprietary System 3			▰	▰										



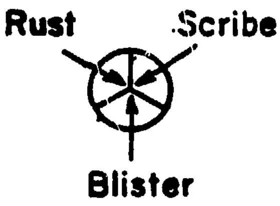
Scribe rusting or undercutting in 1/32" (0.08mm)

▢	0,1	Excellent
▩	2,3	Good
▨	4-7	Fair
■	≥ 8	Poor

Table 12. Qualitative Summary of Salt Fog Data - 16,000 Hours



Topcoat	Tie-Coat \ Primer	Post Cured	INORGANIC Water Reducible			INORGANIC Solvent Reducible				ORGANIC			Metal-lized
		IA	IB₁	IB₂	IB₃	IC₁	IC₂	IC₃	IC₄	II₁	II₂	II₃	
Vinyl	None	●	●	●	●	●	●	●	●	●	●	●	●
	Wash Primer	●	●	●	●	●	●	●	●				●
	Mist Coat		●	●		●	●	●					●
Epoxy	None	●	●	●	●	●	●	●	●	●	●	●	●
	Wash Primer	●	●	●	●	●	●	●	●				●
	Reduced Coat		●	●		●	●	●					
Chlorinated Rubber	None	●	●	●	●	●	●	●	●	●	●	●	●
	Wash Primer	●	●	●	●	●	●	●	●				●
	Reduced Coat		●	●		●	●	●					
Coal Tar Epoxy	None	●	●	●	●	●	●	●	●	●	●	●	●
	Wash Primer	●	●	●	●	●	●	●	●				●
	Mist Coat		●	●		●	●	●					
Latex	None	●	●	●	●	●	●	●	●	●	●	●	●
	Wash Primer	●	●	●	●	●	●	●	●				
	Reduced Coat		●	●		●	●	●					
None	None	●	●	●	●	●	●	●	●	●	●	●	●
Proprietary System I		●	●	●	●	●	●	●	●	●	●	●	
Proprietary System 2			●	●	●								
Proprietary System 3			●	●								●	



Average Durability Ratings

○ > 10,000hrs Excellent

▨ > 5,000 hrs Good

▤ > 2,000 hrs Fair

● < 2,000 hrs Poor

REDUCED TIME FRAME FOR PREDICTING COATING PERFORMANCE

Bernard R. Appleman
Steel Structures Painting Council
4400 Fifth Avenue
Pittsburgh, PA 15213

Summary of Paper Given at
Workshop on Performance Prediction for Coatings

Naval Civil Engineering Laboratories
Port Hueneme, CA 93043
September 15, 1986

Probably the most reliable means for predicting how well a coating will perform under a given set of conditions is its past performance under the same or similar conditions. For heavy-duty industrial maintenance coatings, designed to last 10 to 20 years, such a test protocol is neither practical nor affordable. There are, however, techniques for deriving the required information in a shorter period of time.

One of the major objectives in a coating development and evaluation program is to determine the time until failure occurs (this is normally defined as the point at which the coating system is no longer serving its intended function and requires repainting). For maintenance paints, failure is normally based on macroscopic visual defects such as rust, or paint delamination over a substantial portion of the surface (e.g., 20% of the surface showing greater than or equal to 3% rusting). As noted above, for high-quality coatings, this condition occurs after approximately 100,000 hours (approximately 11 years).

There are several approaches to obtaining performance data in a shorter time period.

1. Observe early macroscopic damage under natural exposure

For example, one can look for very small pinpoints of rust, or tiny blisters, or use instruments for detecting corrosion under the film.

2. Observe microscopic damage on natural exposures

Film properties that may have predictive value include permeability, electrochemical impedance spectra, and internal strain.

3. Observe macroscopic failure in artifical accelerated environments

Common accelerated chambers which cause paints to fail relatively rapidly include salt spray and environmental weathering chambers.

4. Observe early macroscopic or microscopic damage in accelerated environments

This approach combines 1 and 3 or 2 and 3 above, and would potentially produce degradation in the shortest time period.

Approach 1 is currently being investigated by SSPC as described below.

Approach 2 has been discussed by several other speakers at the NCEL Workshop on Performance Prediction for Protective Coatings. Approach 3 is extensively used by paint manufacturers, users, and testing agencies, and is widely criticized for its lack of reliability. Approach 4 is being investigated in a joint program by SSPC and National Bureau of Standards (NBS) under sponsorship by the Federal Highway Administration and the National Shipbuilding Research Program.

Figures A, B, C, and D illustrate how the various approaches can reduce the time for evaluations. Graph A illustrates Approach 1, in which damage (which is less than failure) occurs at 10,000 hours versus the actual failure occurring at 100,000 hours. Graph C shows a linear progression of damage over the log of time. This line will not coincide with the line showing macroscopic damage, because different properties are being evaluated. Graph C illustrates the reduction in time by looking at 2 or more levels of damage. Graph B shows representative plots of the degradation versus the log of the time. The three lines represent different levels of intensity of the artifical stress factors. The leftmost line represents the most severe conditions and the rightmost the least severe conditions. By looking at several levels of stress (e.g., several temperatures), one can cause the failure to occur at reduced time intervals.

Graph D also depicts degradation in an artificial exposure, but applies the principle of microscopic damage levels. Depending on the severity of the stress and the sensitivity of the microscopic technique, it is possible to obtain performance information in a very short period of time.

Early Degradation in Natural Exposures

SSPC has applied the approach of early macroscopic examination to a set of U.S. Navy data on 5-year exposures at a severe marine site. The Navy test evaluated six paints and 10 surface preparations. For this analysis we will focus on the variation among the six paints. The major parameters evaluated were as follows:

- o Degree of rusting on a logarithmic scale of 1-10 (SSPC-Vis 2/ASTM D610
- o Distance of undercutting from the scribe in 1/32". (Scribe is a bared area approximately 1/16" x 4".

- o General protection: compilation of all defects rated on a logarithmic scale of 1-10.

One illustration of the use of early degradation is shown in Figure E. These two plots show the cumulative failure distribution of an alkyd paint (the cumulative failure distribution is the total number of systems that have reached a prescribed degradation or failure criterion at different time periods). The upper figure uses a failure criterion of 5, i.e. failure when 3% of the surface shows degradation. The lower curve is based on a failure criterion of 8.7, i.e., all panels having greater than or equal to 0.05% of the surface degraded. These data demonstrate that these two distribution curves have similar shapes. However, much important data for the lower curve was missed because no readings were taken at 3 and 9 months. Thus, in order to apply this technique, one needs to obtain more frequent readings during the early stages of the evaluation. Additional experiments have been initiated using a much more rigorous approach to obtain early degradation information.

Survival Analysis of Paint Degradation

These data were also examined using the statistical approach of survival analysis. Survival analysis examines the proportion or fraction of coatings which survive (i.e., do not fail) for various time intervals. By analysing the survival behavior of different coatings, it is possible to differentiate and rank the coatings tested.

Table 1 shows the result of survival analysis on the six paints in this experiment. The second column gives the percentage of the test panels that had failed after 54 months, ranging from 45% for the epoxy to 100% for the coal tar epoxy and alkyd. Failure is considered to occur when either the rust rating reaches a 7 or the scribe equals 8/32".The third column is the mean time for the panels of a given paint to reach the failure.

Table 2 shows the ranking from best to worst of the six coatings included in this test. Three sets of failure criteria were analyzed. These criteria are based on a combination of ratings; for example, the first criterion was time until either the rust rating reached a level of 9 or the scribe rating reached a level of 2/32". The other two criteria were rust rating of 8, scribe rating of 4/32", and rust rating of 7, scribe rating of 8/32", respectively. The table shows that the ranking among the coatings was very similar for the different criteria selected. In other words, the ranking obtained using the criterion that gave the earliest indication of degradation (rust of 9, scribe of 2/32") was a good predictor of the ranking of the coatings at the criterion showing higher degradation (rust of 7, scribe of 8/32"). NOTE: The latter criterion is the more usual definition of "failure" for most industrial maintenance coatings.

SUMMARY

Predicting performance of coatings is an extremely challenging and difficult problem. There are several techniques available for obtaining information at an early stage. There is considerable effort underway by various research groups in developing new artificial exposure cycles, in advancing the techniques for microscopic and electrochemical characterization of paint films, and in more detailed observation and evaluation of coatings in natural environments. It is important to recognize the complexity of the problem and to develop the multi-discipline and cooperative industry-government effort required to generate real progress in this area.

BRA:aeb
11/6/86

TABLE 1

SURVIVAL ANALYSIS OF 54-MONTH OUTDOOR PAINT EXPOSURES

Failure Criterion: Rust 7 or Scribe 8/32"

PAINT	% FAILED (54 Months)	MEAN FAILURE TIME
EPOXY	54	54 Months
LATEX	63	42
VINYL	80	41
ZINC	84	36
COAL TAR	100	32
ALKYD	100	32

TABLE 2

COMPARING RELATIVE PERFORMANCE WITH DIFFERENT FAILURE CRITERIA

FAILURE CRITERION	RUST RATING	9	8	7
	SCRIBE RATING	2/32	4/32	8/32
	RANKING*			
	1	EPOXY	EPOXY	EPOXY
	2	VINYL *	VINYL	VINYL
	3	LATEX	LATEX	LATEX
	4	COAL TAR	COAL TAR	COAL TAR
	5	ALKYD	ZINC	ZINC
	6	ZINC	ALKYD	ALKYD

*Bar between coatings indicates that differences are statistically significant at 95% level.

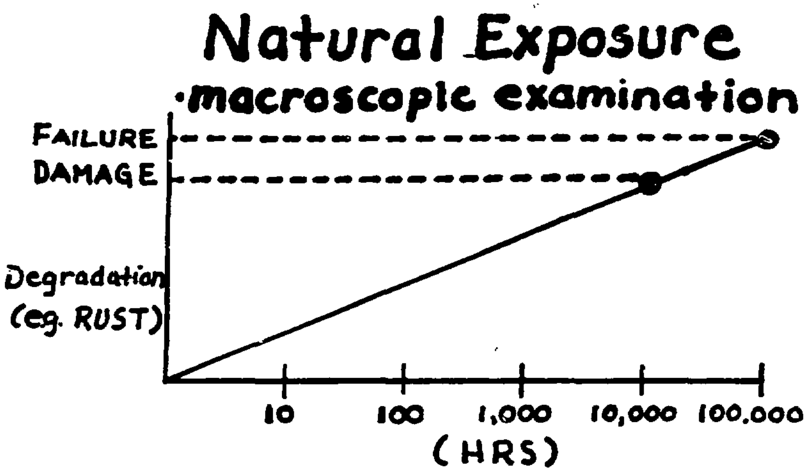


Figure A

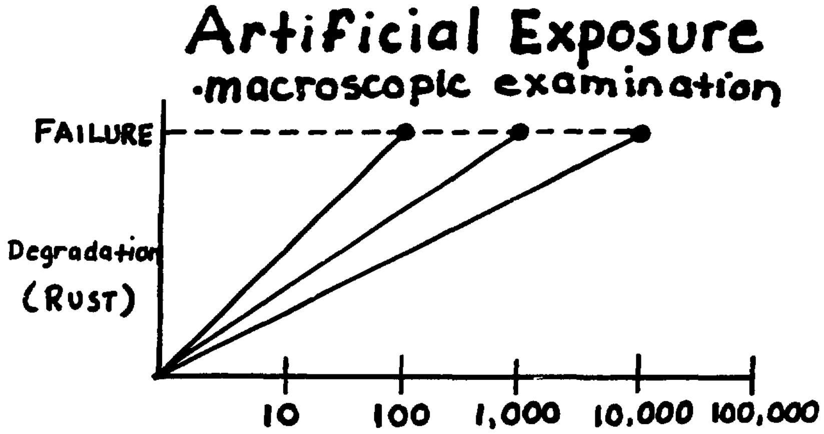


Figure B

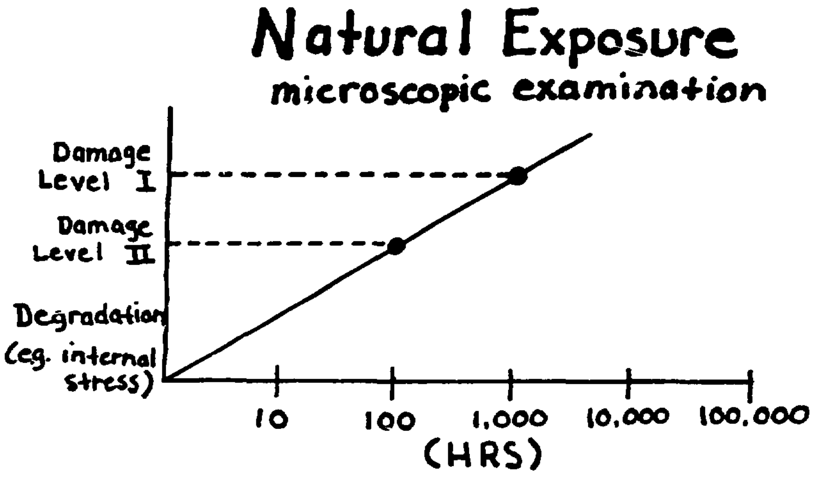


Figure C

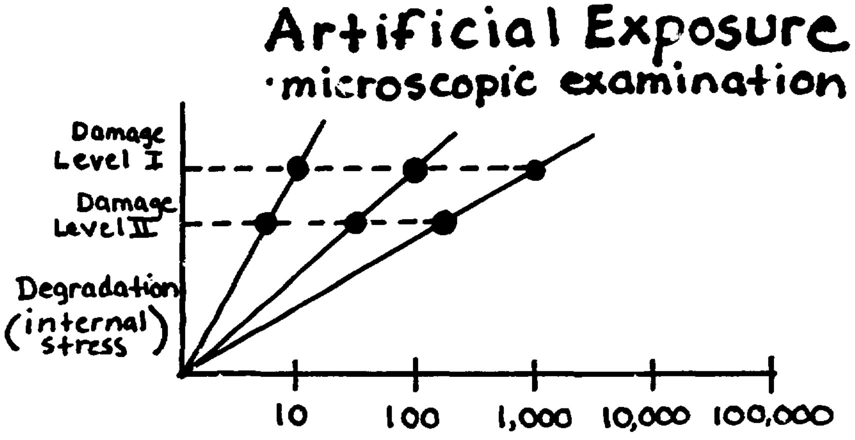


Figure D

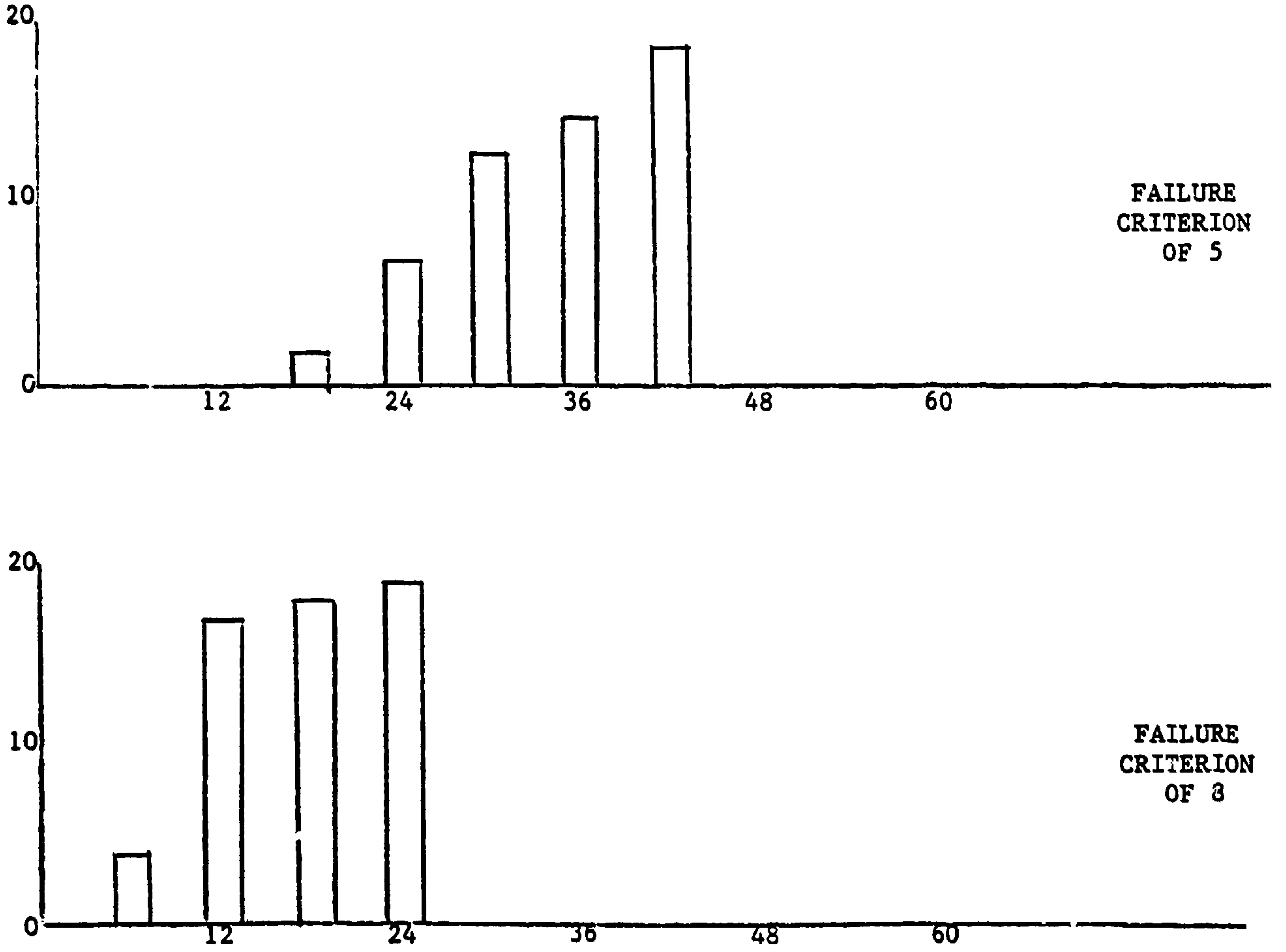


Figure E. Cumulative failure distribution alkyd (general protection).

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