



Project Summary

Preliminary Exposure Study to Determine the Effects of Acid Deposition on Coated Steel Substrates

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This report describes the progress that has been made within the Coatings Effect Research Program that the Environmental Protection Agency conducts for Task Group VII within the National Acid Precipitation Assessment Program. This project involves the evaluation of the effects of acidic pollutants on painted metal substrates. The project examined a commercially available alkyd paint/primer system applied to a low carbon steel substrate exposed under a variety of simulated acidic conditions to determine the micro/macro effects of such exposure. This report details the results which include the screening and development of sensitive analytical techniques and the use of these techniques to investigate effects of SO₂ on alkyd painted steel coupons during laboratory exposure. The techniques that were identified as those most sensitive and applicable during the study include tensile adhesion testing, electrochemical impedance spectroscopy (EIS), and x-ray photoelectron spectroscopy (XPS). A novel electrochemical monitor was developed during this program that allowed the continual monitoring of coating degradation during chamber exposure. It was further found that a good correlation existed between tensile adhesion strength measurements and electrochemical impedance parameters. The program determined that the rate of degradation of the alkyd painted steel coupons was

accelerated in the presence of SO₂. This effect was most pronounced on samples that contained defects (scribes), that were allowed to form condensed dew during the exposure period, and that had a horizontal orientation during exposure.

This Project Summary was developed by EPA's Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title. (See Project Report ordering information at back.)

Introduction

The Atmospheric Research and Exposure Assessment Laboratory of the Environmental Protection Agency (EPA) has conducted a program entitled, Effects of Acid Deposition on Coated Steel Substrates for Task Group VII, Effects on Materials and Cultural Resources. This Task Group is one of several groups that conducted research within the National Acid Precipitation Assessment Program.

This report reviews the progress that was made to develop and select analytical techniques that are appropriate to identify early micro/macro failure processes associated with acidic deposition on coated steel substrate systems and to use these techniques to evaluate such damage. The candidate techniques were those that would evaluate changes in the painted steel coupons that would lead to such macroscopic failures. Those determined to be the most appropriate for our

painted steel system include tensile adhesion testing, electrochemical impedance spectroscopy, and surface analytical techniques. The recent focus of the program involved refined types of exposures, i.e., controlled atmosphere in an environmental chamber and the use of those analytical techniques deemed most appropriate in year one to examine the incremental effects of acid deposition on painted metal substrates.

Technical Approach

The first year of this program involved the completion of four primary tasks: the design and construction of an environmental test chamber, the selection of an initial coating system for study and the development of a method for accelerated cure of the system, preliminary sample exposures (primarily via immersion), and technique screening. The second year of the program involved the use of the most promising analytical techniques in refined types of exposures to evaluate the damage to painted steel substrates exposed to acidic environments.

Environmental Exposure Chamber

The environmental test chamber is composed of a 4" diameter, 2 ft. long sample compartment which can accommodate up to 78 1" x 1" x 1/16" painted steel coupons mounted flush to the chamber wall. It is capable of controlled introduction of pollutants and regulation of conditions of temperature and relative humidity. Since flow rates in the chamber are not sufficient to ensure turbulent flow, baffles have been incorporated between sample sections to promote mixing and minimize the development of a boundary layer. The inside walls of the chamber are quartz, and the remainder of the system that is exposed to the gas is teflon. The environmental exposure system is monitored and controlled using a computer, to collect the data and to control the 60 1/min. mass flow controllers (wet stream) and the sample heater/chiller unit, which regulates the sample temperature.

Sample Preparation

All test panels made from steel (ASTM A 569 CQ). Coupons of two different sizes (4" x 6" x 1/16" and 1" x 1" x 1/16") were used in these studies. The coupons were solvent degreased and grit-blasted to a white metal finish. A commercially available alkyd primer/topcoat paint system, typically used for steel storage tanks, was selected for these studies. The primer/top coat

system, which does not contain sulfur, was spray-applied onto the clean coupons. The front side of the coupons was coated with a layer of primer followed by a single or double layer of topcoat. The back side of the coupons was coated with one layer of primer and two layers of topcoat. The edges were coated with primer and brush coated twice with topcoat. Free-standing paint films (200-250 μ m) were prepared by pouring the paint onto a teflon plate, spreading it out using a doctor blade, and allowing to dry on the plate overnight at room temperature under standard laboratory conditions. All the coupons and films were then oven cured in air at 100°C for 1 hr, after a gradual heat up rate (taking approx. 70 min.) from room temperature to 100°C. Specimens had dry film thicknesses of either 120-170 μ m (later studies) or 250-300 μ m (immersion studies and early chamber studies). Some specimens contained a scribe extending diagonally across the specimen according to ASTM D-1654. Detailed description of the techniques that were used to provide reproducible specimens for the exposure studies are provided in the report.

Promising Analytical Techniques

A number of analytical techniques, including tensile adhesion, XPS, SEM, TGA, etc., have been applied to characterize degradation of chamber-exposed and aqueous-immersed painted steel coupons. EIS was also used to examine the electrochemical properties of the paint/substrate system. An atmospheric electrochemical monitor (ATMEIS) was developed for conducting these measurements during atmospheric exposures. EIS was the only analytical method, used within this program, that was appropriate for *in-situ* testing in the atmospheric exposure chamber. The fact that samples remain in the chamber throughout such studies makes EIS invaluable in determination of the onset and extent of degradation and establishing the relative contributions from each pollutant/condition.

Results and Discussion

Painted steel coupons were immersed in one of four different environments: aerated solutions of either nitric acid, sulfuric acid, or distilled water, or a deaerated solution of sulfurous acid. The acidic solutions were maintained at pH 3 throughout the exposure time. Free standing paint films were also exposed to each solution. It should be emphasized that all immersion studies were

conducted on samples containing a single layer of topcoat on the front side of the sample and a double layer of topcoat on the back and edges of the sample.

After two weeks of exposure, the edges of the panels in the nitric and sulfuric acid baths began to show very slight rust stains. The edges of the panels exposed to the sulfurous acid solution did not appear to have been attacked however, small blisters began to form on the surface. At later exposure times each of the exposed sample coupons exhibited blisters which appeared to increase in number with time. The blisters were filled with an aqueous solution whose pH is approximately 8.

ED-XRM line profiles were made across primer/paint cross-sections for as-prepared samples and for samples exposed for 1, 4, and 8 weeks. Samples exposed to water, sulfuric and nitric acids exhibited no indiffusion or leaching of material (elements with $Z > Na$). In contrast, samples exposed to sulfurous acid exhibited an indiffusion of S through the paint and primer and a leaching of primer constituents starting after 1 week of exposure. The comparison of the ED-XRM line profiles and the XPS measurements suggests that the S from the sulfurous acid penetrates the paint and primer films readily and does not accumulate at the intact paint-electrolyte interface.

EIS was also used extensively to characterize immersed samples throughout the exposure time in each of the three acids. From initial impedance values, 5 hours after exposure, evidence of pinholes was apparent. EIS data throughout the exposure period were dominated by the presence of preexisting pinholes, predominately located at the edges of the samples. A cell which does not expose the edges of the sample to solution was subsequently used for EIS analyses of immersed specimens to avoid the contribution of pinhole defects. Samples exposed in this cell exhibited very high impedance value (10^{10} ohms cm^2) a few hours after exposure, and did not show evidence for appreciable defects until 1-2 weeks after exposure. These data confirmed that defects are largely localized on the edges of the samples.

A primary goal of the initial immersion studies was the screening and development of techniques that would be appropriate for chamber and field exposure studies. EIS is a desirable technique to monitor paint degradation since it is quite sensitive and essentially nondestructive. Our efforts involved the design and

testing of an atmospheric electrochemical monitor (ATMEIS) to be used to generate EIS data during atmospheric exposure. The ATMEIS monitor consists of a painted steel coupon upon which a gold electrode (covering less than 10% of the front surface of the sample coupon) is electron-beam deposited. The impedance of the substrate/coating system is determined in a two electrode measurement using the steel substrate as one electrode and the electron-beam-deposited gold as the second electrode. The monitor can be used, therefore, in the absence of a remote reference or counter electrode. The monitor was developed to assess the degradation of organic coatings in atmospheric exposures simulating acid deposition. A description for the preparation of the monitor is presented in the report.

The monitor relies on the assumption that the impedance of the interface of the deposited electrode lying on the surface of the coating is low relative to the impedance of the coating and the steel-coating interface; an assumption which has been verified. This enables a two electrode measurement rather than a conventional three electrode measurement to be completed. The two electrode approach is valid, because placement of the deposited electrode at the surface of the coating enable its entire interface with the coating to be wetted and used, resulting in a low interfacial impedance relative to the coating or the steel-coating interface. The primary value of this monitor is that it has the potential of being used for completely *in-situ* monitoring of atmospheric or vapor phase coating deterioration on a real-time basis and/or on real structures. Such a method is currently unavailable.

Although the ATMEIS monitor was designed to be used for atmospheric monitoring of coating degradation, preliminary evaluation and validation of the monitor was conducted using immersion exposures. Results from exposures for time periods up to several months demonstrate that the EIS data are essentially identical regardless of whether 1) remote reference and counter electrodes are used, 2) the gold electrode is used as the reference/counter combination with the sample in the aqueous acid electrolyte, or 3) the gold electrode is used as the reference/counter combination with the sample removed from the electrolyte in air.

In addition, the ATMEIS monitor has shown behavior which is nearly identical to that of an as-prepared sample (conventionally coated without a sputter coated gold electrode) for equivalent

exposure times. Within the error associated with sample to sample variation and measurement constraints, there is no significant difference in the behavior of samples with or without the monitor. Thus, the presence of the gold electrode on the sample surface does not appear to affect the normal chemistry/degradation process of the coated metal sample.

Tensile adhesion tests were used to measure the cohesive/adhesive strength of the paint system as a function of time in each exposure environment. Studs were bonded to the painted steel prior to and/or following exposure. The force required to separate the steel and the paint was measured. The failure type and locus of failure in the unexposed coupons was cohesive in the primer. After one week exposure, no change in the tensile strength was noted for the water, nitric, and sulfuric acid-exposed samples, and failure continued to be cohesive in the primer. Some decrease in strength (approx. 30%) was seen for the sulfurous acid-exposed samples, and failure was partially cohesive in the primer and partially cohesive in the paint with the strength being inversely correlated with fraction of paint failure. The nitric and sulfuric acid-exposed specimens retained their strength at 4 weeks immersion, but lost most of it by 8 weeks. The water and sulfurous acid-exposed specimens lost their tensile strength by 4 weeks. In each case, strength was dependent on the time from removal of specimens from immersion to time of measurement, the lowest strength being seen if the measurement was completed shortly after removal from exposure. Tests performed a few days after removal from immersion indicated a partial regaining of strength. Presumably this time dependence was a result of the paint/primer system losing some of its absorbed water once it was removed from the immersion environment. The locus of failure of the degraded samples generally changes to the metal-primer interface. XPS analysis of spots commonly found on failure surfaces following long exposures revealed Fe, indicating the onset of corrosion of the substrate.

Chamber Exposures

Chamber exposures of alkyd painted steel coupons to 1-ppm SO₂ with an air flow of 60 l/min. at a relative humidity of 95% were conducted. Control experiments without SO₂ were also performed. Samples were either kept at a constant temperature (20-23°C) for dry deposition or were thermally cycled

(alternating 12hr periods at 25-28°C and 15-18°C) for both wet and dry deposition during the exposures. The samples were removed at various time intervals (in the middle of the dry cycle). Samples designed for *in-situ* EIS monitoring were also included in the latter experiments. It should be noted that all chamber-exposed samples except those for *in-situ* EIS monitoring during the chamber run contain two layers of topcoat on both sides of the sample. The *in-situ* EIS samples contain a single layer of topcoat on the front side of the specimen.

As the samples were removed from the environmental chamber, some blistering occurred on the samples used in the final chamber studies (these were the samples with the dry film thicknesses of 120-170µm). Since these samples were, on average, the thinnest of all the samples examined, the occurrence of blistering was likely related to coating thickness. In addition, after ambient laboratory storage for a few days, brown spots appeared on all (independent of thickness) the SO₂, dew-exposed samples that were mounted horizontally (with the top surface exposed). The discoloration is likely an example of a synergistic effect between condensed moisture and SO₂. The brown spots appeared after removal from the chamber only on specimens with condensed dew that were mounted horizontally. The discoloration may be attributed to a moisture-induced reaction with the adsorbed S whose local concentration has been increased as a result of the evaporation of condensed dew. On specimens that are mounted vertically, the dew drips off and removes much of the S from the paint surface. However, on horizontal surfaces, not only does the S remain on the surface, but as the dew evaporates during the dry cycle, parts of the surface dry first with the S concentrating in the remaining wet areas. The discoloration does not occur until the absorbed moisture, as indicated by the weight gain of each specimen, is lost after a few days in the desiccator.

XPS measurements show that all the nominally dry samples adsorbed SO₂ from the test atmosphere. As one would expect, no S was detected on paint surfaces exposed only to high humidity (control run). The rate of adsorption was greatest initially with 1-2 at.% S present on the surfaces after the first few days; the S concentration subsequently takes the remainder of the 28-day period to approximately double. There is no orientation dependence, but samples that were pre-exposed to UV exhibit ~70%

greater uptake of S than samples that were not pre-exposed. High-resolution XPS spectra indicate that the S is in the form of a sulfate.

The results from the samples exposed to dew are very different. First, there is a strong orientation dependence – samples that were mounted vertically exhibit very little S adsorption (<0.5 at.%) whereas samples that were mounted horizontally exhibit up to 4 at.% S adsorption. Second, the amount of S adsorption on the horizontal samples varies greatly across the surface – the brown areas on horizontally mounted samples have high S concentrations (comparable to that of the dry samples), white areas have significantly less than brown areas, but have higher S uptake than the samples that were mounted vertically. Again, the S was in the form of a sulfate.

The tensile adhesion tests indicate a degradation of the mechanical properties of the paint system during the chamber exposures. Initially, the tensile strength is high (5-6 MPa) with the failure occurring cohesively in either the primer or the top coat. However, upon exposure to SO₂, the strength decreases, until the average value is approximately one-third of the initial value. Concurrent with this weakening of the paint system is a shift of the locus of failure from within the paint system to the primer metal interface.

The mechanical properties of the paint system also degrade during the control run, but at a slower rate. SO₂-exposed samples exhibited a significant loss in strength even after exposures as short as one day. Even though there was more variation in control samples, strength losses occurred much more gradually over the 28-day period and final strength values were higher than those witnessed for SO₂ exposure.

The relationship between locus of failure and strength remains constant regardless of variations in test method or exposure condition. As the specimens are exposed in the chamber, the tensile strength decreases significantly and the locus of failure shifts from within the polymer system to the metal/primer interface. The decrease in tensile strength appears to be dominated by a loss or weakening of adhesion between the substrate and the primer and that any reduction in the cohesive strength of the paint system plays a secondary role. This mechanism of failure appears to be the same with and without the presence of SO₂, but SO₂ increases the rate at which the de-adhesion occurs.

Decreases in near DC impedance correspond well to changes in the

mechanical properties. ATMEIS data are given for two different samples and tensile adhesion values are averages of at least 3 specimens. Locus of failure in the tensile specimens occurs initially within the paint system but shifts to the metal primer interface at later exposure times. Visual examination of the failure surface indicates that this failure is associated with corrosion at the metal/primer interface. Thus, EIS is detecting corrosion at the interface.

The relationship was also observed between EIS data obtained with the ATMEIS monitor and tensile adhesion strength for samples exposed to the same environment. This provides encouragement that EIS data may be used as an indicator of mechanical properties and the changes in these properties due to degradation. Although one other study reports similar effects, we are not aware of any studies which have evaluated the extent of this correlation for the same samples.

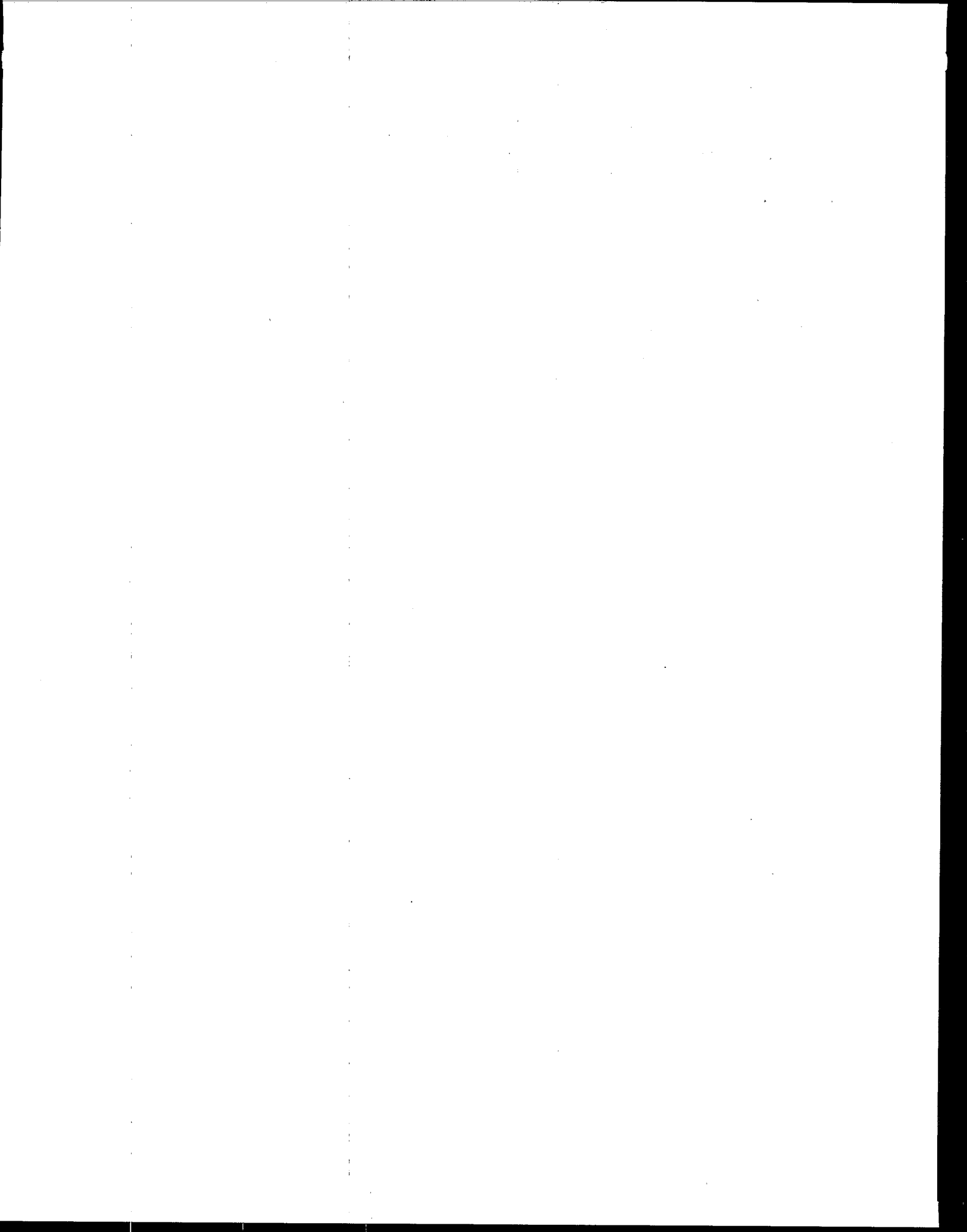
Conclusions

Major findings for this study are summarized as follows:

- Specific analytical techniques capable of detection of coating degradation at early exposure times have been either identified or developed. A good correlation exists between non-destructive electrochemical (EIS) and mechanical test methods indicating new possibilities for evaluation of coating degradation.
- Under aqueous conditions S penetrates the paint film upon exposure to sulfurous acid but does not penetrate the film upon exposure to sulfuric acid. In addition, the presence of water, in immersion exposures, overrides the effects of the individual pollutants.
- Exposure to 1 ppm SO₂ at 95% RH causes significantly more deterioration of coated metal substrates over exposure to 95% RH in the absence of SO₂. This deterioration is manifested as localized discoloration, damage at defects, and changes in tensile adhesive strength and locus of failure in chamber-exposed samples as a function of exposure time. These discolored regions which occur only on samples on which dew condensed and was allowed to dry are areas of high S concentration. Significant blistering and rusting occurred on samples containing intentional defects. This damage was most severe for samples that were dew cycled and

mounted horizontally during chamber exposure.

- Data from chamber exposed samples incorporating the ATMEIS electrochemical monitor also indicates coating deterioration as a function of exposure time to 1ppm SO₂ at 95% RH with diurnal cycling.
- Pre-exposure of samples to UV and/or diurnal cycling (during exposure) can affect the severity of this degradation as indicated by the discoloration and the amount of S detected on the surface.



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John W. Spence is the EPA Project Officer (see below).

The complete report, entitled "Preliminary Exposure Study to Determine the Effects of Acid Deposition on Coated Steel Substrates," (Order No. PB 90-201 799/AS; Cost: \$15.00, subject to change) will be available only from:

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