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CORROSION CONTROL THROUGH A BETTER UNDERSTANDING OF THE METALLIC SUBSTRATE/ORGANIC COATING INTERFACE

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Principal Investigator: Henry Leidheiser, Jr.
Co-Investigator: Richard D. Granata

Zettlemoyer Center for Surface Studies
LEHIGH UNIVERSITY
Bethlehem, PA 18015

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REPORT OVERVIEW

The research carried out during the period, October 1, 1988 - September 30, 1989, included the following subject areas:

(1) Application of positron annihilation spectroscopy to coatings;

(2) Appraisal of coatings using electrochemical impedance spectroscopy as a function of temperature;

(3) The nature of alkali metal ions within organic coatings as studied by solid state nuclear magnetic resonance.

(4) The mechanism of corrosion inhibition by lead pigments in coatings.

(5) Coatings as a means to detect cracks in structure.

Positrons, [illegible], Epoxy [illegible], [illegible], [illegible], [illegible] Lead, [illegible], [illegible] Coatings, Corrosion [illegible]

Significant progress has been made in all five subject areas but this annual report is limited primarily to a summary of the corrosion inhibition by lead pigments, area (4), and brief overviews of work-in-progress for areas (1) and (2).

PUBLICATIONS DURING PERIOD, OCTOBER 1, 1988 - SEPTEMBER 30, 1989

"Positron Annihilation Studies of Corrosion Protective Coatings," H. Leidheiser, Jr., C. Szeles, and A. Vértes, Polym. Mater. Sci. Eng. 58, 44-47 (1988).

"Polymer Studies of a New Pretreatment Method," H. Leidheiser, Jr., and W. Bilder, Polym. Mater. Sci. Eng. 58, 176-77 (1988).

"Inhibition in the Context of Coating Delamination," H. Leidheiser, Jr., Corrosion 89 Paper No. 142, New Orleans, LA, Apr. 17-21, pp. 142/1-7.

"Corrosion Inhibition of Steel by Lead Pigments: The Steel-Lead Galvanic Couple in Acetate Solutions," J. I. Mickalonis and H. Leidheiser, Jr., Corrosion 45(8), 631-36 (1989).

SUBJECT AREA 1

TEMPERATURE-DEPENDENCE OF POSITRON ANNIHILATION PARAMETERS IN POLYAMINE-CURED EPOXY COATINGS

Richard C. MacQueen, Richard D. Granata, and Henry Leidheiser, Jr.

ABSTRACT

Positron Annihilation Spectroscopy (PAS) was used to study the microstructural properties of a polyamine-cured epoxy coating on steel. The ortho-positronium lifetime in this coating was found to increase with temperature (20°to 80°C) and return to near its original value after thermal cycling. Work is underway to explain these changes in terms of the coating's free volume.

INTRODUCTION

Positron Annihilation Spectroscopy (PAS) has been used to determine defect and vacancy properties in solids and liquids for the past 20 years [1]. When a positron is injected into a solid, it can abstract an electron from the medium to form a neutral atom, positronium (Ps). Ps can be formed in either a triplet state (ortho-Ps) or a singlet state (para-Ps), depending on the spin combination of the electron and the positron. In a vacuum the average lifetime of ortho-Ps is 140 ns [2]. In condensed medium, the lifetime of ortho-Ps is shortened by three quenching processes: conversion, chemical reaction, and pick-off. In the absence of paramagnetic, oxidizing and reducing species, pick-off annihilation is the dominant mode of annihilation of ortho-Ps in condensed matter. In polymers, three lifetimes are often found, which range from 100 ps to 5 ns [3]. The longest of these lifetimes (τ_3) is due to the pick-off annihilation of ortho-Ps.

The free volume of a polymer is the sum of individual void volumes (molecular-level cells and cavities). Formation and annihilation of ortho-Ps occurs mainly in the polymer free volume. The free volume theory states that the rate at which pick-off annihilation occurs is inversely proportional to the size of the free volume sites [4]. In other words, as the size of the individual cavities increases, the lifetime of the ortho-Ps in that cavity also increases. The fraction of ortho-Ps's that formed after a lifetime, τ_3, is given by the area under the curve and is referred to as intensity, I_3. This intensity, I_3, is therefore a measure of the number of sites available for formation and annihilation of ortho-Ps. Since the lifetime, τ_3, is a measure of the relative size of an individual free volume site and intensity,

I_3, is a measure of how many sites are available, the product, $\tau_3 I_3$, is a measure of the total free volume of the medium.

In previous studies, PAS has been used to measure the free volume in polymers as a function of pressure, crystallinity, and temperature [5-7]. Jean et al. [8] have determined that the free volume holes of an amine-cured epoxy polymer (bulk) ranged from 0.025 to 200 nm^3 over a temperature range of -78° to 250°C. However, there have not been any studies to date on the temperature dependence of positron annihilation parameters in epoxy coatings. In this report, the positron annihilation parameters in a polyamine-cured epoxy coating on steel are given for the temperature range of 20° to 80°C.

EXPERIMENTAL

The epoxy was prepared by mixing bisphenol A resin with polyamine hardener in a 1:1 (v/v) ratio. The coatings were made by applying 2 mℓ of the epoxy to 5×5 cm steel panels and spinning for 7 s at 1000 rpm. These samples were allowed to air dry 8 h at room temperature and the average thickness of these coatings was determined to be 7 mil. The steel panels were SAE 1010 steel abraded with 240 grit sandpaper and rinsed with distilled water and ethanol, respectively.

The positron source was 10 μCi ^{22}Na sealed between two 0.3 mil Kapton foils. The lifetime spectrometer was a standard fast-fast coincidence system based on fast plastic scintillators, RCA 8575 photomultipliers, and EG&G Ortec electronics. Elevated temperature measurements were made in a specially designed oven consisting of an aluminum box wrapped with heating tape and surrounded by fiberglass insulation. The temperature was kept constant to ±1°C using a thermocouple placed in contact with the sample.

In a typical experiment, the positron source was placed between two samples such that the coating side was in contact with the source. This arrangement was mounted inside the oven. The oven was placed between the detectors. Spectra were taken at room temperature, 40°, 60°, 80° and room temperature, respectively. Each spectrum contained 50K counts in the peak channel and was fitted to three lifetime components using POSITRONFIT [9].

RESULTS AND DISCUSSION

The positron annihilation parameters of polyamine-cured epoxy on steel are shown in Figure 1. The figure is divided into three sections. The top and center sections are I_3 and τ_3, respectively. The bottom section is the mean positron lifetime, $\bar{\tau}$. The values identified as RT1 are those for the first room temperature measurements and the values identified as RT2 are those for the second room temperature measurements after the coating has been subjected to the higher temperatures. The error bars shown are the standard deviations of each of the measurements as calculated by POSITRONFIT.

The intensity of the ortho-Ps lifetime I_3 remained nearly constant within experimental error throughout the temperature range studied. The ortho-Ps and mean lifetimes τ_3 and $\bar{\tau}$ increased with temperature values and returned to nearly their original room temperature values after being exposed to the higher temperatures. These results indicate that the number of voids in polyamine-cured epoxy on steel remained constant in this temperature range, but the average size of these voids increased with temperature reversibly.

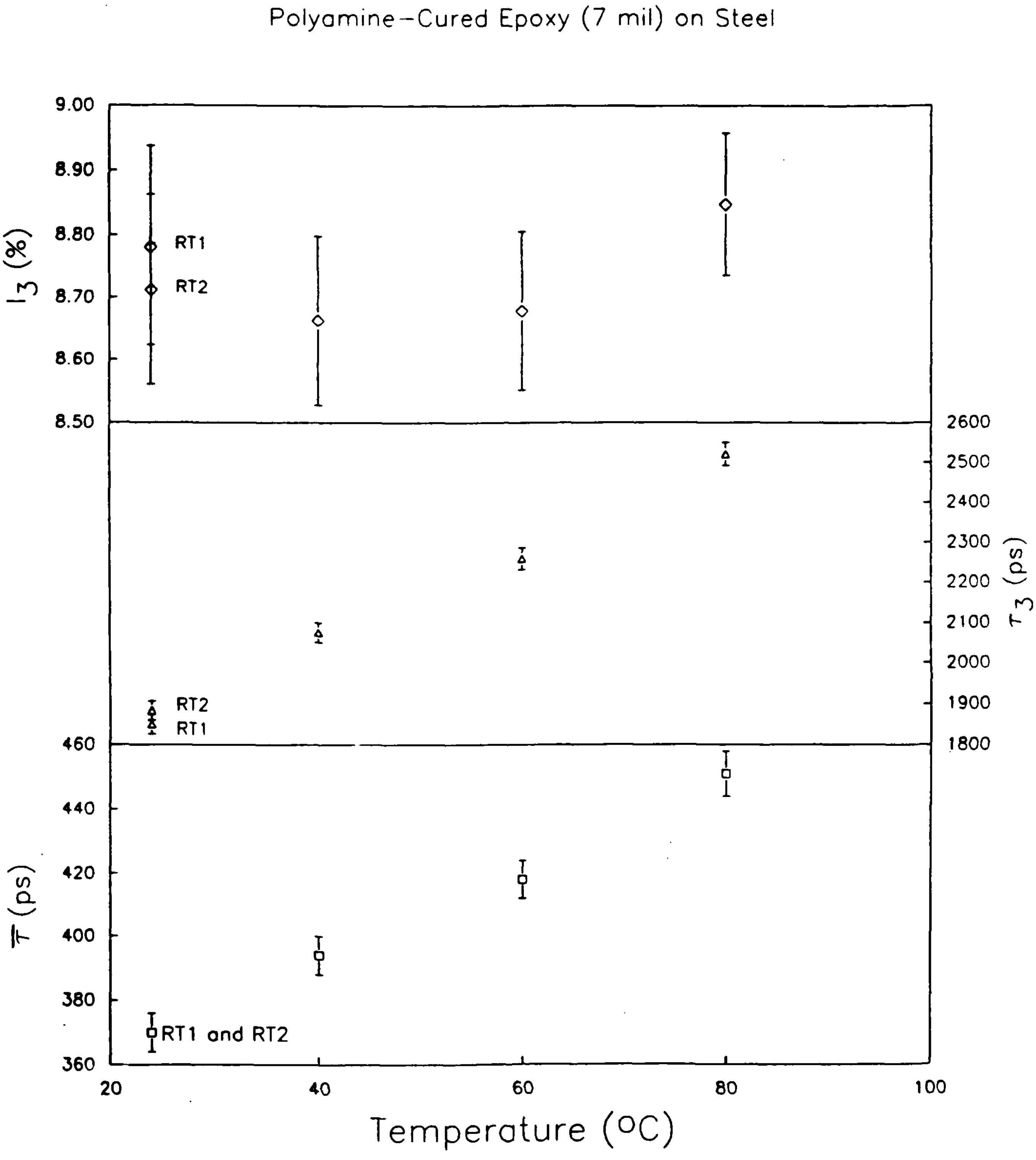

Fig. 1. Positron annihilation parameters in polyamine-cured epoxy on steel over a temperature range of 20° to 80°C.

CONCLUSIONS

PAS is being developed for use in the study of microstructural properties of organic coatings. The free volume of polyamine-cured epoxy on steel increases with temperature (20° to 80°C) and returns to near its original value after thermal cycling.

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SUBJECT AREA 2

TEMPERATURE DEPENDENCE OF THE LOW FREQUENCY IMPEDANCE OF POLYMERIC COATINGS

Kevin Kovaleski, Richard D. Granata, and Henry Leidheiser, Jr.

ABSTRACT

Electrochemical impedance data have been obtained for eleven polymeric coating systems subjected to distilled water at room and elevated temperatures. These coatings fell into two distinct classes: those that showed a very large change in the low frequency impedance when temperature was increased and those that showed a relatively small change in the low frequency impedance when temperature was increased. Coatings that were cured at 85°C or below exhibited the large changes, while the three that were cured at 190°-200°C (polybutadiene, a polyimide, and a polyester) exhibited the much smaller changes. An understanding of the origin of the large differences among the coatings in the low frequency impedance as a function of temperature is important and related to coating service life. Several mechanisms are being considered. The glass transition temperature of the polymer as the controlling factor has been studied, but no simple relationship was determined. The preferred mechanism for temperature dependent coating impedance is related to the presence or absence of unreacted hydrophilic components in the cured coating. These may be residual solvents or, in the case of epoxies and urethanes, unreacted components.

INTRODUCTION

Electrochemical impedance methods offer a convenient way of evaluating the performance of organic coating/metal systems. Many of these applications are found in the literature [1-3]. Electrochemical Impedance Spectroscopy (EIS) has exhibited high capability for predicting the performance of coated metals in an aggressive environment. Our studies and those of S. Tait reported at the April 1989 Symposium on Advances in Corrosion Protection by Organic Coatings held in Cambridge, England, indicate that coatings give good protection when the low frequency impedance is greater than 10^7 ohms for 1 cm^2 measured area. In many systems, a decrease of the low frequency impedance to 10^7 ohms for 1 cm^2 measured area takes several months of exposure to an aggressive environment. This work was originally undertaken in an effort to generate information about the protective quality of a coating in a much shorter time period than several months. This report describes the electrochemical impedance properties as a function of temperature of eleven different coating systems listed in Table I.

EXPERIMENTAL

Epoxy-1 (Table I) samples were prepared from 10×20×0.05 cm 1010 SAE steel panels. The panels were wet ground with 240 grit SiC paper and rinsed with ethanol. Epoxy-1 primer MIL-P-24441/1 was applied by draw bar at a thickness of 0.015 cm wet. Some panels were allowed to air-cure overnight. The others were cured at 85°C for 1 h. Two coats of epoxy-1 topcoat MIL-P-24441/5 were applied by draw bar at 0.018 cm wet thickness. The first topcoat

Table I

Coatings Used for the Temperature-Dependent Impedance Tests

Coating	Baked[a]	Air-dried[b]	Added Solvent[c]
1. Epoxy-1(EP1NEATD): primer mil-p-24441/1 topcoat mil-p-24441/5 1 coat primer 2 coats topcoat	No	Yes	No
2. Epoxy-1(EP1NEATB)	Yes	No	No
3. Epoxy-2(EP2NEATD): Dow D.E.R. 671-X75 (Unirez 2415 Batch 8708-0221) 1 coat	No	Yes	No
4. Epoxv-2(EP2SOLVD)	No	Yes	Yes
5. Epoxy-2(EP2SOLVB)	Yes	No	Yes
6. Epoxy-2(EP2NEATB)	Yes	No	No
7. Polybutadiene(PBD) 1 coat	Yes	No	No
8. Polyester Enamel(PE) 1 coat	Yes	No	No
9. Polyimide (PI) 1 coat	Yes	No	No
10. Plythane 800 (800) Aliphatic Urethane MAB Paints 052-165 052-069 1 coat	No	Yes	No
11. Plythane 800 (880) Urethane/Acrylic MAB Paints 010-165 010-069 1 coat	No	Yes	No

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Table I (Cont'd.)

Notes:

[a] Epoxies: 85°C for 1 h.
Polybutadiene: 195° for 30 min.
Polyester Enamel: 190° for 20 min.
Polyimide: 85°C for 12 min and 200°C for 20 min.

[b] Samples were allowed to cure in air for 1 week.

[c] Solvent used was Cellosolve™ (ethylene glycol, monoethyl ether). Solvent was 5% by weight.

was allowed to air-cure overnight and the final coat was allowed to air-cure 1 week. For heated-cured primer, the first topcoat was cured at 85°C for 1 h and the final coat was cured 1 h at 85°C. The panels were cut into 5 cm squares. Cured film thicknesses ranged from 0.017 to 0.024 cm.

Substrates for urethane coatings were prepared as described above. The urethanes were applied with a thickness of 0.010 cm wet. The panels were allowed to air-dry 1 week. The panels were cut into 5 cm squares. Final cured-film thicknesses ranged from 0.004 to 0.009 cm.

Substrates for epoxy-2 coatings were prepared as described above, but were cut into 5 cm squares before applying the coating. The epoxy-2 was applied by spin-coating and allowed to either cure at 85°C for 1 h or air-cure at room temperature for 1 week, as shown in Table I. For some samples, Cellosolve™ was added to the epoxy-2 (5% by weight) before application. Cured-film thicknesses ranged from 0.006 to 0.012 cm.

Polybutadiene samples were prepared as described above. The polybutadiene was applied by spin-coating, followed by a 30 min cure at 195°C. Cured-film thicknesses ranged from 0.002 to 0.003 cm.

Polyester and polyimide samples were prepared in a similar manner as the polybutadiene samples. Polyester was cured 20 min at 190°C and the cured-film thickness was 0.006 cm. Polyimide was cured 12 min at 85°C followed by 20 min at 200°C giving a cured-film thickness of 0.001 cm.

Impedance data were obtained from a system consisting of an EG&G Princeton Applied Research Corp. Model 173/179 potentiostat with computer-controlled Solartron 1250 frequency response analyzer. The impedance spectra were determined from 65.5 kHz to 3.1 mHz. The amplitude was 15 mV above 100 mHz and 50 mV below 100 mHz.

The electrochemical cell was a glass cylinder clamped and O-ring sealed to the sample surface. The seal exposed 8.8 cm^2 of sample surface to the distilled water test medium. The reference electrode was Ag/AgCl and a carbon rod served as the counter electrode.

Studies were conducted on three sets of samples, each at a different elevated temperature (40°, 60° and 80°C). An impedance spectrum was taken at room temperature. The sample was incubated at the test temperature for 1.5 h and an impedance spectrum was taken at the elevated temperature. The sample was equilibrated at room temperature for 1.5 h and another spectrum was recorded. Samples were equilibrated at ambient laboratory conditions (22°C and 50% RH) for up to 2 weeks and final spectra recorded.

Differential Scanning Calorimetry (DSC) tests were conducted on coating samples using a Mettler DSC 30 interfaced with a Mettler TC10A TA processor to determine glass transition ranges for each system. These ranges are shown in Table II.

Table II

Estimated Glass Transition Temperatures for the Test Coatings

Coating	T_g Range (°C)
1. EP1NEATD	69.0 - 76.3
2. EP1NEATB	59.5 - 60.1
3. EP2NEATD	51.3 - 53.4
4. EP2SOLVD	56.3 - 61.8
5. EP2SOLVB	57.4 - 62.4
6. EP2NEATB	39.6 - 53.8
7. PBD	-42.2 - -28.9
8. PE	32.8 - 41.6
9. PI	219 - 221

Data generated from impedance measurements are summarized in Figures 1-4 for the different coating systems. The four sets of data for each coating, at each of the elevated temperatures, are given as bar charts. The open bar at the extreme left is the impedance at 0.0031 Hz for the first room temperature measurement. The solid bar, second from the left, is the impedance at the indicated temperature. The diagonal-hatched bar, third from the left, is the impedance after the sample returned to room temperature. The cross-hatched bar, fourth from the left, is the impedance after the coating was exposed to air for 7 days at room temperature.

Note that the 11 coatings fell into two distinct classes, those that showed a very large change in the low frequency impedance when the temperature of the water was increased and those that showed a relatively small change in

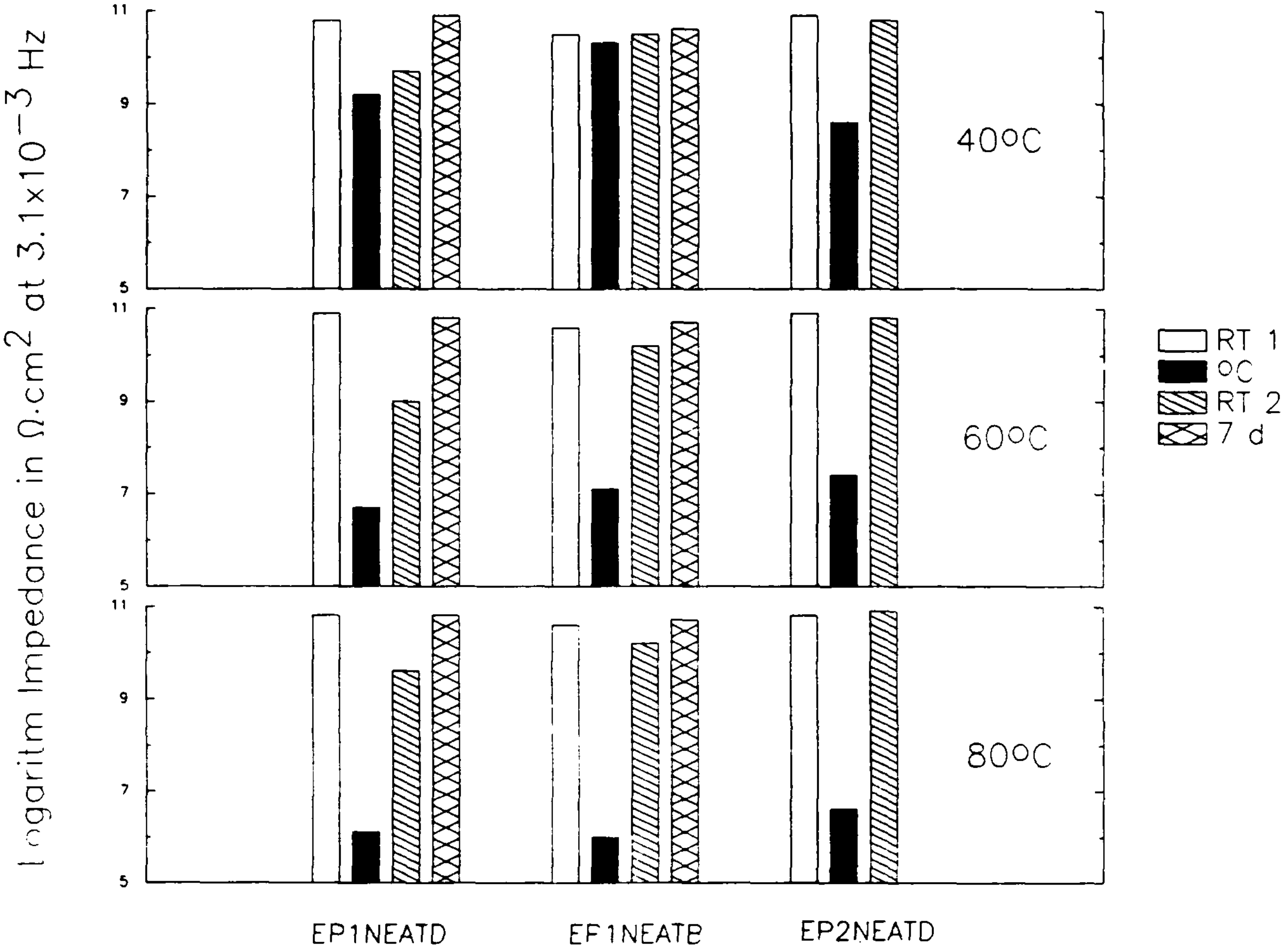

Fig. 1. The temperature dependence of the impedance at 0.0031 Hz of three different epoxy coatings on steel while immersed in distilled water.

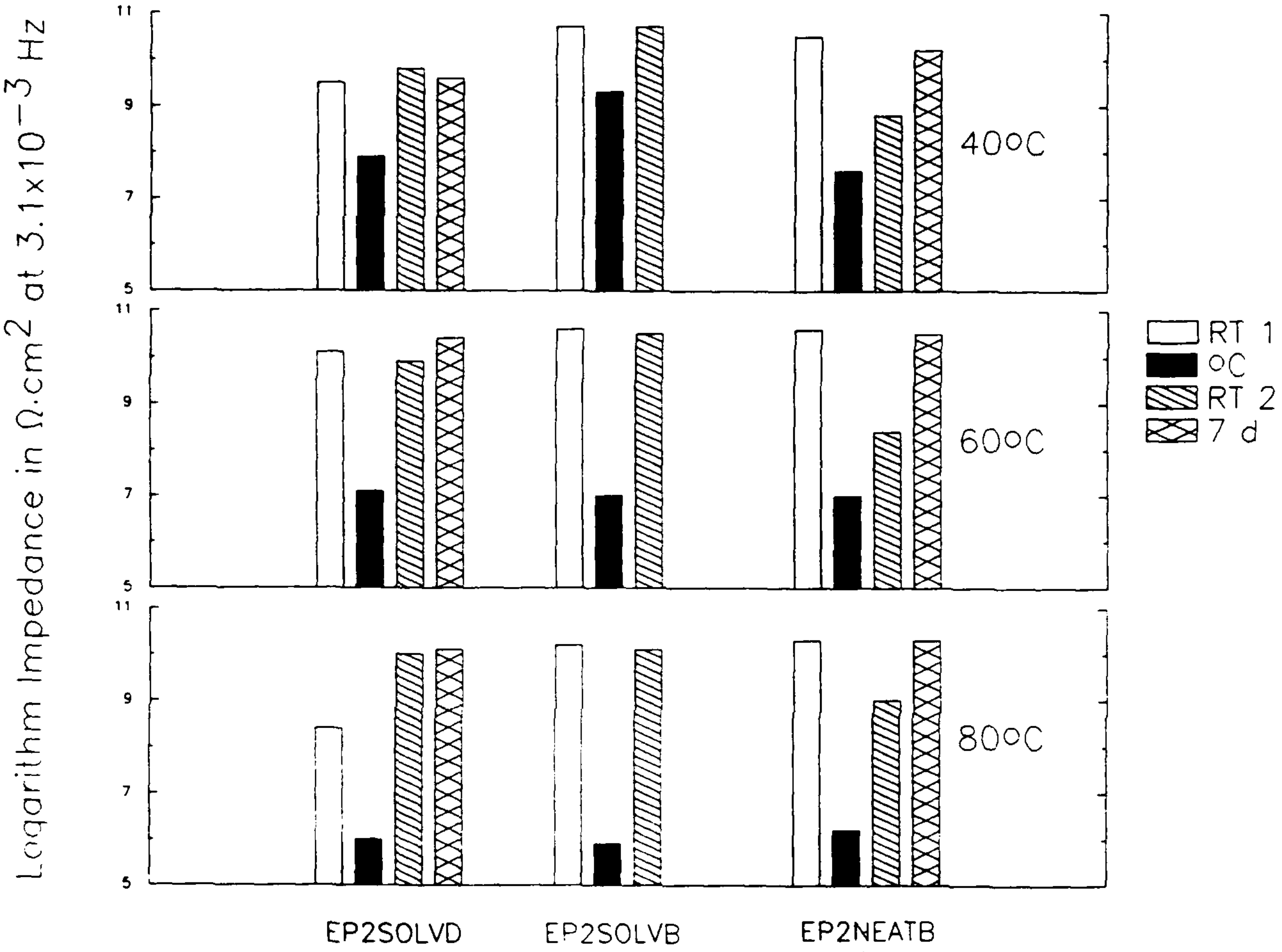

Fig. 2. The effect of solvent on the temperature dependence of impedance at 0.0031 Hz of an epoxy coating on steel while immersed in distilled water.

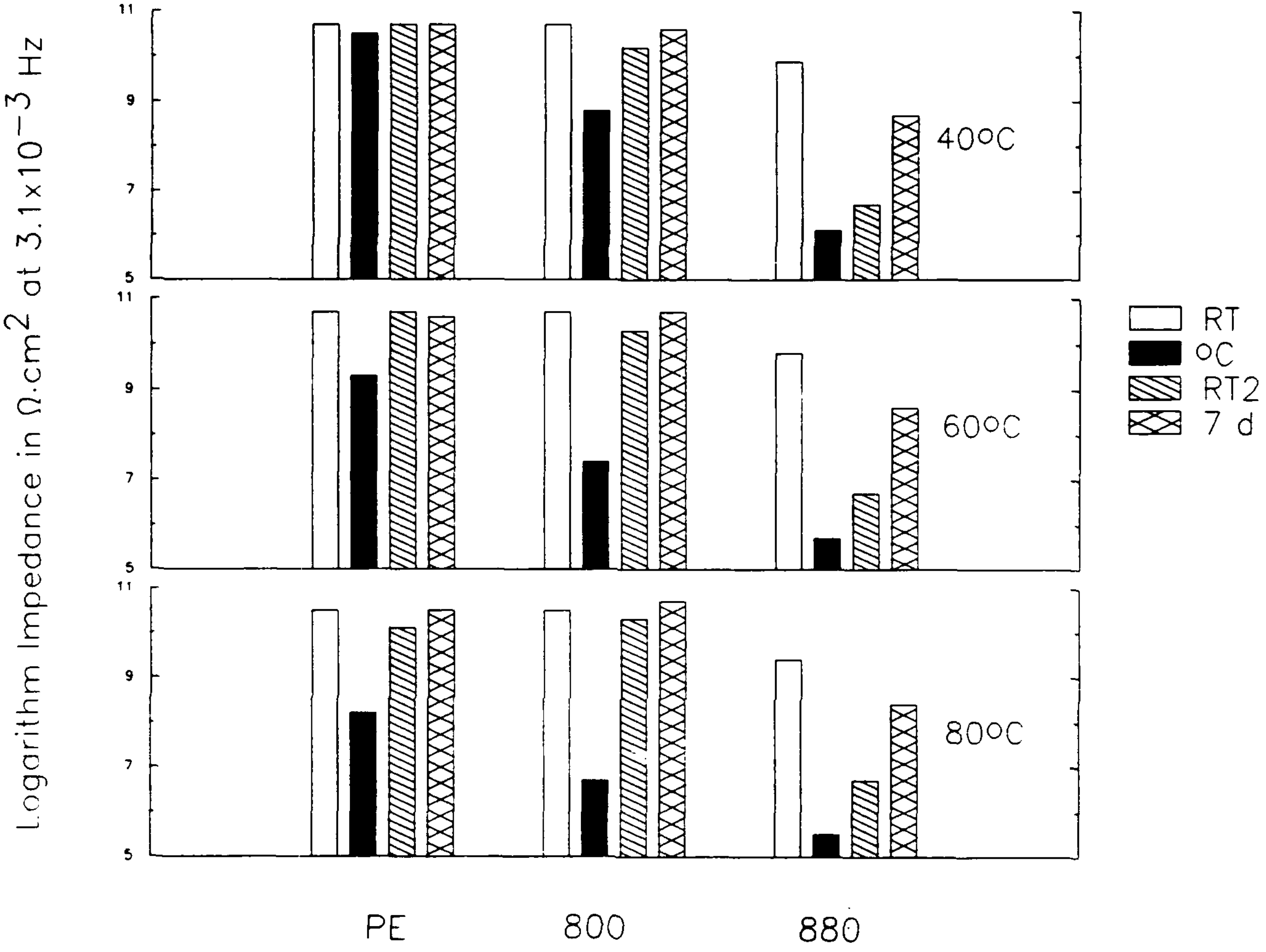

Fig. 3. The temperature dependence of the impedance at 0.0031 Hz of three different coatings on steel while immersed in distilled water.

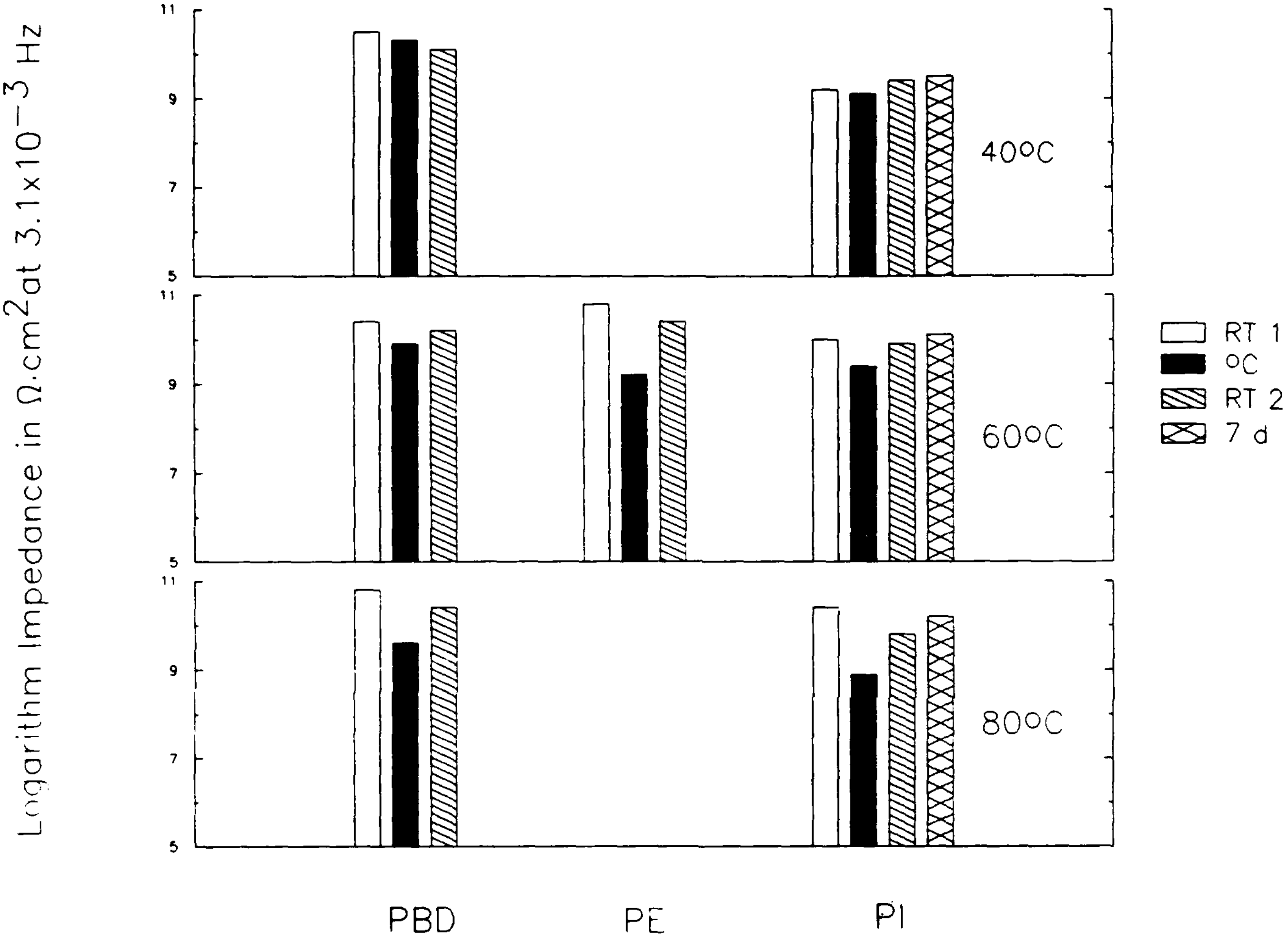

Fig. 4. Data for three different coatings, all baked at approximately 200°C, in which there was only a small change in the impedance at 0.0031 Hz as temperature was increased. Data were generated while the coated steel was immersed in distilled water.

the low frequency impedance when the temperature of the water was increased. All the coatings that were cured at 85°C or below exhibited large changes in the low frequency impedance with increasing temperature while the three that were cured at 190°-200°C (polybutadiene, a polyimide, and a polyester), as shown in Figures 3 and 4, exhibited a much smaller change.

An understanding of the origin for the large differences among the coatings in the low frequency impedance as a function of temperature should result in the establishment of a strong relationship to coating failure mechanism for coatings subjected to thermal transients in normal service. From the data in Table II, the glass transition temperature (T_g) does not show a direct relationship to the observed phenomena. The present mechanism under scrutiny is that the major factor in determining the temperature dependency of the impedance may be the presence or absence of unreacted hydrophilic components in the cured coating. These may be residual solvents or excess reactive components.

CONCLUSION

Impedance data for 11 different coatings showed that the coatings could be grouped into two distinct classes: those that showed a very large change in the low frequency impedance and those that showed a relatively small change when the temperature of the water was increased. The coatings exhibiting the large change were cured at 85°C or below, while those exhibiting a small change were cured at 190°-200°C. The present mechanism under study is that the major factor affecting this temperature dependence of the impedance is the presence or absence of unreacted hydrophilic components in the cured coating.

Additional systems will be selected to confirm or refute this hypothesis. Should the additional data confirm this hypothesis, quantitative studies will be pursued.

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SUBJECT AREA 4

THE MECHANISM OF CORROSION INHIBITION BY LEAD PIGMENTS IN ORGANIC COATINGS

John Mickalonis and Henry Leidheiser, Jr.

ABSTRACT

A mechanism for corrosion inhibition by lead pigments in coatings is proposed that applies to situations where there is (a) a large separation of anodic and cathodic sites, (b) a small separation of anodic and cathodic sites, (c) an oxygen deficiency at the metal/coating interface and (d) an alternate wetting and drying cycle.

INTRODUCTION

We propose herein an hypothesis for the mechanism of inhibition of corrosion of steel by lead pigments in coatings. The concepts draw heavily on the ideas of Mayne and co-workers [1-4] and of Lindqvist [5] but the conclusions are based largely on our own electrochemical observations in a model system chosen to be representative of the aqueous phase present at a steel/coating interface. A summary is also given of the special properties of lead pigments that are responsible for the excellent corrosion inhibition provided by these materials.

Eight different proposed mechanisms for the corrosion inhibition by lead pigments are listed in Table I along with the references in which the mechanism is described. Mechanisms 1, 2, 3, 4, 5 and 8 describe processes that undoubtedly play a role in some circumstances but none of these is sufficiently general to explain the inhibition process in detail. The concepts of Mayne and co-workers and of Lindqvist, however, are consistent with much of our experimental data and our efforts are concerned with refining these concepts and applying them to hypothetical situations existing at a steel/coating interface.

Table I

Mechanisms Proposed for Inhibition of Steel Corrosion by Lead Pigments

Number	Mechanism	Reference
(1)	Formation of Lead Soaps with Consequent Improvement in Mechanical Properties of Coating	[6]
(2)	Scavenging of Sulfur Dioxide by Pigment	[7]
(3)	Reduction in Diffusion Rate through Coating	[8]
(4)	Buffering of Aqueous Environment at Metal Interface	[9]
(5)	Solublized Pigment Serving as Adsorbed Anodic Inhibitor	[10]
(6)	Depolarization of the Oxygen Reduction Reaction to Maintain Iron in the Interfacial Oxide in the Ferric State; Blocking of Anodic Sites	[1-4]
(7)	Deposition of Lead; Maintenance of Insoluble Ferric Oxide; Polarity Reversal; Autocatalytic Action	[5]
(8)	Insolubilization of Sulfur by Lead Pigment at Steel/ Coating Interface: Note: Applies to rusty steel only.	[11]

Rationale for Experimental Studies

Experimental work was performed in seeking evidence for the proposed mechanism of corrosion inhibition. The rationale for the use of the model system and the model electrolyte used in the experimental work is given below.

Model System. Steel corrosion, according to Evans [12], results from the electrochemical interaction of separate anodic and cathodic sites on the steel surface. The lead species interact with these sites and inhibition occurs. Previous investigators suggested that metallic lead also played a role in this inhibition, so the interaction between lead and steel is important. Therefore, the mechanism by which lead inhibits the corrosion of steel involves the interactions of the anodic and cathodic regions on the steel surface with metallic lead or soluble lead species.

These interactions were experimentally modeled in this study by various galvanic couples. The anodic and cathodic regions on a steel surface were modeled by electrically coupling steel electrodes in different pH solutions. Anodic and cathodic sites beneath a coating are known to produce acidic and alkaline electrolytes, respectively [13-15]. The interaction of soluble lead species with the steel surface was studied with steel-steel couples exposed to a test solution containing lead acetate. The lead was added in an ionic form since lead was shown to be present in this form in extracts from lead pigments [9,16]. Lead-steel couples were used to model the interactions between metallic lead and steel. Both acidic and alkaline solutions were used because the local environmental conditions under which lead forms are unknown.

Model Solution. The composition of the aqueous phase at the steel/coating interface is dependent on the composition and properties of the coating and the exterior environment. The primary anion of the aqueous phase under the coating may be a constituent leachable from the coating since anions appear to move through protective organic coatings at lower rates than alkali metal cations. Many protective coatings contain carboxyl groups [18] and curing and corrosion processes often develop such groups in the vicinity of the metal surfaces [18-20]. Sodium acetate was selected as the primary anion of the model solution for several reasons. First, the acetate anion is a short chained carboxylate which is one of the many carboxylates formed as a degradation product between linseed oil binders and lead pigments [17]. Second, the inhibitive action of sodium acetate is not as effective as the longer chained carboxylates, nor is it as corrosive as sodium formate [13]. The inhibition is also a function of composition [21], so a low concentration, 0.1M, was chosen to minimize the inhibitive effect. Finally, the pH of the acetate solution can be altered by the addition of acid or base without precipitation of the anion.

Other anions such as chlorides and sulfates are probably present at a steel/coating interface as indicated by the diffusion data for coatings [22] and by the difficulty of preparing a truly clean surface. These ions were not included in the model solution because they accelerate corrosion and chlorides are competitive with lead ions for anodic sites on the steel surface during underpotential deposition of lead [23].

The difference in pH at the anodic and cathodic sites results from the reactions occurring at each site. The cathodic reaction under a coating is oxygen reduction since oxygen readily diffuses through a coating. This reaction produces hydroxyl ions which increase the pH. Hydrogen evolution may be the dominant cathodic reaction when the oxygen concentration is limited and this reaction also leads to an increased pH. Schwenk [13] showed that the pH of the electrolyte under cathodic blisters in sodium acetate solutions was between 8 and 10. Ritter and Kruger [14] reported pH values as high as 13-14 near cathodic sites under cathodic polarization. A pH of 10 was chosen for the model solution to represent a cathodic site since this value is near the middle of the range of reported values and local cathodic sites may not develop a very high pH in some cases due to the closeness of acidic anodic sites.

The pH of the aqueous phase near anodic sites is acidic because of the oxidation of the substrate and the resulting hydrolysis which increases the concentration of hydrogen ions in solution. Schwenk [13] reported that the solution in blisters formed under anodic conditions had a pH of 4. Similar values (pH 4-5) were found for steel crevices and other occluded cells which are also anodic sites [21]. The pH of the model solution was adjusted to 4.5 or 5 in this study to simulate the aqueous phase near anodic sites.

The Mechanism for Corrosion Inhibition by Lead Pigment

The inhibitive process of soluble lead species is integrated with both the formation of an aqueous phase at the steel/coating interface and the subsequent corrosion reactions. The effectiveness of the inhibition is due to the continual chemical reactivity of lead under the changing conditions at a steel/coating interface. The interfacial conditions proceed through various stages including the formation of an aqueous phase; the initiation, progression and cessation ("healing") of corrosion; and the wet/dry cycling during exposure. The inhibitive mechanism is composed of several components, each one being activated by a particular interfacial condition. The complete inhibitive process under a coating involves the following: (1) the formation of an aqueous phase, (2) the solubilization of lead pigments, (3) the initiation of steel corrosion, (4) the inhibition of steel corrosion by lead species during a wet cycle, and (5) the inhibition of steel corrosion by lead species during healing or the drying cycle. The inhibitive mechanism is presented with justification for the outlined steps based on the results of this investigation and those of previous investigators.

1. The Formation of an Aqueous Phase

An aqueous phase forms at the steel/coating interface by the passage of water through the coating or through defects within the coating. Water passes readily through many organic coatings as shown by Yaseen and Funke [24]. Leidheiser et al. [25] using aluminum Payne cups found that water permeated free films of organic coatings at rates of the order of 0.005 mg-cm/cm^2/day. Leidheiser and Kendig [15,26] reported changes in the permittivity, capacitance and resistance of a coating during exposure to aqueous salt solutions. These changes were related to the water uptake by the coating. Coatings with defects or spots of low resistance (10^6-10^8 ohms/cm^2) were found by Mayne and Mills [27] to correlate with areas of corrosion on the steel substrate. This correlation of defects to corrosion indicated a greater ease of transmission of both water and ions through pathways in the coating.

The composition of the aqueous phase at the interface may be quite complex because of the various components that can either diffuse through the coating, dissolve from the coating, be present initially at the interface or form during the corrosion process. These components include oxygen, carbon dioxide, sulfur dioxide, chlorides, sulfates, carboxylates and soluble lead species. The soluble lead species are formed from the breakdown of lead pigments within the coating as discussed below. Oxygen and carbon dioxide readily penetrate polymers. Actual rates through a coating probably differ since concentration profiles across a coating are expected to differ from those of a free film. Thomas [28] reported that rust formation beneath a blister increased twofold when the test solution was saturated with oxygen. The coating is also penetrated by sulfur dioxide, which may serve as a precursor to a soluble sulfate. Svoboda et al. [7] showed that this rate was reduced in the presence of pigments.

Ions such as chlorides and sulfates either penetrate through a coating or are present at the interface from impurities on the steel surface. Ion penetration through organic coatings was observed by Schwenk [13] and Parks and Leidheiser [29] in polarized and freely corroding samples. Chloride and sulfate ions also form impurities on the surface of the steel and enhance water penetration by osmotic forces [13].

Carboxylates are probably present initially as an anion in addition to chloride and sulfate ions. Many protective coatings contain carboxylate groups, especially linseed oil paints which form degradation products with pigments [17]. Corrosion and curing processes often develop carboxyl groups in the vicinity of the metal surface [18-20]. As recently discussed by Leidheiser and Deck [18], carboxylate species are found at or near the interface for polybutadiene and polyimide systems on cobalt.

The initial pH of the aqueous phase that forms beneath the coating is probably near neutral. Lindqvist [5] reported slightly alkaline pH values (pH

7-8) for extracts from epoxy and chlorinated rubber coatings pigmented with red lead. Extracts from alkyd and linseed oil paints which were also pigmented red lead had more acidic pH values (pH 5-6). These acidic values resulted from degradation products of the binders. The degradation products included a large number of carboxylic and dicarboxylic acids [17]. The results of the referenced studies indicate that the aqueous phase that forms at the steel/coating interface is a conductive and corrosive electrolyte. The exact composition depends on the properties and composition of the coating, the surface preparation techniques and the exterior environment.

2. The Solubilization of Lead Pigments

The presence of soluble lead species in the aqueous phase is necessary for inhibition. Several investigators [4,9,10,16,30] reported that aqueous extracts of lead pigments alone were inhibitive against the corrosion of steel. Lindqvist [5] found that lead species within a coating were mobile by measuring the lead dissolution rate from several coatings. The rates were constant over a three-month period after initially high values. The rate was a function of the type of coating with rates of migration from the coating decreasing in the following order: linseed oil > alkyd > chlorinated rubber > epoxy. The dissolution rates in the linseed oil and alkyd paints were higher because of the formation of soluble degradation products, for example azelaic acid [17].

Lindqvist and Vannerberg [31] reported finding metallic lead in a black surface layer that formed at a steel/coating interface after a three-month exposure to a sodium perchlorate solution. The coating was an alkyd paint pigmented with red lead, so metallic lead was not present initially in the coating. Thomas [11] reported similar results for coated steel panels exposed for three months in a marine/industrial environment. The steel panels were rusted prior to the initial application of the alkyd primer containing red lead. After exposure, a lead species was detected in the rust layer near the paint/rust interface. Therefore, soluble lead species form from the pigments within the coating and diffuse to the interface.

3. The Initiation of Steel Corrosion

The corrosion process of steel in aqueous solutions is known to be electrochemical in nature [12]. The anodic reaction is the oxidation of the substrate. The cathodic reaction varies with the environment, but oxygen reduction and hydrogen evolution are the two common reactions. Leidheiser and Kendig [15] showed that steel corrosion under a coating was also electrochemical nature. A defect was found to be central to the area of degradation. This area was the anode and the surrounding region was the cathode. The coating was detached from the substrate at the cathode but the substrate remained unattacked. The separation of the anodic and cathodic sites produces a pH difference in the solution at these sites as corrosion progresses. Acidic values develop at anodic sites from the hydrolysis of ferrous or ferric ions in solution. The iron ions are produced by the oxidation reaction. The pH at cathodic sites becomes more alkaline due to the production of hydroxyl ions from oxygen reduction. In chloride-bearing solutions, the pH in a steel crevice or an occluded cell is approximately 4-5 in the absence of oxygen. The pH of the aqueous phase near cathodic sites is as high as 13-14 when a cathodic potential is applied [35]. Schwenk [13] observed similar pH differences under anodic and cathodic blisters formed in pigment-free alkyd resin coatings after a few months' exposure in a 0.2M sodium chloride solution.

The corrosion process of steel beneath a coating is controlled by the cathodic reaction. Leidhesier and Kendig [15] concluded that the cathodic reaction was rate limiting because a significant increase in the deterioration of coated steel was observed after externally coupling the sample to platinum. Cathodic control was also observed in the present study with steel (pH 4.5/steel pH 10) couples where the galvanic potential of the couple was similar to the open-circuit potential for steel in a pH 4.5 solution. Steel-steel couples in the presence of soluble lead species and the lead-steel couples also had potentials close to the anodic potentials. Therefore, the corrosion process beneath a coating is controlled cathodically and progresses by a separation of anodic and cathodic sites.

4. The Inhibition of Steel Corrosion by Lead Species during a Wet Cycle

The inhibitive process of soluble lead species occurs during a wet cycle. The wet cycle results from the exposure of a coating to rain, an aqueous environment or a high relative humidity atmosphere. The rate-controlling mechanism is determined by different conditions which may exist at the steel/coating interface during this cycle. These conditions are categorized as (a) a large separation of anodic and cathodic sites on the steel surface, (b) a small separation of anodic and cathodic sites, and (c) an oxygen deficiency at the interface. The lead species interact differently with the steel under each of these conditions to bring about inhibition.

The first step in each of these mechanisms is similar, i.e., the initiation of corrosion. The steel surface is composed of regions which act as anodes and cathodes. The cathodes polarize to a potential similar to that of the anodes since the corrosion process is under cathodic control.

(a) Mechanism #1 - A large separation of anodic and cathodic sites.

The separation of the anodic and cathodic sites allows the solution pH near these sites to develop distinctly acidic and alkaline values. Inhibition proceeds by the following sequence of steps:

Step 1. A lead species forms at cathodic sites by underpotential deposition (UPD)

Step 2. The cathodic current decreases

Step 3. The galvanic current decreases

Step 4. The corrosion rate decreases

Step 1 - The cathodic sites are polarized to potentials more noble than the equilibrium potentials for bulk lead deposition (E_n); lead deposits on the steel surface by UPD. The potentials of steel(pH 4.5)/steel(pH 10) couples in solutions with different lead ion concentrations are anodic to the lead deposition potential as shown in Table II. Lead species were detected by XPS and AES on the cathodes of these steel-steel couples. Metallic and oxidized forms of lead were identified. UPD is a probable mechanism for the formation of the lead deposits under these conditions. The characteristics of these deposits are similar to those which form by UPD. These characteristics include the uniformity of coverage, the lack of discrete particles and the proportional relationship between surface and solution concentrations of lead. The subsequent oxidation of the lead species is related to the thinness of a layer deposited by UPD and the negative free energy associated with the

Table II

The Potentials of Steel(pH 4.5)/Steel(pH 10) Couples in 0.1M Acetate Solution in Comparison with Lead Deposition Potentials

Lead Concn. (M)	Potential of Couple		Open Circuit Potential		Lead Deposition Potential
	Initial	Final	pH 4.5	pH 10	
0	-0.588	-0.612	-0.630	+0.075	--
2 × 10^{-6}	-0.563	-0.522	-0.540	+0.095	-0.536
1 × 10^{-3}	-0.497	-0.497	-0.514	+0.100	-0.457

oxidation process. The formation of these deposits by precipitation appears unlikely since the deposits were not visually observed and the inhibition was potential dependent.

The formation of a lead species by UPD explains the experimental findings of previous investigators, who did not have present-day sensitive surface analysis techniques, where lead was not detected on coated steel surfaces after exposure. The result of Mayne and Turgoose [1] in which only a small amount of lead was found at the perimeter of a drop, i.e., the cathodic sites, is reasonable if lead deposits formed by UPD.

Step 2 - The lead deposits inhibit oxygen reduction at the steel surface and decrease the cathodic current density. The inhibition of oxygen reduction by lead deposits results from a lower reaction rate or i_L for lead than for steel. The resulting reduction in the cathodic current density was observed on cathodic polarization curves at potentials corresponding to the galvanic potentials of steel-steel couples. The reaction was a function of the lead concentration in solution, the greater the surface coverage by the lead deposit, the greater the inhibition of oxygen reduction and the larger the reduction of the cathodic current density. The structure of the lead deposit may also affect the kinetics of oxygen reduction. Adzic and Despic [36] reported that UPD deposits of lead inhibited oxygen reduction on platinum. These lead deposits, therefore, act as cathodic inhibitors.

Step 3 - The galvanic current at anodic sites on the steel surface is reduced by the cathodic current. The reduction in the cathodic current density in the presence of lead parallels the reduction in the galvanic current density as shown in Table III. A contributing factor to the reduced galvanic current density was also the local cell action on the anode of the

Table III

Cathodic Polarization Parameters for Steel in a pH 4.5 Solution with Lead Acetate[a]

Test Cond.[b]	n	Lead Concn. (M)	Corr. Poten. (mV)	Corr. Current Density[c] ($\mu A/cm^2$)	Limiting Current Density[d] ($\mu A/cm^2$)
1	4	0	-604 [1]	47 [4]	--
	3	2×10^{-6}	-590 [2]	18 [4]	63 [17]
	3	1×10^{-3}	-521 [1]	10 [2]	61 [5]
2	2	0	-584 [6]	245 [14]	265 [20]
	3	$4\text{-}6 \times 10^{-6}$	-554 [1]	210 [40]	230 [60]
	1	1×10^{-5}	-546	280	280
3	2	0	-598 [6]	25 [1]	--
	2	2×10^{-6}	-566 [0]	1 [0.2]	4 [0.3]
	2	1×10^{-3}	-502 [0]	1 [0.5]	33 [3]

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[a] The parameters are average values where n is the number of samples. Standard deviations are in brackets.

[b] The numbers correspond to the following test conditons: (1) unstirred solutions and CO_2 control, (2) stirred solutions and CO_2 control, and (3) unstirred solutions and deaerated.

[c] Corrosion current densities listed for test condition 3 were determined by the extrapolation of the Tafel region for hydrogen evolution back to the open-circuit potential.

[d] Limiting current densities were measured at a potential of -750 mV for test condition 1 and at -650 mV for 2 and 3.

couple. The local cathodic current on the anode had only a small effect, however, since the weight loss of an electrode in the pH 4.5 solution was less when coupled (Table IV). The decrease in the galvanic current density was accompanied by a change in the controlling process. In the absence of soluble lead species the process in unstirred solutions was either diffusion limited or reaction limited, i.e., activation control. The process was solely under activation control in the presence of soluble lead species.

Step 4 - The lower galvanic current density, due to cathodic inhibition by the soluble lead species, decreases the corrosion rate. The lower weight losses observed for the anodes of the steel-steel couples were indicative of the reduced corrosion rate in the presence of soluble lead species.

(b) Mechanism #2 - A small separation of anodic and cathodic sites.

The small distance between anodic and cathodic sites reduces the pH difference of the aqueous phase between these sites such that the pH near the cathode and the anode probably approaches a neutral value. Inhibition proceeds by the following sequence of steps:

Step 1. Lead deposition occurs at cathodic sites in addition to oxygen reduction, the sum of which increases the cathodic current density.

Step 2. The anodic current increases; the anodic potential is increased into the passive region.

Step 3. The corrosion rate is reduced because of the formation of a protective oxide.

Table IV

Weight Losses of Coupled and Uncoupled Steel Electrodes - Unstirred Solutions and CO_2 Control[a]

Lead Concentration (M)	Wt. Loss of Coupled Electrodes (mg/cm^2) Anode pH 4.5	Wt. Loss of Coupled Electrodes (mg/cm^2) Cathode pH 10	Wt. Loss of Uncoupled Electrodes (mg/cm^2) pH 4.5	Wt. Loss of Uncoupled Electrodes (mg/cm^2) pH 10
0	1.7 [0.3]	<-0.1[b]	0.8 [<0.1]	-0.2
2×10^{-6}	1.0 [0.2]	0.2	0.8 [0.1]	0.3
1×10^{-3}	0.8 [0.2]	<0.1	0.6 [0.2]	-0.3

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[a] Weight losses are the average of two to four measurements. Standard deviations are in brackets for the coupled and uncoupled electrodes in the pH 4.5 solution.

[b] Minus sign indicates a weight gain.

Step 1 - The deposition of lead at cathodic sites along with oxygen reduction increases the current density. The deposition of metallic lead was visually observed as faceted particles which deposited from solutions containing the high lead concentration. Metallic and/or oxidized lead species were found by AES and XPS on the anodes of steel-steel couples and uncoupled electrodes in the pH 4.5 solution. The lead deposited at cathodic sites since the faceted particles were metallic. An increased density of particles was also found near macroscopic defects on samples from the scratch test or at pits on samples from the immersion tests. Pits or scratches are generally anodic sites with surrounding regions being cathodic sites.

Mayne and coworkers previously reported the presence of lead species on steel exposed to lead-containing solutions, although the sites on the steel surface were not identified. The results from Mayne and Turgoose [1] showed that at the center of drops (pH 5-7) lead deposits had a similar distribution to deposits of the azelate anion which indicated a possible close proximity of anodic and cathodic sites although the region was primarily anodic.

Oxygen reduction and lead deposition occurred simultaneously on cathodic polarization in the pH 4.5 solution as indicated by polarization curves. The increase in the cathodic current resulted from both the deposition of lead and the increased surface area for oxygen reduction. Appleby and Mayne [4] also found that oxygen reduction was increased for steel electrodes rubbed with metallic lead in an 0.1N sodium azelate solution at a pH of 4.8. These authors, however, attributed this increase to the greater ease of the reaction on a lead surface than on steel surface. In the present study both lead and steel in stirred solutions were found to readily depolarize the oxygen reduction reaction, but i_L was lower for lead than for steel.

Step 2 - The increased current produced by the lead cathodes as a result of a larger surface area increases the current flowing to the anodic sites. The overpotential for passivation was reduced from 690 mV in the absence of soluble lead species to 500 mV for the high lead concentration as shown in Figure 1. These effects of lead, which depend on concentration, lower the energy barriers for passivation.

Step 3 - The corrosion rate decreases because the anodic sites on the steel surface are polarized into the passive region. A smaller weight loss was observed for a coupled steel electrode exposed to the high lead concentration (Table IV). Corrosion current densities, however, decreased with increasing lead concentration for unstirred acidic solutions (Table V). The surface roughness of steel after exposure was observed to decrease when lead was in solution, possibly indicating a reduced attack of the surface due possibly to a thicker oxide.

This mechanism is in agreement with that proposed by Mayne and coworkers [1-4] and similar to part of the autocatalytic mechanism proposed by Lindqvist [5]. The overall effect of lead in this mechanism is similar to that of oxygen. Oxygen depolarizes the cathodic reaction and maintains the surface oxide on the anode in repair.

(c) Mechanism #3 - Oxygen deficiency at the interface.

An oxygen deficiency at the interface occurs from several circumstances, i.e., a coating with excellent barrier properties or exposure of a coating to oxygen-deficient environments. Inhibition proceeds by the following sequence of steps:

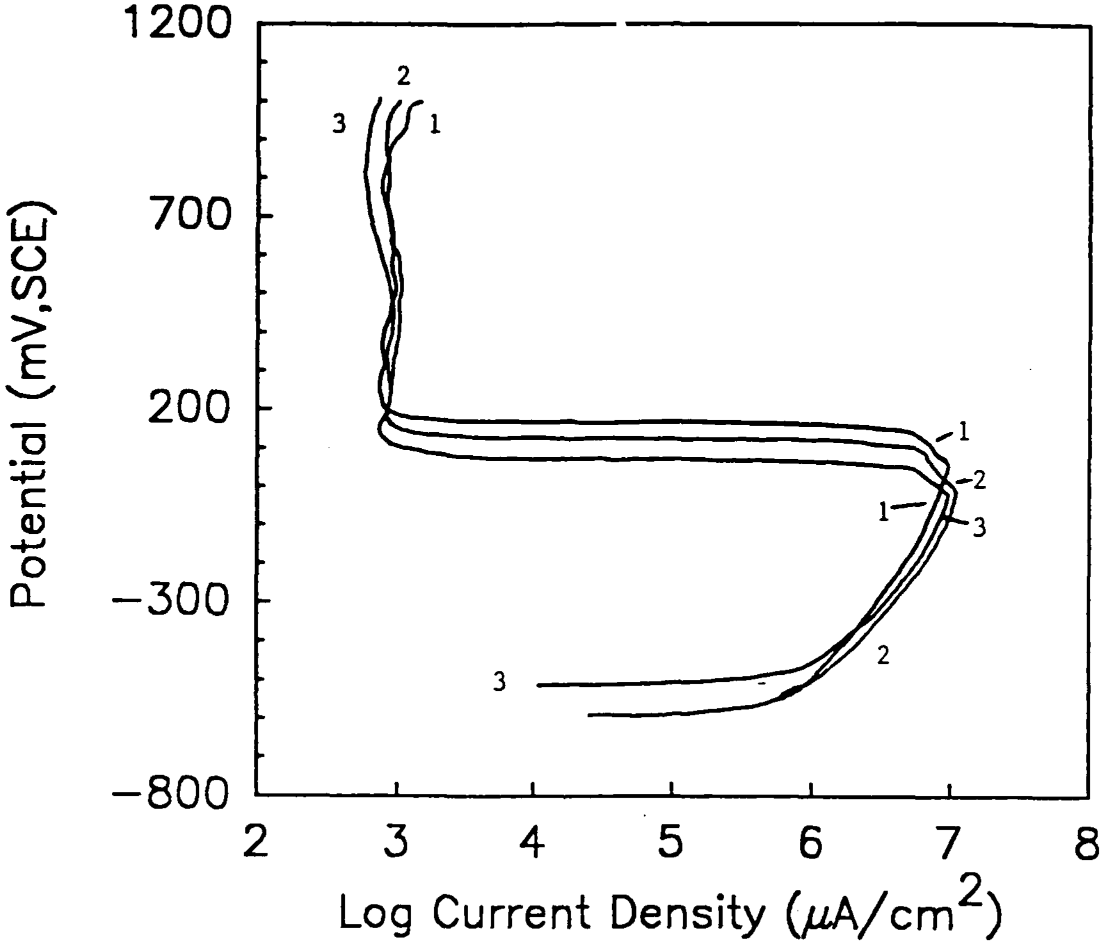

Fig. 1. Anodic polarization curves for steel in unstirred 0.1M sodium acetate solutions at a pH of 4.5 with the following lead acetate concentrations: (1) 0M, (2) 2×10^{-6}M, and (3) 1×10^{-3}M.

Table V

Solubility Products and Solubility Limits of Lead Compounds[a]

Compound	Reactants	Solubility Product or Limit		
		4.5	7.0	10.0
$PbCO_3$	H_2CO_3, Pb^{+2}	7.4×10^{-6}	7.4×10^{-11}	7.4×10^{-17}
	HCO_3^- , Pb^{+2}	1.0×10^{-7}	3.2×10^{-10}	3.2×10^{-13}
$PbSO_4$	HSO_4^- , Pb^{+2}	4.3×10^{-11}	1.3×10^{-13}	3.2×10^{-13}
$Pb(OH)_2$	Pb^{+2}	4.4×10^{4}	4.4×10^{-1}	4.4×10^{-7}
	$HPbO_2^-$, H^+	1.3×10^{-10}	4.2×10^{-8}	4.2×10^{-5}
$PbCrO_4$[b]			5.4×10^{-7}	
$Pb_3(CO_3)_2(OH)_2$[b]			6×10^{-6}	
$Pb_3CrO_4(OH)_2$[b]	CrO_4^{-2}, OH^-, Pb^{+2}		2.1×10^{-32}	
$PbClOH$[b]	Cl^-, OH^-, Pb^{+2}		$1.7\text{-}9.7 \times 10^{-14}$	

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[a] The values were taken from the following references: $PbCO_3$, $PbSO_4$, and $Pb(OH)_2$ (P. Delahay, M. Pourbaix, and P. Van Rysselberghe, Proceedings of Second Meeting of CITCE, Milan, 1951, 15); $PbCrO_4$, $Pb(CO_3)_2(OH)_2$, $Pb_3CrO_4(OH)_2$ and $PbClOH$ (W. F. Linke, Solubilities of Inorganic and Metallic Organic Compounds, Vol. 2, ACS, Washington, DC, 1965, 1256).

[b] Solubility limits are given in molar units (M).

Step 1 - Hydrogen evolution and lead deposition occur at cathodic sites on the steel surface.

Step 2 - Hydrogen evolution is suppressed at lead deposits.

Step 3. The corrosion rate is decreased.

Step 1 - Hydrogen evolution and lead deposition replace oxygen reduction as the dominant cathodic reaction. This change in reaction is observed experimentally by a change in the cathodic polarization behavior. For unstirred solutions, the polarization curve for steel in 0.1M sodium acetate solution at pH 5 displayed a Tafel region for hydrogen evolution at low over-potentials, as opposed to the diffusion-limited current for oxygen reduction that was observed for stirred solutions. A Tafel region for hydrogen evolution was also observed for unstirred deaerated solutions. Lead deposition occurred on steel surfaces during cathodic polarization in deaerated pH 4.5 solutions in the presence of soluble lead species. The deposition occurred at a limiting current density (Figure 2). Faceted lead particles were also observed on the surface for freely corroding steel samples under deaerated conditions.

Oxygen reduction occurred when oxygen was present. The cathodic polarization behavior of steel in unstirred solutions containing lead showed a limiting current density attributed in part to oxygen reduction. In the absence of lead, the polarization behavior showed only a Tafel region. Weight loss data suggested that both oxygen reduction and hydrogen evolution occurred.

Step 2 - The hydrogen evolution reaction is suppressed at the cathodic lead deposits. The suppression of hydrogen evolution on steel electrodes in

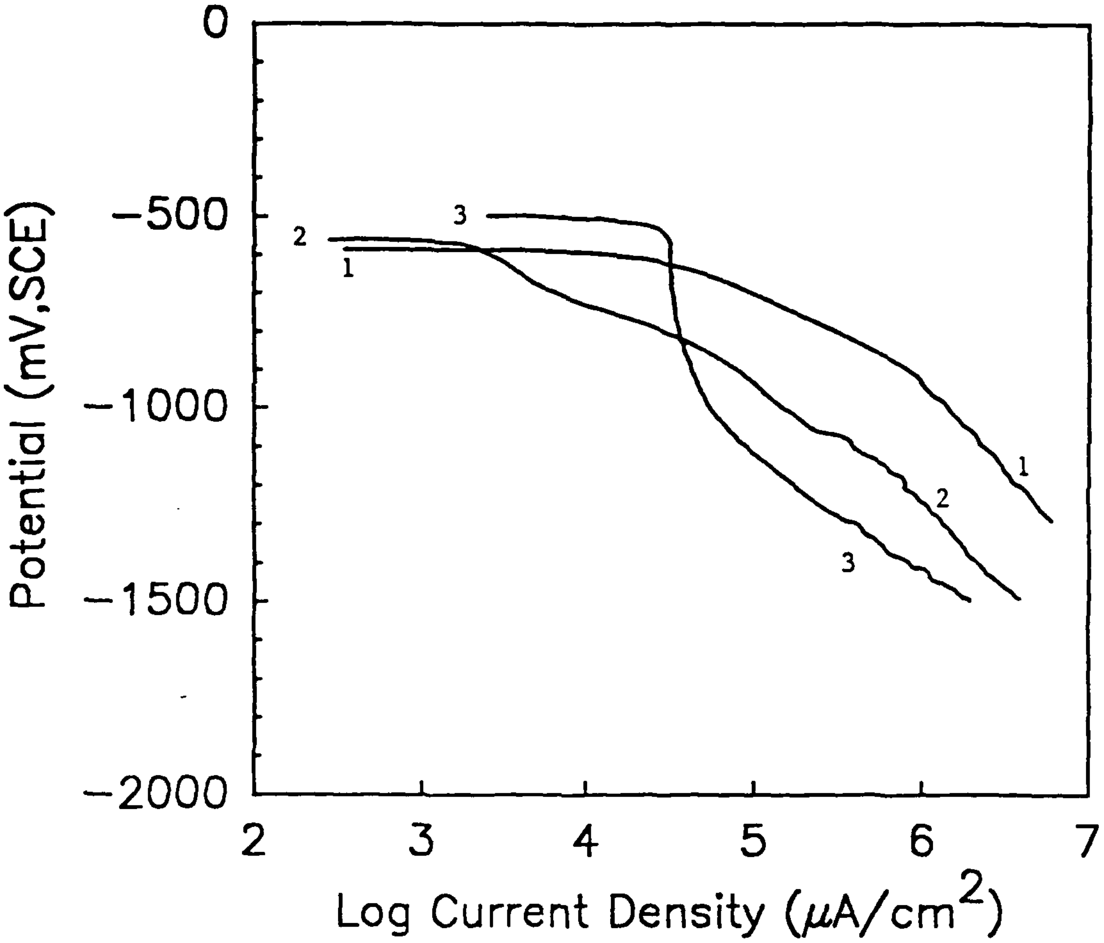

Fig. 2. Cathodic polarization curves for steel in unstirred 0.1M sodium acetate solutions at a pH of 4.5 under deaerated conditions with the following lead acetate concentrations: (1) 0M, (2) 2×10^{-6}M and (3) 1×10^{-3}M.

lead-containing solutions was observed by the more active values of E_H from that when lead was not present. E_H became more active with increasing concentration of lead. This result was observed for all the test conditions, i.e., stirred and unstirred solutions and deaeration. The concentration dependence of E_H was indicative of a greater percentage of the steel surface being covered with lead deposits.

Step 3 - The corrosion rate of the steel decreases because the rate of the cathodic reaction decreases. The corrosion current density associated with hydrogen evolution was found to decrease in the presence of lead for the deaerated solutions (Table III, test condition 3). Similar correlations of a reduced corrosion rate and corrosion current density to the suppression of hydrogen evolution were previously reported for lead deposits on steel in low pH solutions by Lafranconi et al. [22] and Jüttner [23].

This mechanism is controlling only under certain circumstances. First, the pH of the aqueous phase must be sufficiently acidic because in alkaline solutions hydrogen evolution is not significantly affected by the presence of lead. E_H was similar for stirred and unstirred solutions when lead was or was not present. Second, lead deposition increases the cathodic current so if a sufficiently high lead concentration is present, corrosion of the steel substrate increases. The combination of i_L and i_{corr} for a given lead concentration is representative of the corrosion rate in deaerated solutions. The combined current densities were greater for the high lead concentration than when lead was not present. The combined current density for the low lead concentration, however, was significantly less than that in the absence of lead ions in solution.

5. The Inhibition of Steel Corrosion by Lead Species during the Drying Cycle

The inhibitive process which occurs during the drying cycle results from a change in the solubilities of lead compounds. These compounds precipitate onto the steel surface as the interfacial conditions change and the solubility limits of the compounds are reached. The precipitated deposits that form during the drying process provide inhibition by barrier-type protection. In rewetting part of the cycle these deposits provide a ready supply, or reservoir, of soluble lead species immediately at the interface. These elements of the inhibitive mechanism extend the effectiveness of lead over the lifetime of the aqueous phase.

Lead forms compounds with many common constituents of the aqueous phase including chlorides, sulfates, carbonates, hydroxyl ions and oxygen (Table V). The solubilities of many of these compounds are a function of the pH and generally decrease with increasing alkalinity. This pH dependence was observed by the abundance of precipitates in the pH 10 solution and by the lack of precipitates in the pH 4.5 solution. The solubilities of these compounds extend over a range at a particular pH; e.g. at pH 7 $PbClOH$ has a low solubility of $10^{-14}M$ and $Pb(OH)_2$ has a high value of $10^{-1}M$. These characteristics of lead compounds potentially provide an array of precipitates that function inhibitively over the pH range of the aqueous phase at the steel/ coating interface.

The cessation of corrosion results from the inhibition by the soluble lead species. Oxides reform or thicken at anodic regions and decrease the anodic reaction. The aqueous phase becomes less acidic as the anodic reaction slows and becomes more localized. The anodic sites become more polarized such that anodic control of the corrosion process occurs. The lead compounds under these conditions precipitate by two pathways. First, the decreased acidity of the aqueous phase decreases the solubility of these compounds. The compounds precipitate on the steel surface and form a barrier-type layer which increases the diffusion distance for ions to and from the surface. The precipitates act as an additional resistance to corrosion. Second, the anodic polarization provides the conditions for the formation of oxides from $HPbO_2^-$. The concentration of $HPbO_2^-$ increases as the pH increases. The anion by ionic migration is attracted to the anodic sites. PbO precipitates if a sufficient concentration of $HPbO_2^-$ is obtained or Pb_3O_4 forms by oxidation of the anion. These precipitation mechanisms are proposed since a lead species was found on uncoupled electrodes after a 24-hour exposure in a pH 10 solution. The reinforcement of the oxide was indicated by a more noble E_{corr} for steel and a lower current density during anodic polarization in lead-containing solutions.

Precipitates as a Reservoir of Soluble Lead

As the coating dries out, the volume of the aqueous phase decreases and the concentration of ionic species subsequently increases. The compounds precipitate as their solubility limits are reached. These precipitates act as a supply source or reservoir of soluble lead species when the aqueous phase reforms or increases, but the effectiveness of this process will depend on the solubility of the compounds. The soluble species are available near the surface at points of corrosion. The diffusion time is less than that for lead species diffusing from within the coating. The corrosion process, therefore, does not proceed significantly before inhibition occurs. This mechanism was modeled from the potentiostatic test in which lead compounds were added after a stable cathodic current was obtained. The reduction in the current density depended on the lead compound; the more soluble compound produced the greatest reduction. Mayne [10] found that distilled water after exposure to various lead compounds was inhibitive due to the presence of lead in solution. The inhibitive compounds were primarily the various lead oxides. Compounds such as lead carbonate and sulfate were not inhibitive, but their solubilities are lower than those of lead hydroxide. Large volumes of water were used by Mayne. A greater inhibitive effect probably occurs at the steel/coating interface where volumes are smaller.

6. Lead Pigments - The Ideal Inhibitor

The effectiveness of lead pigments as a corrosion inhibitor and its superior performance over other common inhibitors are requisite to titling a lead pigment as an ideal inhibitor. Six requirements of an ideal inhibitor in organic coatings were summarized by Leidheiser [33]. A corrosion inhibitor should: (1) be effective over a wide range of pH values, ideally from 2 to 12; (2) react with the metal surface to form a low solubility product; (3) have a low but sufficient solubility; (4) have reaction products that do not reduce the coating adhesion; (5) be effective as both an anodic and a cathodic inhibitor; and (6) inhibit the two important cathodic reactions, i.e., oxygen reduction and hydrogen evolution.

The soluble lead species which form from lead pigments do inhibit the corrosion of steel over a wide pH range. Pryor [9] reported that at pH values of up to 10 the corrosion rate of steel was reduced in aqueous extracts of PbO. Mayne and coworkers [1-4] found that the degradation product of lead pigments were inhibitive at pH values down to 5. Lead was also inhibitive in solutions with pH values less than 3, but these test conditions are not typical of those expected at a steel/coating interface. In this study, weight losses of steel in pH 4.5 solutions were reduced when lead acetate was added.

The soluble lead species generally react at the surface more so than with the surface. The soluble lead species deposit as a metal in acidic solutions and precipitate as lead compounds in alkaline media. The potential of the steel surface is also a factor since metal deposition by UPD was found for the pH 10 solution. Many previous investigators [2,5,23,27,33,34] proposed that metallic lead was the surface species involved in the inhibitive mechanism. Some investigators proposed precipitation [35] and adsorption [10] products which result from reactions with the surface were responsible for inhibition. It appears that different reactions occur under different circumstances.

Coating adhesion is probably not affected significantly by the presence of soluble lead species or their reaction products since lead-pigmented paints were once extensively used. Coating adhesion was not reported as a problem with these paints. Lindqvist and Vannerberg [31] reported that a very thin surface layer was found beneath an alkyd paint pigmented with red lead after a three-month exposure. Although the authors did not study adhesion specifically, they noted that paint fragments were retained with the surface layer, which indicated some degree of adhesion.

The soluble lead species and their reaction products act as both anodic and cathodic inhibitors. As a cathodic inhibitor, the lead deposits inhibit both oxygen reduction and hydrogen evolution. The lead deposit that formed on cathodically polarized steel sample in alkaline solutions decreased the current density associated with oxygen reduction. This effect on oxygen reduction decreased the corrosion rate of steel-steel couples in these solutions.

in acidic solutions the lead deposits suppress hydrogen evolution since lead has a large overpotential for this reaction. This suppression would be effective for inhibition in deaerated environments where hydrogen evolution would probably be the dominant cathodic reaction. Anodic inhibition was found to occur in aerated acidic solutions. The oxidation rate was increased in the presence of soluble lead species so that the critical conditions for passivation were met. The oxidation rate was driven by an increased cathodic current due to lead deposition and oxygen reduction.

Lead pigments, along with soluble lead species and their reaction products, fulfill the requirements for an ideal inhibitor. The effectiveness of lead pigments and the soluble products is attributed to their versatility in adapting to the changing conditions at a steel/coating interface. This versatility is shown by the multifaceted inhibitive mechanism. The likelihood of other compounds exemplifying lead pigments seems small. In order to replace lead pigments adequately as a corrosion inhibitor, two or three compounds are probably needed.

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