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De-adhesion at the Organic Coating/Metal Interface in Aqueous Media

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De-adhesion, or delamination, may occur along six different planes in the interfacial regions of a metal/organic coating system: (a) in the metal (anodic undermining), (b) at the metal/interfacial oxide boundary, (c) within the interfacial oxide, (d) within a pre-treatment layer or conversion coating, (e) at the organic coating/interfacial oxide boundary, (f) within the polymer coating. The plane along which delamination occurs is a function of the system and environmental conditions. Five areas where extensive research is required are outlined: studies of the interfacial oxide, nature of the coating/interfacial oxide bond, non-destructive methods for locating bulk water aggregation at the interface, understanding the effects of ions on delamination during cathodic treatment, and understanding the factors which control the generation of a high pH in a region delaminated by a cathodic process.

INTRODUCTION

There are many ways to develop solid/liquid interfaces including melting of a solid, precipitation of a solid, injection of a solid into a liquid, contact of a liquid with a solid, displacement of one liquid/solid interface by another liquid/solid interface, condensation of a solid onto a liquid surface, condensation of a liquid onto a solid surface, melting one component in a two-component systems, etc. Many of these ways are the subject of other talks at this conference. A present interest of our research in the Corrosion Laboratory of the Center for Surface and Coatings Research at Lehigh is a better understanding of the development of solid/liquid interfaces in the interfacial area between a metal and an organic coating. We have thus selected this topic for review at the 5th Ruđer Bošković Summer Conference on the Chemistry of Solid/Liquid Interfaces.

Organic coatings are applied to a metal surface in order to obtain a combination that takes advantage of the physical properties of the metal and the chemical properties of the coating. The coating is most often applied to protect the substrate metal from corrosion, although the optical, electrical, thermal, and acoustic properties of the coating are also of importance. The

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protective nature of the coating depends upon the maintenance of a sub-state/coating bond under adverse environmental conditions. When this bond loses integrity and bulk water develops at the interface, the coating lifetime is limited and the system does not meet all the requirements placed upon it.

It is well known that many types of chemical attack lead to preferential deterioration of a system along a boundary. Several examples are cited from the corrosion literature. Many instances of the cracking of stressed metals along grain boundaries have been recognized microscopically[1]. Heat treatment of austenitic stainless steels containing carbon leads to the formation of $Cr_{23}C_6$ at grain boundaries and a consequent reduction of the chromium in the alloy immediately at the boundary. The passive nature of the alloy is lost to the boundary and intergranular attack occurs[2]. The exfoliation of aluminum alloys is a consequence of attack along compositional boundaries in the metal[3]. Stressed intermetallic compounds are preferentially attacked by distilled water and electrolytes along specific planes[4]. Weathering leads to attack at the boundary of epoxy-coated, chromated aluminum[5]. It is clear that an interface is a specially prone location for breakdown.

It is the purpose of this presentation to point out that the development of an aqueous phase at a metal/organic coating interface can occur along different planes in the interfacial region. Also, suggested areas for research will be outlined.

EXACT LOCATION OF DE-ADHESION

Organic coatings are applied to metal surfaces both with a protective pretreatment or directly to the metal without pretreatment. In the absence of pretreatment, all metals with the possible exception of gold and several of the precious metals have an interfacial oxide at the metal/organic coating interface. The presence of this oxide has been confirmed by emission Mössbauer spectroscopy in the case of polybutadiene coatings on cobalt[6], but there is no reason to doubt its presence in other systems in which direct experimental evidence is lacking. The pretreatment may be a thick coating, as in the case of iron or zinc phosphate, or it may be thin as in the case of chromated surfaces or those coated with a complex mixed oxide by proprietary formulations. In these cases the composition of the interfacial oxide or phosphate is controlled in order to improve the corrosion resistance of the systems.

A coated metal thus consists of three main layers: metal substrate, interfacial oxide or other compound, and the organic coating. The metal/organic coating system may delaminate by attack within any of the three different phases or at the two boundaries. See Figure 1. Each of these cases will be discussed separately and examples will be cited from the literature.

All organic coatings are permeable to the constituents that are important in a corrosion reaction, namely, ions, water, and oxygen; they differ only in the rate at which the coating permits migration from the coating/environment interface to the coating/substrate interface. This permeability allows the development of an aqueous phase at localized regions of the interface under conditions where an imperfection in the coating/substrate bond exists or by hydrolysis of the coating/substrate bonds at points of weakness or excessive stress. Once an aqueous phase is present, electrochemical reactions, such as corrosion, may occur. The anodic half reaction, $Me - ne^- = Me^{+n}$, and cathodic half reaction, $H_2O + 1/2\,O_2 + 2\,e^- = 2\,OH^-$, occur at those locations where the
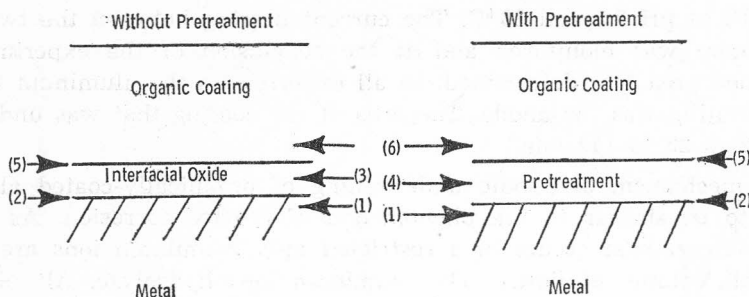
Figure 1. Schematic representation of the six planes along which delamination may occur in an organic coating/metal substrate system. Note that relative thicknesses of oxide and pretreatment layers and the organic coating are not to scale.

kinetics favor them. Thus a high pH may be generated at specific locations and the alkalinity may be injurious to the system with consequent enlargement of the area occupied by the aqueous phase at the interface. The chemistry of the system and the resistance of the three phases to the alkaline environment often determine where the predominant deterioration occurs.

Mode #1 — Attack of the Metal.

This phenomenon also has been termed »anodic undermining« by Koehler[7]. There is little published experimental information on attack of the metal beneath the organic coating and beneath the interfacial oxide. The most convincing evidence that attack of the metal can occur without destruction of the oxide film is found in the work of Yahalom, Ives, and Kruger[8]. These workers studied the pitting of stainless steel foils in chloride media. They observed that the oxide film that was originally present on the stainless steel surface was detected by electron microscopy on the floor of the pit. In several cases the stainless steel was completely dissolved in small areas leaving the oxide film from both original surfaces still adhering to the foil.

According to Koehler[7] »anodic undermining is a most significant type of failure mechanism for the corrosion of organic-coated metals.« Tinplate, where a thin coating of tin serves as a sacrificial coating for the underlying steel, is specially prone to anodic undermining in those cases where an organic coating is over the tin. A defect in the organic coating on a tin plate food container allows the tin to dissolve selectively from between the steel and the organic coating starting from the defect[9]. Reduction processes taking place through the organic coating or on other available cathodes provide the driving force for the anodic reaction.

Aluminum, when protected with an organic coating, is also prone to anodic undermining. A laboratory test[7] illustrates anodic undermining. A sample of aluminum was heavily coated with an organic coating and a small defect was made in the coating by pressing a scribe through it. This sample was coupled to a second aluminum sample that had not been coated and the bimetallic couple was exposed to air-saturated citrate buffer solution with

0.5% NaCl at pH 3.5 and 38 °C. The current passing between the two pieces of aluminum was monitored and at the conclusion of the experiment the undermined area was determined. In all experiments the aluminum with the organic coating was the anode. The area of the coating that was undermined ranged from 25 to 140 mm².

The mechanism of anodic undermining of organically-coated aluminum appears to be similar to the phenomenon of crevice corrosion. As a small amount of corrosion occurs in a restricted area, aluminum ions are formed in a small volume of liquid. The aluminum ions hydrolyze, $Al^{+++} + H_2O = Al(OH)^{++} + H^+$, with the formation of a low pH. The low pH leads to an autocatalytic effect with aluminum being attacked at a greater rate and the pH falling as a consequence of the greater aluminum ion concentration. Undermining, in preference to pitting, occurs according to Koehler »because of the greater restriction on diffusion processes at such an anode as compared with the anode at the base of a pit.«

Anodic undermining has been observed in commercial paint systems with an iron phosphate pretreatment, whereas it was absent in systems in which a zinc phosphate pretreatment was used. Wiggle, Smith and Petrocelli[10] have attributed this contrasting behavior to the fact that iron phosphate pretreatments tend to be more porous than zinc phosphate pretreatments. In their experiments the porosity of a zinc phosphate pretreatment was 0.2% and the iron phosphate was about 23%.

Filiform corrosion is a special from of anodic undermining. This type of corrosion consists of thread-like filaments that form beneath an organic coating, and beneath an oxide coating in some instances. It is specially prevalent beneath organic coatings on steel, galvanized steel, aluminum, and magnesium substrates. Good summaries of this phenomenon have been presented by Hoch[11] and Koehler[12]. It will not be discussed further here.

*Mode #2 — Attack at Metal/Interfacial Oxide Boundary.*

The author is not aware of any organic coating systems in which delamination has occurred as a consequence of attack at the metal/interfacial oxide boundary. However, the corrosion literature includes a number of cases in which attack at this boundary seems to occur at a very rapid rate. For example, when an abraded spherical single crystal of copper is electropolished in 42.5% phosphoric acid containing sufficient dissolved copper to give a deep blue color, the oxide formed on the surface during abrasion peels off the surface and is carried to the bottom of the vessel by convective flow. The fragments of oxide are sufficiently large that they must have been released from the surface by rapid attack at the oxide/copper boundary.

Professor U. R. Evans of Cambridge University brought a degree of curiosity and sophistication to the field of corrosion science in the early and mid-1900's that it had not previously had. He developed simple techniques and applied these to an understanding of complex phenomena. One of his

interests was the passive film that formed on iron under strongly oxidizing conditions. He proved that passive iron had a film on its surface that was resistant to attack in oxidizing solutions. He isolated the film from iron by scratching the surface in a cross-hatch pattern and then exposing the iron to a solution of bromine in methanol. This medium rapidly attacked the oxide/iron interface and the film floated off the surface.

Mode #3 — Attack of the Interfacial Oxide.

The outstanding example of this type of delamination mechanism has been provided by Gonzalez, Josephic, and Oriani[13]. These workers were concerned with the fact that scratched lacquer coatings on low carbon steel delaminated when exposed to a citric acid-sodium chloride electrolyte while a similar lacquer coating on a steel that had been coated with chromium- -chromium oxide did not delaminate. They proposed that the interfacial oxide was an intimate part of the overall corrosion reaction. It was proposed that the anodic reaction, $Fe = Fe^{++} + 2e^-$, took place in the scratch and the cathodic half reaction took place within the oxide that adjoined the scratch,

$$\gamma - Fe_2O_3 + 6H^+ + 2e^- = 2Fe^{++} + 3H_2O.$$
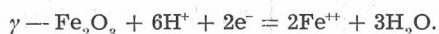
This reaction was first proposed by Evans[14] to explain the rapid disappearance of interference colors of oxidized iron upon immerision in acid solution with a pH of less than 4.

Since the oxide is very thin, of the order of 50 Å (5 nm), the hydrogen ions consumed by the cathodic reaction are not readily made up by diffusion, so a rise in pH occurs locally. As the pH rises, $Fe(OH)_2$ is precipitated and the reaction is stifled. In the presence of complexing ions, such as citrate, the ferrous ions are complexed and no precipitation of $Fe(OH)_2$ occurs. The chromium-chromium oxide interfacial layer cannot participate in a similar cathodic reaction because of the thermodynamic stability of Cr_2O_3 under the experimental conditions used.

Mode #4 — Attack of Pretreatment Layer.

Corrosion performance of an organic coating/metal system is often improved by a metal pretreatment step that precedes the application of the organic coating. A common type of pretreatment involves the formation of a phosphate coating, either zinc phosphate or iron phosphate, on the surface. The beneficial effects of this type of pretreatment result from a combination of corrosion inhibition, barrier-layer protection of the metal, and a roughened surface that promotes good adhesion between the substrate and the organic coating.

Wiggle, Smith and Petrocelli[10] have studied paint adhesion failure mechanisms on steel and have paid particular attention to failure involving the pretreatment. They used phosphate surfaces that were coated with an epoxy ester prime coat and an acrylic topcoat. They were primarily concerned with loss of adhesion because of corrosion and used a test in which a painted panel

was scribed through to the metal and the lateral rate of delamination was determined as a function of time of immersion in an aerated solution of 5% NaCl. In the case of the zinc phosphate pretreatment the prime mode of delamination was attack of the zinc phosphate by the alkaline medium generated by the cathodic reaction which occurred adjoining the scribe mark. Delamination in the case of the iron phosphate coatings was very small under the same experimental conditions. The de-adhesion with the zinc phosphate pretreatment was attributed to the dissolution of the phosphate and the absence of such dissolution in the case of the iron phosphate on the basis of microscopic studies and independent dissolution studies. Evidence for the effect of alkali on the rate of dissolution of these two phosphates is summarized in Table I.

TABLE I

Rate of Dissolution of Zinc Phosphate and Iron Phosphate in Different Alkaline Media[10]

Type of Phosphate	Alkaline Medium	pH	Rate of Phosphate Dissolution from a Pretreated Surface
Zinc	0.01M NaOH	12	0.02% of total phosphate/minute
Zinc	0.1M NaOH	12.8	6%
Zinc	1M NaOH	13.8	200%
Iron	1M NaOH	13.8	Negligible; rate became significant at 5M NaOH

Contamination of the steel surface can also affect the quality of the pretreatment and its ability to resist delamination in a scribe test. Iezzi and Leidheiser[15] have presented evidence that carbon contamination of the steel surface, not removed by standard cleaning procedures, leads to inadequate nucleation of the zinc phosphate pretreatment layer and the formation of a phosphate that is relatively porous. Such a porous phosphate does not resist the alkaline environment well and delamination occurs to a greater extent than with a non-contaminated surface.

Mode #5 — Attack at the Organic Coating/Interfacial Oxide Boundary.

Attack at this location does occur under some circumstances, but knowledge of the mechanism and the cause for its infrequent appearance is not available. One of the rapid quality control tests used to determine the integrity of the metal/organic coating bond is to expose the coated metal to a hot aqueous solution (60—100 °C) for a period of time and then immediately determine the adherence of the coating to the substrate. In unusual circumstances the coating loses adherence and it may be readily stripped from the metal. However, if the coating is allowed to cool and dry out completely, the adherence is normal. Thus, the phenomenon is reversible. The strength of the bond is high before exposure to water and also high after a water-exposed sample is completely dried.

This reversibility in adherence is worthy of an important research effort because of its intriguing scientific nature and because of its great commercial significance.

Mode #6 — Attack of the Polymer.

Many polymers are subject to saponification when exposed to strongly alkaline media. The high pH generated when the cathodic reaction occurs under a polymer film suggests that delamination as a consequence of attack of the polymer coating near the metal surface is a real possibility. The question of whether attack of the polymer is involved in delamination has been addressed by Hammond, Holubka, and Dickie[16]. These workers studied both an epoxy ester primer and a polyethylene terephthalate top coat and found that both were subject to saponification by strong alkali.

They prepared coatings based on this system and utilized a test that involved scribing the coated panel and immersing it in oxygen-saturated 5% sodium chloride solution while in electrical contact with a zinc counter electrode. At the end of the test, adhesive tape was applied to the scribe mark and the delaminated sections on the sides of the scribe mark were removed. An analysis of the surface was made by means of X-ray photoelectron spectroscopy. It was concluded that bonds within the polymer were broken by the strong alkaline environment which results from making the scribed panel the cathode vs. a zinc anode. Fragments of polymer remained on the metal surface and carboxylated fractions were detected on the polymer surface that had been directed towards the metal prior to delamination.

The authors noted that saponification is a »significant pathway for adhesive loss«. We agree with this conclusion and feel that it is logical that the strong alkaline environment in the cathodic regions will attack the polymer. We also feel that the hydroxyl ions must be generated at the metal surface so that the failure mode must involve both separation at the polymer/metal interface as well as separation by cohesive failure within the polymer itself. Saponification thus provides an alternate pathway for the delamination process to proceed along the surface. Scanning Auger spectroscopy of the delaminated surface may provide information to determine if there are patches of metal surface and patches of surface to which polymer fragments still adhere after the delamination.

SUGGESTED AREAS OF RESEARCH

This summary indicates that the delamination process may occur predominantly in any of 6 locations within the interfacial boundary region as diagrammatically illustrated in Figure 1. Before any complete mechanism for a delamination process is proposed for a specific system, it is incumbent on investigators to determine the exact location where the separation process dominates. The available surface analysis techniques such as Auger and X-ray photoelectron spectroscopy allow one to determine if polymer fragments remain on the metal surface after delamination. In the most favorable cases, scanning Auger spectroscopy will allow one to determine if the polymer fragments completely cover the metal surface or if they remain in patches. Cross sectional studies using electron microprobe analysis in a delaminated region permit one

to determine if the pretreatment is adherent to the metal substrate or to the organic coating. This basic information should be generated in all studies.

It is apparent also that the major plane along which delamination occurs is a function of the system being studied. Anodic undermining predominates in some cases and cathodic delamination by alkali generation in other cases. Anodic undermining is expected to be determined largely by whether or not the kinetics favor separation in site of the anodic and cathodic half reactions for the corrosion process. Where large separations are not favored, the anodic and cathodic sites fluctuate within the confines of a defect and the anodic reaction spreads normal to and laterally from the center of the defect. When the kinetics of the corrosion reaction in a particular system favor large separations of the anodic and cathodic half reactions, the pH becomes very high at the periphery of a delaminating area and cathodic delamination dominates.

A better understanding of the delamination process as a consequence of corrosion or the application of an applied potential is a major concern of many research laboratories at the present time. For the purposes of this review, I am singling out five questions that are considered to be the most important in reaching a better understanding of metal/organic coating systems exposed to an aggressive environment in which deterioration of the system occurs by delamination.

Studies of the Interfacial Oxide.

Non-destructive techniques that permit studies of the chemistry of the oxide between the metal substrate and the organic coating need to be developed. Techniques that permit studies of the oxide while it is exposed to an aqueous media are specially required. Ritter and Kruger[17] of the National Bureau of Standards are applying ellipsometric methods to this problem. This technique allows a determination of the thickness of the oxide and the refractive index of the oxide. The refractive index may be utilized to speculate concerning the chemical composition of the oxide. The major limitation of the technique is that it is not applicable to opaque coatings or to coatings that excessively scatter the incident radiation. Optimum results in ellipsometry are obtained with very bright and smooth surfaces and such surfaces are not generally used as a substrate for an organic coating. Nonetheless the technique can be applied to a wide variety of substrates and transparent coatings and it may have special application in studies of changes in the thickness of the oxide during curing of the coating.

Mössbauer spectroscopy holds promise for studying the oxide in very special situations[6]. Concentration of a Mössbauer-active isotope, such as Co-57, in a thin film at the interface permits one to follow changes in the chemical nature of the emitting species as a function of thermal treatment or exposure to an electrolyte. Mössbauer spectroscopy suffers under the limitation that only a very few candidate materials are available and thus it is of restricted applicability. It does have the advantage that information can be generated with organic coatings that are opaque.

Optical reflectance spectroscopy may be applicable in some systems in which the interfacial oxide has a strong absorbance in a certain wavelength region and there is negligible absorbance by the coating and water present in the coating at the same wavelengths.

Nature of the Coating/Interfacial Oxide Bond.

The bond between the organic coating and the interfacial oxide appears to be the point of breakdown in certain circumstances. It is of special interest to determine the nature of this bond and how the bond is affected by water molecules that migrate through the coating. A potentially fruitful concept is that advocated by Fowkes[18,19] in which the bond is considered to have largely an acid/base character. Bond strength is strong when the oxide is acidic in nature and the bonding groups in the polymer are basic in nature, or when the oxide is basic and the polymer bonding groups are acidic. This acid/base concept should be tested with the objective of selecting surface treatments and polymer coatings where the bond strength can be maximized both in the absence and presence of water molecules in the coating.

Non-Destructive Methods for Locating Regions of Bulk Water Aggregation at Interface.

Water exists in polymers and polymeric coatings in two forms: (a) mobile, unaggregated water and (b) aggregated water. When aggregated water contains a sufficient number of molecules to have the properties of bulk water and when this aggregated water exists at the metal/coating interface, the conditions exist for the electrochemical reactions to occur that are involved in the corrosion reaction. The corrosion reaction is kinetically favored when the anodic and cathodic half reactions can occur at those sites where the activation barrier is minimal for each half reaction. An aqueous phase is necessary to permit charge transfer between the two reaction sites. In the absence of the aqueous phase, the corrosion reaction does not readily occur.

Procedures for determining the presence of bulk water in coatings are badly needed. Standish and Leidheiser[20] have found that the presence of bulk water in very low concentrations at a polyethylene/metal interface leads to unique capacitance and conductivity behaviors when electric measurements are made as a function of temperature. An example of the effect of aggregated water at the polyethylene/metal interface is given in Figure 2. Johnson and colleagues[21] at Bell Telephone Laboratories are also carrying out similar electrical measurements in order to identify the presence of bulk water within polymers. Such measurements are useful, but the necessity of cooling the coating/substrate system to a low temperature makes the test a destructive one and restricts its usefulness. An electrical measurement at room temperature that identifies bulk water in low concentrations and quantifies its location precisely is badly needed. A probe technique that characterizes the electrical properties on a localized basis[22] shows promise for identifying the locale of aggregated water, but an electrical signal that identifies aggregated water at room temperature is still being sought.

Understanding Ion Effects on Delamination during Cathodic Treatment.

An accelerated test for determining the tendency of a coating to delaminate by corrosion involves the introduction of a coating defect by pricking the surface with a sharp instrument, followed by making the system the cathode in an electrolyte. Research at Lehigh is utilizing this technique for polybutadiene coatings on steel substrates. The delaminated region is determined as
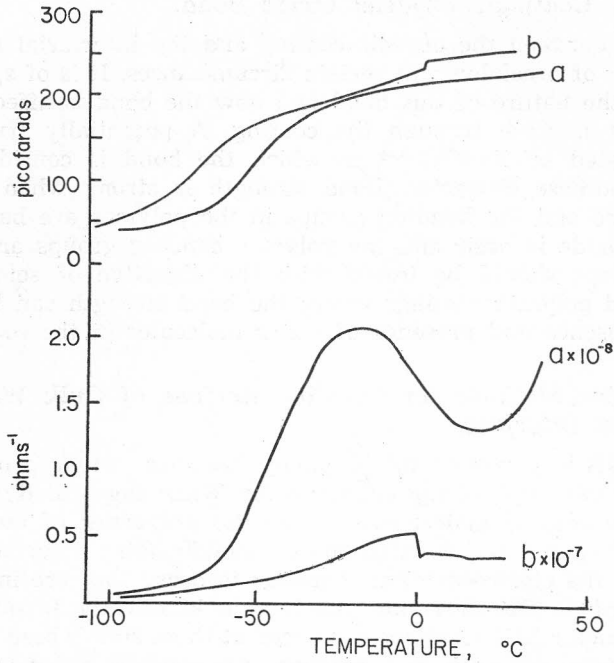
Figure 2. Dielectric values for (A) a polyethylene film and (B) a polyethylene film with a layer of deionized water at the polymer/electrode interface. Top curves represent capacitance and lower curves represent equivalent parallel conductivity.
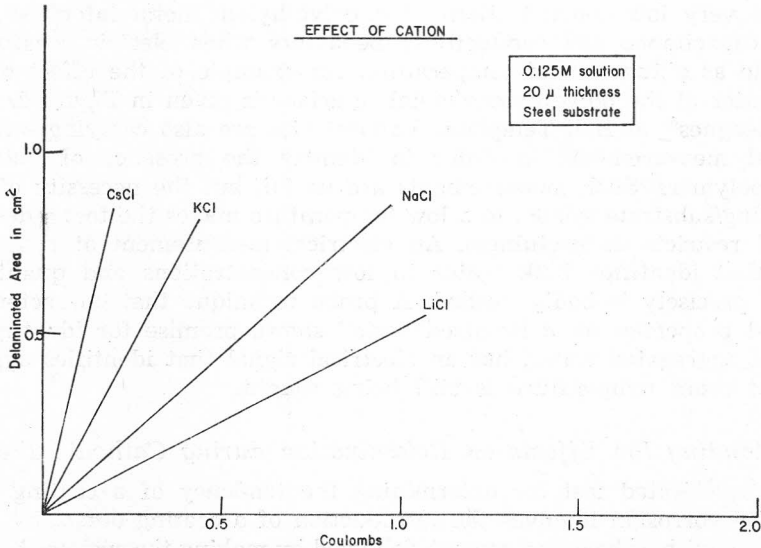

Figure 3. Delamination of a polybutadiene-coated steel surface when made the cathode in four different electrolytes as a function of the number of coulombs passed through a small defect in the surface. Note that results are a function of the cation.
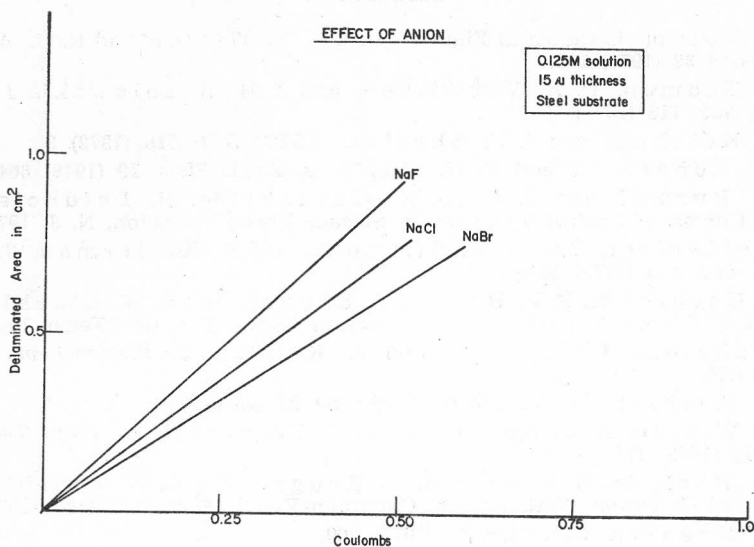
Figure 4. Delamination of a polybutadiene-coated steel surface when made the cathode in three different electrolytes as a function of the number of coulombs passed through a small defect in the surface. Note that results are a minor function of the anion.

a function of the number of coulombs passing through the interface. Data are given in Figure 3 for different cations and in Figure 4 for different anions. The strong cation dependence of the delamination remains unexplained at the present time. Present research is focused on determining whether the cation dependence is a function of the coating chemistry.

Factors Controlling Generation of High pH in Delaminated Area.

As stated earlier, when the cathodc reaction, $H_2O + 1/2 O_2 + 2 e^- = 2 OH^-$, occurs underneath the coating in an area adjoining the anodic corrosion site, a very high pH is generated. The magnitude of the pH generated is a function of many variables including the following:

(1) Rate of diffusion of water and oxygen to reaction site.

(2) Rate of diffusion of generated OH^- away from site.

(3) Rate at which cations can reach area and provide charge neutralization of the generated OH^- ions.

(4) Volume of liquid in region where OH^- ions are generated.

(5) Buffering reactions that might occur.

(6) Polymer/liquid interactions.

The situation is very complex and many kinetic factors come into play. What is specially needed is a method for determining which of the many kinetic factors are rate controling.

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SAŽETAK

Pojava deadhezije na granici faza organska prevlaka/metal u vodenim otopinama

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Opisano je šest osnovnih presjeka na granici faza organska prevlaka/metal u vodenim otopinama na kojima dolazi do pojava deadhezije (delaminacije, odvajanja) slojeva. Do pojave deadhezije dolazi, ovisno o uvjetima i vrsti organske prevlake i osnovnog metala, u različitim presjecima. U radu se posebno opisuje fenomenologija slijedećih presjeka: a) u metalu — zbog anodinog nagrizanja ispod oksidnog sloja; b) na graničnom sloju metal/metalni oksid — zbog stvaranja posebne oksidne faze; c) u oksidnom sloju — zbog otapanja oksida u kiselim medijima; d) u posebno obrađenom površinskom sloju — u slučaju fosfatiziranih slojeva, zbog njihova otapanja; e) na granici faza organski sloj/površinski oksid — zbog slabljenja molekularnih adhezijskih sila utjecajem vodenih molekula; f) u samomu organskom sloju — zbog kemijske reakcija organske baze s komponentama otopine. Za pretkazivanje zaštitnih, antikorozivnih svojstava graničnog sloja potrebno je poznavanje mehanizama adhezije raznorodnih vrsta. U radu se upućuje na tematiku istraživanja koja bi bila u stanju razjasniti neke fenomene. Posebno se spominju tehnike elipso-

metrije, Mössbauerove spektroskopije, optičke refleksne spektroskopije te mjerenja difuzije molekula vode kroz granični sloj. Za proučavanje utjecaja molekula vode od značenja su elektrokemijske metode, kao npr. mjerenje napetosti za dielektričko probijanje. Autor je razvio i kulometrijsku metodu u katodnoj polarizaciji, i pokazao da je za određivanje postojanosti sloja važan mehanizam stvaranja područja visokog pH u zoni početne delaminacije.

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