MATERIALS STUDIES FOR PREVENTING CORROSION IN CONDENSING ENVIRONMENTS

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By

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16. Abstract (Limit: 200 words) This R&D effort is being focused to provide information regarding corrosion resistance, heat transfer, material cost, fabrication method and cost; and product reliability since all are important in the final design and production of a heat exchanger. Results to date indicate that organic and inorganic-type polymer coating systems applied to low cost metals such as mild steel and aluminum provide good corrosion protection. The thermal stability of these polymers plus the identification of the interfacial requirements needed to utilize them with reactive filler materials should also make their use as bulk composites feasible.				
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RESEARCH SUMMARY

Title	Material Studies for Preventing Corrosion in Condensing Environments
Contractor	Associated Universities, Inc. Brookhaven National Laboratory GRI Contract No. 5090-260-1948
Principal Investigator	L.E. Kukacka
Report Period	October 1990-September 1991 Annual Report
Objective	Determination of the fundamental interfacial requirements for low-cost, organic and inorganic materials resistive to corrosion in condensing furnace exhausts.
Technical Perspective	The 1987 National Appliance Energy Conservation Act requires that new gas furnaces exceed 78% efficiency by 1992. Reductions in the initial cost of more efficient gas furnaces may help to maintain their competitiveness. Corrosion can occur in high efficiency furnace systems due to wet/dry cycles that concentrate aqueous chloride on the surface of heat exchangers, vents, and flue linings. As a result, expensive, difficult to fabricate, AL 29-4C stainless steel is currently used to prevent corrosion in secondary heat exchangers. Costs below \$2-3/ft ² (18 gauge material) for easily fabricable materials would reduce the cost of finned tube condensing heat exchangers by ~50%. This research is investigating organic and inorganic approaches to reducing the cost and improving the lifetime of these components.
Results	<p>Polymer coatings on heat exchangers and other types of chemical process equipment are used commercially on a routine basis, thereby suggesting that their use can be cost effective. Polyphethylene sulfide (PPS) and other types of polyaryl-type polymers such as polyphenylethersulfone (PES) and polyphenyletheretherketone (PEEK) were selected for study in this program due to their high melting points (>295°C) and acid resistance. All have common chemical features consisting of aromatic backbone chains coupled with oxygen, ketones, and/or sulphur. They are commercially available and can be applied as coatings using standard spray, dip and fluidized bed processes. When the polymers are mixed with fillers, extrudable composite tubing can be produced.</p> <p>Screening test performed at Battelle Columbus indicated that BNL-supplied specimens consisting of a PPS topcoat dip applied to a carbon steel substrate containing a polyelectrolyte [p(AA)]-modified zinc phosphate (Zn·Ph) conversion coating, had excellent durability in condensing flue gas environments. The durability displayed was equal or better</p>

than that obtained from a commercially supplied two layer PPS coating applied to Al using a fluidized bed technique. All other materials tested failed. Therefore, initial work at BNL was focused on the PPS system. Studies on PPS/Al and polyzirconosiloxane (PZS)/Al systems were also initiated.

The results from the first years work indicate that the utilization of a <5 micron thickness of the BNL-developed Zn.Ph as a chemically resistant coupling material between PPS and mild steel, produces a well bonded durable coating system. The PPS/Zn.Ph interaction also provides reaction phases at the PPS/metal interface which are more resistant to chemical attack, thereby providing extra protection in the event of pin holes in the coating or cracks forming due to mechanical and thermal stresses.

PPS coatings applied to Zn.Ph-modified mild steel by first dipping the substrate into a PPS-alcohol slurry and subsequently heating in air at 300° and 350°C, exhibited bond strengths ~37% greater than those for PPS/steel interfaces. This improvement is attributable to three factors: 1) gas-solid interactions between SO₂ emitted from the PPS and oxidized Fe compounds to form FeS, 2) a polymer-to-polymer reaction between PPS and the poly(acid) anhydride existing on the outer surface of the Zn.Ph, and 3) mechanical anchoring resulting from the melted PPS penetrating into the open surface microstructure of the Zn.Ph layer.

When PPS was applied to unmodified surfaces of 6061-T6 aluminum, a hydrolyzable compound Al₂(SO₄)₃ was formed at the interface. Exposure of specimens for 8 days to a 80°C pH 3 H₂SO₄ solution containing 0.1 M NaCl resulted in complete delamination of the PPS film apparently due to the formation of Al₂(OH)₄SO₄·7H₂O.

Studies in which PZS coatings were applied to aluminum commenced. These coatings were formed by hydrolysis-polycondensation-pyrolysis synthesis of acid-base catalyzed sol precursors. Preliminary data indicated that thin (~1 micron), impermeable and hydrophobic films can be produced which should provide good corrosion protection. The proportion of Si-O-Si to Si-O-Zr linkages in the film and the pH of the sol precursor are important parameters.

Technical Approach

A mechanistic approach is being used to obtain the fundamental knowledge needed to meet the research goals. Information elucidating interactions that occur between organic and inorganic polymer binders and reactive fillers in composites, and at polymer/conversion coating/metal and pre-ceramic/metal interfaces is being obtained. Decomposition mechanisms occurring upon exposure to the test environments are also determined. State-of-the-art analytical techniques being used in these studies include scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM),

X-ray photoelectron spectroscopy (XPS), X-ray powder diffraction (XRD), fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), thermal mechanical analysis (TMA), and Auger electron spectroscopy (AES).

Test variables for the coating systems include metallic substrate composition, method of surface pretreatment, coating composition, and thickness. For the composites, variables include the composition and concentration of reinforcing particles and fibers, reinforcement surface pretreatment method, and polymer binder composition. Mechanical properties such as bond, flexure, tensile, and peel strengths, and impact resistance, are being measured in accordance with the appropriate ASTM Standards.

All of the data will be used to develop models which will describe the most effective interaction mechanisms, intermediate phase assemblages, and microstructure features at the interfaces and interphases responsible for the achievement of good interfacial bonding, strength and durability.

Project
Implications

Brookhaven National Laboratory (BNL) is establishing a fundamental basis for an improved, low-cost, corrosion-resistant, condensing heat exchanger for high efficiency gas furnaces. During the first year's research, BNL significantly advanced the understanding of the interfacial chemistry of polyphenylene sulfide (PPS) coated mild steel and obtained initial results for PPS and polyzirconosiloxane (PZS) coated aluminum. In addition to determining interfacial structure, composition, and chemistry, BNL established mechanisms of degradation at the coating-substrate interface under various conditions of pH, salt concentration, and cathodic polarization. BNL developed: a zinc phosphate layer between PPS and steel to improve adhesion and minimize corrosion in the event of exposure of the interfacial region; and a dip method, which may minimize cost and enable coating of difficult geometries. Future research will study novel, thermally conductive composite materials and continue to examine PPS and PZS on aluminum surfaces. GRI plans to continue support of this research.

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I. INTRODUCTION

The 1987 National Appliance Energy Conservation Act requires that new gas furnaces exceed 78% efficiency by 1992. In order to help maintain the competitiveness of units meeting this criterion, it is essential that cost-effective materials of construction be available.

The corrosiveness of the fluids present in condensing heat exchangers for high efficiency gas furnaces is well documented.^[1,2] All traditional metals used for heat exchangers, and even some more exotic and much more expensive alloys are corroded by the acidic environments encountered. Some high temperature engineering plastics such as polyacrylsulfones, polyetherimides and polyketones exhibit good corrosion resistance to these environments, but their costs make them uneconomical for use as bulk materials^[3]. Ceramics are brittle, and exhibit similar cost constraints. Conventional chemical coupling systems needed to bond polymers to steel and aluminum substrates often undergo hydrolytic decomposition, therefore making the use of polymeric coatings for corrosion protection unreliable.

Earlier work^[4-7] at Brookhaven National Laboratory (BNL) identified several material systems which appeared to have potential for being low-cost solutions to this corrosion problem, therefore reducing the first cost increase of a condensing furnace over an induced draft noncondensing unit. The goal of one of these programs which was sponsored by the Army Research Office (ARO), was to obtain physico-chemical data needed to synthesize low cost organic crystalline and pre-ceramic-type polymer coatings which could provide corrosion protection to cold-rolled metals, clad aluminum, and magnesium upon exposure to acids, and alkali electrolytes containing high concentrations of Na^+ and Cl^- ions at temperatures up to 200°C.

The results indicated that upon exposure to concentrated Cl^- ions at 200°C, failures of conventional organic coatings applied to metallic substrates occur as a result of 1) the high segmental mobility of the molecular chains, 2) alkali catalyzed hydrolysis of polymers, 3) localized delamination caused by the cathodic half reaction $\text{H}_2\text{O} + 1/2 \text{O}_2 + 2\text{e}^- \rightarrow 2\text{OH}^-$, which occurs under the coating in conjunction with the anodic half reaction $\text{Fe} \rightarrow \text{Fe}^{++} + 2\text{e}^-$, which takes place at the defect, 4) in conjunction with failure mode 3, alkali-catalyzed degradation of the polymers at the polymer-metal interface, and 5) interfacial dissociation of the metal oxide layer resulting from the chemisorption of Cl^- ions that penetrate the organic film.^[4] Using these

results, it appeared possible to define the requirements for the molecular design of optimized protective systems which will yield hydrolytically stable coatings for use in pH 2 to 11 environments. These requirements include 1) formation of a highly cross-linked structure having low segmental mobility at 200°C, 2) elimination of functional groups in the material network in which any two atoms selected from N, O, and S are joined to the same carbon atom, and 3) formation of hydrophobic reaction products at the film-metal interface in order to inhibit cathodic reactions. It is assumed that all of the above design requirements must be attained in order to produce a protective film that will meet the requirements for high efficiency gas furnaces.

A noteworthy success in this earlier ARO-sponsored work was the development of polyelectrolyte-modified zinc phosphate (Zn·Ph) crystal conversion coatings for steel.^[5] This BNL-patented process was the recipient of a 1988 R&D 100 Award, and it has subsequently been licensed to two commercial firms. The Zn·Ph coating is prepared by immersing steel for approximately 5 to 20 min in a zinc phosphate solution containing a moderate amount of poly(acrylic acid) at approximately 80°C. A thin (1-2 micron), flexible and ductile conversion coating is formed which has excellent corrosion resistance and adhesion with polymeric topcoats. The thickness of the crystal coating can be varied by changing the immersion time.

In order to establish the technical feasibility of using the Zn·Ph technology to impart corrosion protection to condensing heat exchangers, test specimens were supplied to Battelle Columbus for evaluation in a heat exchanger that reproduced the environment present in a condensing furnace. The samples supplied by BNL consisted of 15.9 mm - o.d. mild carbon steel tubing, the outer surface of which had been modified by the application of the Zn·Ph. An ~1 mil thick PPS topcoat was then dip applied. Spin casting would be applicable for the placement of uniform dense coatings on inner tube surfaces. The results from this corrosion test series^[2] indicated that eight of the ten materials evaluated degraded in two months and were judged unsuitable for use in condensing heat exchangers. Only the BNL-supplied tubes and aluminum tubes coated with PPS by a commercial firm experienced no discernible degradation.

Pre-ceramic-type coatings consisting of polytitanosiloxane (PTS) polymers also appear to have potential for gas furnace condenser applications. These polymers are characterized by a three-dimensional network structure of

Ti-crosslinked polysiloxane. These polymers are synthesized by hydrolysis-polycondensation or hydrolysis-polycondensation-pyrolysis reaction processes starting with clear precursor sol solutions consisting of monomeric organosiloxanes, $\text{Ti}(\text{OC}_2\text{H}_5)_4$, methanol, water, and hydrochloric acid. Deposition of films is accomplished by dipping the substrate into the precursor solution and subsequent heating. Although dependent upon the species of the organosiloxane used, heating at $\geq 300^\circ\text{C}$ is generally necessary to produce a hydrophobic PTS network structure. Key variables in the production of high quality thin (0.2 - 1.0 micron) coatings are the organosiloxane to $\text{Ti}(\text{OC}_2\text{H}_5)_4$ ratio and the extent of the densification of the Si-O-Ti bonds in the PTS network.^[6]

PTS coatings applied to mild steel substrates containing the Zn·Ph conversion coating may represent another candidate protective coating system. In this case, improved bonding of the PZS to the steel may possibly be obtained and the Zn·Ph would provide additional low cost corrosion protection in the event of crack formation within the ~1 micron thick PZS layer, or the coating-metal interface becomes exposed.

Polymer-matrix composites presently under investigation for use as corrosion resistant materials in geothermal processes, may also be suitable for GRI needs.^[7] These materials exhibit a corrosion resistance to hyper-saline brine (300,000 ppm total dissolved solids) at 250°C comparable to that of Hastelloy C. The cost is only marginally greater than that of carbon steel^[8], and possibly four times less than AL-29-4C, an alloy judged acceptable for concentrated condensate.^[9] Applications as corrosion resistant coatings or as bulk materials appear technically feasible.

Research to acquire the fundamental knowledge necessary to design, synthesize and evaluate low cost composite bulk materials; and composite, Zn·Ph and pre-ceramic coating systems which will provide corrosion protection to cold-rolled steel and aluminum substrates upon exposure to harsh condensing fluids was initiated by BNL under GRI sponsorship on October 1, 1990. Attainment of these objectives will result in a comprehensive understanding of the principles governing the role of matrix to reactive additive or reinforcement interfaces and the interphases, and how they affect the mechanical and physical properties of organic and inorganic matrix composites and their ability to bond to metallic substrates.

A mechanistic approach is being used to obtain the fundamental knowledge needed to meet the research goals. Information elucidating interactions that occur between organic and inorganic polymer binders and reactive fillers in composites and at polymer/conversion coating/metal and ceramic/metal interfaces is being obtained. Decomposition mechanisms occurring upon exposure to the test environments are also being determined. Techniques being used in these studies include scanning electron microscopy (SEM) coupled with the energy dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), X-ray powder diffraction (XRD), fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), thermal mechanical analysis (TMA), and Auger electron spectroscopy (AES).

The planned 3 year program has been structured into four tasks: Task 1, Fundamental Studies; Task 2, Property Determinations; Task 3, Prototype Component Fabrication and Testing; and Task 4, Documentation. Work on Tasks 1, 2 and 4 commenced in FY 1991 and will be continued in 1992. Tasks 3 and 4 will be completed in FY 1993.

This report summarizes accomplishments in FY 1991. Fundamental data that characterize the interactions at PPS/steel, PPS/Zn·Ph/steel, PPS/Al, and polymetallosiloxane (PMS)/Al interfaces are given. Transport kinetics and decomposition mechanisms occurring upon their exposure to harsh acid environments are also discussed.

II. PROJECT OBJECTIVE

The objective of the research being performed is to acquire the fundamental knowledge necessary to design, synthesize, and evaluate low cost composite bulk materials; and composite Zn·Ph and pre-ceramic coating systems which will provide corrosion protection to cold-rolled steel and aluminum substrates upon exposure to harsh condensing fluids. Attainment of these objectives will result in a comprehensive understanding of the principles governing the role of matrix to reactive additive or reinforcement interfaces and the interphases, how they affect the mechanical and physical properties of organic and inorganic polymers and composites, and their ability to bond to metallic substrates. Such an understanding will significantly extend the science of polymer coatings and composite materials, and lead to the

production of systems with enhanced strength, toughness, durability and impermeability, as compared with those available today.

A near-term benefit of the research to the Gas Research Institute (GRI) will be the identification of low cost materials of construction for use in gas furnace condenser applications. This will reduce the first cost increase of a condensing furnace over induced draft noncondensing units, and provide basic information needed for use in solving other gas industry materials needs.

III. SPECIFIC OBJECTIVES FOR YEAR

The specific objective of the work scheduled to be performed in the first year of the three year program was to commence the accumulation of fundamental data that will lead to the development of models of the reaction product assemblages and bonding modes at matrix-reinforcement and coating-substrate interfaces. Such an understanding is essential for the design and construction of cost-effective and durable composites or coating systems for condenser applications and other gas industry needs.

IV. CURRENT YEAR WORK PLAN

Work was planned for Task 1, Fundamental Studies; Task 2, Property Determinations; and Task 4, Documentation. Descriptions of the work scheduled within each of these tasks are given below.

Task 1. Fundamental Studies

Data elucidating interactions that occur at polymer/conversion coating/metal and pre-ceramic/metal interfaces were to be obtained. Transport kinetics and decomposition mechanisms resulting from exposures to test environments were also to be determined. Test variables were to include metallic substrate composition, method of surface pretreatment and coating composition.

Task 2. Property Determinations

Based upon the results from the fundamental studies performed in Task 1, corrosion-protective systems were to be designed and test specimens fabricated for use in characterizations of their mechanical, physical and chemical properties at conditions simulating those expected in gas furnace condenser applications.

Task 4. Documentation

Quarterly progress reports and an Annual Report were to be prepared. Participation at the 1990 and 1991 Inorganic Chemistry Program Reviews was planned.

V. WORK ACCOMPLISHED

Experimental studies commenced on October 1, 1990. Earlier screening tests performed at Battelle Columbus under GRI sponsorship indicated that BNL-supplied specimens consisting of a PPS topcoat applied to a surface modified carbon steel substrate, had excellent durability in condensing flue gas environments.^[2] Therefore, our initial investigations were focused on the interactions occurring within this system. Subsequently, interactions at PPS/Al and PZS/Al interfaces were also elucidated. Each system is discussed separately below.

PPS was chosen for study in this program since high temperature hydrolytically stable acid resistant films can be produced. Also, its molecular structure $[-\text{C}_6\text{H}_4-\text{S}-]_n$ meets the criterion of not having a functional group in which two atoms of S, O, or N are attached to the same carbon atom. When heated to temperatures above the melting point of approximately 290°C, high molecular weight structures are produced through mechanisms of crosslinking and chain extension.^[10-12] It is also known that oxidized metal surfaces have a strong affinity for the chemisorption of organic polymers containing functional groups.^[13] Therefore, it was anticipated that the fusing-curing process for the PPS would also result in thermal oxidization of the metal beneath the PPS, thereby enhancing the bond. Specimens cured in oxygen-free environments would be expected to yield lower values.

A. PPS/Steel Interfaces

Experiments were conducted to determine how the reaction products formed in oxygen (O₂) and nitrogen (N₂) environments at the critical interfacial contact zone between PPS and various metals influence adhesive bonding. X-ray photoelectron spectroscopy (XPS) was used as the primary analytical tool in these experiments.

Three metal substrates; AISI 1010 cold-rolled steel (CRS), AISI 304 stainless steel (SS), and G-90 galvanized steel (G-S) were used. Prior to

application of the PPS, the metal surfaces were wiped with acetone-soaked tissues to remove any surface contamination. The "as received" PPS was a tan colored powder having a high melt flow and a melting point of 288°C. This was mixed with isopropyl alcohol at a ratio of 45 parts PPS to 55 parts isopropyl alcohol by weight to form a slurry. The metal substrates were dipped into the slurry at 25°C and then heated in either O₂ or N₂ at 300°C for 3 hr. This fused the PPS and volatilized the alcohol. The temperature was then increased to 350°C for 2 hr in order to increase the macromolecular structure and to crosslink it.

The chemical compositions and states present on the bulk PPS, cleaned surfaces of the three metallic substrates, and on the bond failure side of PPS coated substrates were determined from the peak areas and binding energies (BE) obtained from XPS analyses. A V.G. scientific ESCA 3MK II spectrometer was used. An Al K α (1486.6 eV) X-ray source operated at a constant power of 200 W was used to provide excitation radiation and the vacuum in the analyzer chamber of the instrument was 10⁻⁸ Torr. The atomic concentrations of the chemical elements were determined by comparing the XPS peak areas which were obtained from the differential cross-sections for core-level excitation.^[14] To set a scale for the high-resolution XPS spectra, the BE was calibrated with the C_{1s} of the principal hydrocarbon-type carbon peak fixed at 285.0 eV as an internal reference. A curve deconvolution technique was employed to find the respective chemical components from the high resolution spectra of each element.

Strips of the various metals were also bonded together using a 1 to 3 mil film of PPS as an adhesive. The strips were 50 mm long and 15 mm wide, and the overlapped area was 150 mm² (10 by 15 mm). Lap shear tensile strength measurements of metal-to-metal adhesives were then made in accordance with ASTM Method D-1002.

The results from lap shear bond strength measurements for metal-to-metal PPS adhesive joints are shown in Figure 1. The data clearly indicate that the presence of O₂ during the curing of the PPS enhances the bonding to SS and CRS substrates, the former yielding the highest value. The PPS/G-S system cured in air exhibited the lowest bond strength.

To clarify the reasons for the above results, XPS was used to analyze failure surfaces prepared by pulling the PPS films from the substrate surfaces by tensile stresses. Reference data were obtained by first determining the

chemical compositions and states of bulk PPS and the acetone cleaned metal surfaces. These data are given in Table 1 and Figure 2. Referring to Table 1, the S/C atomic ratio of 0.19 for the 350°C-cured bulk PPS surfaces was slightly higher than the value of 0.17 computed from the fundamental formula, $-\left[\text{---} \text{C}_6\text{H}_4 \text{---} \text{S} \text{---} \right]_n$, of PPS. The S_{2p} core-level spectrum (Figure 2) for the bulk PPS featured a symmetric curve with a peak at the BE position of 163.8 eV, originating from the S of the S-C bond in the PPS structure.^[14] CRS surfaces disclosed the presence of a large amount of oxygen, which can be associated with the formation of Fe oxides additional to those originally present on the metal. In fact, the main core line at 710.9 eV and the shake-up satellite at a high BE site about 8 eV away from the main line in the $\text{Fe}_{2p3/2}$ region are assignable to the formation of ferric oxide (Fe_2O_3).^[15] As is evident from a high carbon concentration of 58.3%, the SS surface seemed to be covered with carbon-based contaminants which could not be removed by organic solvents. Regardless of coverage with the C contaminant, the $\text{Fe}_{2p3/2}$ spectral feature verified that the underlying Fe compound was mainly Fe_2O_3 . The presence of a concentrated P atom suggested that the surface of the galvanized steel used in this study was treated by phosphate. The $\text{Zn}_{2p3/2}$ spectrum for the G-S substrates denoted the presence of a single Zn component at the BE position of 1022.1 eV. Since this BE value corresponds to Zn in a ZnO formation^[16], the dominant Zn compound formed at the outermost surface of G-S was ZnO.

The elemental compositions for failure surfaces obtained by pulling N_2 and O_2 -cured PPS films from a CRS substrate are given in Table 2. In N_2 , the interface chemistry of the PPS side from the CRS substrate was characterized by a small amount of Fe and a large amount of O compared with that of the bulk PPS (Table 1), in conjunction with 7.4% S and 42.5% C. Sulfur originating from the PPS was detected on the interfacial substrate surface. Since the Fe and O elements that remained on the PPS side were associated with the Fe_2O_3 and/or the interfacial reaction products, the locus of failure might have occurred in either the mechanically mixed layer of PPS and Fe_2O_3 , or in the reaction product layer formed by interaction between PPS and Fe_2O_3 .

Strikingly different results were obtained from the O_2 -treated samples. Much more Fe was left on the interfacial coating sides, and no S was found on the failed CRS sides. Therefore, a cohesive failure mode which occurred through the Fe_2O_3 layers close to the PPS was indicated. In terms of achieving a good bond, the introduction of O_2 into the interfacial zones seemed to

promote interactions between the PPS and Fe_2O_3 . These reaction products appear to be much stronger than those of Fe_2O_3 layers.

To support these findings, inspections of the high-resolution S_{2p} spectra for both the PPS and CRS interfacial sides of N_2 -treated samples and the PPS interface for the O_2 -samples were made (Figure 3). The asymmetric feature of the resultant S_{2p} region for the N_2 -treated PPS interface revealed two resolvable Gaussian components at 161.8 and 163.8 eV. From the surface reference spectra (see Figure 2), the shoulder peak at 163.8 eV is attributable to S in the PPS. Literature data^[17] indicate that the principal line at 161.8 eV, which represents the main chemical component, can be ascribed to the formation of ferrous sulfide (FeS) as the reaction product at the interfaces between the PPS and the Fe_2O_3 in the N_2 environment. The shoulder peak near 710.9 eV, reflecting the Fe in the FeS ^[18], was also observed in the $\text{Fe}_{2p3/2}$ region (not shown). Since the negative ion mass spectra (not shown) of the oxidized PPS surfaces indicated the presence of intense sulphur trioxide (SO_3) signals, such sulphur-related iron compounds can be formed by interfacial gas-solid reactions between the Fe_2O_3 and SO_2 and SO_3 gases emitted from PPS at high temperatures. An additional prominent line was seen at 168.5 eV. This corresponds to a shift of about 6.7 eV to the higher BE site than that of FeS on the N_2 -treated CRS interface. A shift of 6.7 eV is large enough to distinguish the presence of ferrous sulphate (FeSO_4)^[19] from FeS . FeSO_4 can be formed through the following reaction^[20]: $\text{Fe}_2\text{O}_3 + \text{SO}_3 + \text{SO}_2 \rightarrow 2\text{FeSO}_4$. In comparison with the data from the PPS side, a distinctive S_{2p} spectral feature can be seen on the O_2 -treated PPS interface. We concluded that there was no evidence for the presence of FeS at 161.8 eV, while the pronounced peak at 168.5 eV, belonging to FeSO_4 , emerged at the high BE sites. Since the introduction of an abundance of oxygen promotes the conversion of SO_2 to SO_3 ^[21], it is reasonable to rationalize that an enrichment of O_2 catalyst induced SO_3 gas caused the formation of more FeSO_4 than FeS . As a result, the formation of FeSO_4 as the interfacial reaction product appeared to be responsible for the development of strong interfacial bonds.

Table 3 shows the elemental compositions at the cross-section areas of the PPS/SS joint system. In N_2 , the PPS interface removed from the SS was characterized by the absence of Fe and the presence of a small amount of O. Compared with the SS reference surface (Table 1), the interfacial SS surface had 4.4% S, a higher C concentration, and lower O and Fe contents. The

detection of S and a higher concentration of C reflected good adhesion of PPS to the Fe_2O_3 at the outermost surface of SS. Based upon the absence of Fe at the PPS side, a cohesive failure mode, which occurred through the PPS layer adjacent to the Fe_2O_3 , can be proposed for this joint system. Of particular interest is the chemical compositions at the interfaces of the O_2 -induced PPS/SS joint: 1) the presence of S atoms in amounts similar to those observed on the PPS side, and 2) the introduction of a large amount of O into the SS side. These findings suggested that a substantial amount of interaction products containing S, O, and Fe atoms remained at the SS side, whereas there were few residual reaction products adhering to the PPS. Thus, the locus of failure appeared to occur through the reaction product layer near the PPS. Figure 4 shows the S_{2p} region for both interfacial sides after treatment in N_2 and O_2 . The S_{2p} spectrum for the PPS interface in the N_2 -treated joint system features a simple peak containing only a single line at 163.8 eV originating from S in the PPS. There is no indication of peaks at 161.8 and 168.5 eV, which reflect the formation of FeS and Fe_2O_3 , respectively. In contrast, the emergence of pronounced lines at 161.8 and 169.0 eV, while maintaining the major line at 163.8 eV, was observed from the SS interface, thereby accounting for a certain amount of reaction products remaining on the interfacial SS surface. Regarding the reaction products, the new peak at 169.0 eV, corresponding to a position 0.5 eV higher than that of FeSO_4 , was associated with the formation of ferric sulphate $[\text{Fe}_2(\text{SO}_4)_3]$ ^[22], which could be generated by the reaction of Fe_2O_3 with three moles of SO_3 on heating^[23]. These changes in spectral features occurred as O_2 was introduced into the critical interfacial zones. The particular feature of the S_{2p} signal at the SS side was an intense single peak at 169.0 eV, suggesting that only $\text{Fe}_2(\text{SO}_4)_3$ as the interaction product was left on the SS side. The weak line at 169.0 eV was also detected from the PPS interface away from the SS.

Considering that the PPS/SS joint system prepared in O_2 displayed the highest bond strength in this series of tests, we concluded that the extent of PPS adhesive bonding to metal substrates depends primarily on the species, and on the amount of S-related Fe compounds formed as interaction products at the critical interfacial contact zones between PPS and the substrate. The reaction products which play a major role in establishing the bond strength have the following order: $\text{Fe}_2(\text{SO}_4)_3 > \text{FeSO}_4 > \text{FeS}$. Thus, the O_2 -catalyzed reaction

products at the interfaces are responsible for the improvement in bond strength of PPS/metal joints.

Table 4 gives the elemental compositions for both interfacial failure sides in the PPS/G-S joint system. For the sample made in N_2 , the interfacial PPS surface had a composition closely resembling that of the G-S interface. The detection of a certain amount of P, Cr, and Zn on the PPS interface demonstrated that these elements migrate from the substrate to the coating sides during the failure of the bond. The amount of Zn detected on the G-S side was considerably greater, and the amounts of P and Cr substantially less than those observed on the reference G-S surface (see Table 1). This finding suggested that the S in PPS preferentially reacts with the Zn in the substrate, rather than with P and Cr. Hence, failure occurred through the reaction product layers formed at the interface between PPS and G-S. A similar locus of failure was observed on the O_2 -treated adhesion sample; the chemical compositions of both failure surfaces were similar. The only difference was that more P, O, Cr, and Zn remained in the cross-section, while the amounts of S and C were reduced. In particular, the increased amounts of residual Zn and O atoms reflect the formation of oxygen-rich zinc compounds at the interfaces.

To identify the interaction products, we inspected the S_{2p} region for both the interfacial PPS and G-S surfaces (Figure 5). The resultant S_{2p} signal for the N_2 -treated cross-sections had at least two resolvable peaks at 163.8 and 161.9 eV. The former, as the major component, revealed the PPS, and the latter was assigned to the formation of S-related zinc compounds as interfacial reaction products. As reported by several investigators^[15,19,23], the line emerging at a low BE site, ranging from 160.5 to 162.0 eV, commonly relates to metal sulphide compounds. Hence, zinc sulphide (ZnS), reflected by the peak at 161.9 eV, was formed by the reaction of ZnO with SO_2 and SO_3 gases at the PPS/G-S interfacial regions. Since no Fe from the underlying steel was found on either interfacial side, we believe that the adhesion of the ZnS phase, formed as a reaction product, to the zinc layer was much poorer than the adhesion of zinc to the steel substrate.

Compared to the N_2 sample, a quite different S_{2p} signal was obtained from both O_2 -induced interfacial sides. The distinct spectral features were the growth of a prominent line at the high BE position of 169.5 eV, and a considerable attenuation of peak intensity at 161.9 eV at the interfaces. It

is well known^[24] that when ZnS is exposed to air at an elevated temperature, oxidation leads to the transformation of ZnS into zinc sulphate (ZnSO_4). Assuming that such oxygen catalyzed $\text{ZnS} \rightarrow \text{ZnSO}_4$ conversion occurs at the interfaces, the strong line emerging at 169.5 eV was due to the formation of ZnSO_4 . This conversion correlates directly with the marked decay of the ZnS line at 161.9 eV. Therefore, the interfacial ZnS - ZnSO_4 phase transition appears to create detrimental boundary layers which play an active role in the catastrophic loss of bond strength of PPS/G-S joint samples prepared in an oxygen environment.

Tests were performed to determine the durability of steel/PPS adhesive bonds after exposure at 80°C to a pH 3 H_2SO_4 solution containing 0.1 M NaCl. All of the edges on the PPS/metal joints were unprotected, thereby making them more susceptible to acid attack in this extremely harsh environment. Measurements of the lap-shear bond strength were made in triplicate as a function of exposure time. These results, given in Figure 6, indicate a rapid loss of strength. Compared to an initial bond strength of 6.4 MPa, the strength decreased to 4.0 MPa after 1 day and to 0.6 MPa in 8 days. The latter corresponds to a reduction of ~90%. Visual examination of the exposed samples prior to the bond strength measurements indicated partial delamination of the PPS films from the steel.

To elucidate the failure mode of acid damaged PPS/steel interfaces, the chemical composition at the separated PPS and steel interfaces was determined using XPS. These quantitative data are given in Table 5. Comparison with the control indicated that migration of S from the PPS to the steel side and interfacial diffusion of Cl occurred upon exposure to H_2SO_4 . There was no indication of Na resulting from the formation of Na-related sulfur reaction compounds which could possibly diffuse into the interfacial boundary zones. Nevertheless, the locus of failure appeared to occur through the S-incorporated reaction product layers at the interface.

In an attempt to identify the reaction product which caused the bond failure upon acid exposure, the S_{2p} core-level spectra for both the separated PPS and the steel sides were evaluated. These results are shown in Figure 7. The S_{2p} region for both sides showed the emergence of a single peak at a BE of 169 eV. This location represents a 0.5 eV shift from the BE peak of 168.5 eV for FeSO_4 (see Figure 3a) which is formed by interaction between PPS and steel before acid exposure, and may represent the formation of ferric sulphate

[Fe₂(SO₄)₃] formed by the H₂SO₄-catalyzed oxidation of FeSO₄.^[17] Thus, the cause for the bond failure upon exposure to the hot acid solution was the interfacial FeSO₄-Fe₂(SO₄)₃ phase transition.

Unmodified steel substrates containing PPS films were cathodically tested for periods of up to 8 days in an air-covered 1M NaCl solution at 20°C. A very high applied potential of -1.5 volts vs. SCE was used in an attempt to accelerate any deterioration process. This equipment is shown schematically in Figure 8. A defect in the PPS coating was made using a 1 mm-diameter drill bit. After exposure, the specimens were removed from the cell and allowed to dry. The PPS coating was then removed by cutting, revealing a delaminated region which appeared as a light gray area adjacent to the defect. After exposure for 1 day, $\sim 1.3 \times 10^3$ mm² of PPS was delaminated from the original sample area of 10⁴ mm². This progressed to $\sim 6 \times 10^3$ mm² after 8 days.

In an attempt to gain information regarding the reason for the rapid delamination rate, XPS was used to study both sides of the failed interfaces. For use as unexposed controls, PPS films were pulled from steel substrate surfaces by application of tensile forces. Test data from these studies are given in Table 6. For the controls, the interface at the PPS side removed from the steel substrate consisted of 3.5% S, 42.1% C, 44.0% O, and 10.4% Fe. The S element refers to S originating from the PPS while C came from the PPS and contaminants. As mentioned earlier, the Fe and O elements remaining on the PPS side are associated with the interfacial reaction products formed by interaction between the PPS coating and Fe₂O₃ existing on the steel surfaces. Sulfur was not found on the failed steel side. Thus, it appeared that the locus of failure occurred through the reaction product layers close to the PPS.

The cathodically delaminated samples produced markedly different results. These differences are as follows: 1) a large amount of Fe and O was removed from the interfacial PPS sides, while the concentrations of S and C were markedly increased, 2) a small amount of S remained on the steel sides, and 3) a certain amount of Na from the NaCl electrolyte was detected on both the delaminated PPS and steel sides. There was no evidence for the presence of Cl atoms. The first two results show that the cathodic reaction, $\text{H}_2\text{O} + 1/2\text{O}_2 + 2\text{e}^- \rightarrow 2\text{OH}^-$, occurring at the defect in the PPS film, lead to the elimination of Fe-related reaction products. Since the ionic reaction between the OH⁻ ions generated by the cathodic reaction and the Na⁺ ions dissociated

from the NaCl electrolyte yields a high concentration of NaOH in the area of the defect^[24], it is reasonable to assume that the creation of such an alkali environment at the interfacial regions caused NaOH-catalyzed hydrolysis of the interfacial reaction products. Thus, the detection of Na atoms at the delaminated interfaces could be due to the penetration of the NaOH solution through the interfacial layers.

To support this hypothesis, inspections of the high-resolution S_{2p} core-level spectra of the PPS and steel interfacial sides of specimens were made before and after cathodic tests (see Figure 9). The S_{2p} region for the PPS interface of the control samples revealed two major components at 163.8 and 168.5 eV. The former is representative of the principal component, S, from the PPS, while the latter reflects the S in the ferrous sulphate ($FeSO_4$) formed by the interfacial gas-solid reaction between Fe_2O_3 and SO_2 and SO_3 gases emitted from PPS in air at high temperature. Compared to the control, a marked attenuation of peak intensity at 168.5 eV originating from the Fe in the $FeSO_4$ reaction product can be observed on spectrum (b) of the cathodically delaminated PPS side. In spectrum (c), which depicts the delaminated steel side, the presence of the weak line at 168.5 eV verified that a small amount of intermediate $FeSO_4$ adhering to the steel remained at the interfacial steel side. There was no peak at 163.8 eV which would correspond to PPS. Therefore, the major reason for the extreme cathodic delamination at PPS/steel interfaces appeared to be the NaOH-catalyzed hydrolysis of $FeSO_4$ adjacent to the steel surfaces.

B. PPS/Zn·Ph/Steel Interfaces

Studies identical to those described above were conducted using Zn·Ph-modified steel substrates. The conversion solution used to treat the metal consisted of 1.3 wt% zinc orthophosphate dihydrate [$Zn_3(PO_4)_2 \cdot 2H_2O$], 2.6 wt% H_3PO_4 , 2.0 wt% 25% poly(acrylic)acid, [p(AA)], 1.0 wt% $Ni(NO_3)_2 \cdot 6H_2O$, and 93.1 wt% water. The average molecular weight of the p(AA) polyelectrolyte, supplied by the Rohm and Haas Company, was ~60,000. Prior to use, the steel was wiped with acetone-soaked tissues to remove surface contamination from mill oil.

Conventional zinc phosphate conversion processes generally produce a porous iron phosphate phase which provides little resistance to chemical attack. In contrast, the BNL-developed process yields a dense crystalline zinc

orthophosphate coating which is flexible, ductile, chemical resistant, and chemically bonds to polymeric topcoats.

Application of the Zn·Ph conversion coatings was performed by first immersing the steel in the conversion solution at 80°C for up to 20 min. The specimens were then heated in an oven at 350°C for 2 hr to form an anhydrous Zn·Ph layer. The PPS coating was then applied using the procedures described previously. Since earlier ARO sponsored work at BNL had shown that an anhydrous α - $\text{Zn}_3(\text{PO}_4)_2$ phase derived from thermal dehydration of a Zn·Ph hydrate phase had low susceptibility to alkali-catalyzed dissolution^[25], initial work was to verify the formation of this phase on the test specimens. For analysis purposes, Zn·Ph crystal layers were scraped from the steel surfaces before and after heating in air at 350°C. The crystals were then ground to a size of 325 mesh (0.044 mm) and analyzed by X-ray powder diffraction (XRD).

Figure 10 illustrates XRD tracings for the original Zn·Ph, denoted as sample (a), and the anhydrous Zn·Ph (sample b) prepared by heating the original sample at 350°C. Two hydrous crystal phases were distinguishable in the original Zn·Ph layers; namely, zinc orthophosphate dihydrate [$\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$] present as the major component and hopeite [$\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$] as the minor one. The predominating phase of the anhydrous samples was identical to α - $\text{Zn}_3(\text{PO}_4)_2$, and γ - $\text{Zn}_3(\text{PO}_4)_2$ was present as a secondary phase. This result was in agreement with that obtained in an earlier investigation^[25]; that is, $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ is converted into a α - $\text{Zn}_3(\text{PO}_4)_2$ phase during hydration, and the $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O} \rightarrow \gamma$ - $\text{Zn}_3(\text{PO}_4)_2$ phase transition is favored. Based upon this verification, good durability of the PPS/Zn·Ph/steel system in acid and alkali environments was expected.

Durability tests in which the PPS/Zn·Ph/steel system was exposed to a 80°C pH 3 H_2SO_4 solution containing 0.1 M NaCl for periods of up to 8 days were performed. These initial results, summarized in Figure 6, indicated a gradual reduction in bond strength during the first 4 days of exposure. Beyond this time to 8 days, there was little change. Compared to the data for PPS/steel surfaces, also shown in Figure 6, a significant improvement in durability with the PPS/Zn·Ph system is apparent. Since the edges of both sets of test specimens were uncoated, the acid solution had direct access to the PPS/metal interface. Thus, the improved durability exhibited by the PPS/Zn·Ph/steel system can be attributed to the added chemical protection

provided by the Zn·Ph. This will be important if pinholes or cracks in the coating occur.

The results from cathodic delamination tests performed on PPS/Zn·Ph specimens are summarized in Figure 11. The method for performing this test was described previously. Also shown in the Figure are results from previously reported tests for PPS/steel samples. The PPS/Zn·Ph system exhibited a delamination area of $\sim 40 \text{ mm}^2$ after exposure for 8 days, a value ~ 150 times lower than the PPS/steel control.

In an attempt to gain information regarding the failure modes, XPS analyses were performed on both interfacial sides of the PPS/Zn·Ph joint systems before and after the cathodic test. These data are given in Table 7. Similar data for the PPS/steel interface were given in Table 6. For the unexposed samples, the interfacial PPS surface had a composition closely resembling that of the Zn·Ph interface except that S was not present on the latter. The detection of P, Fe, and Zn on the PPS interface indicated that these elements which originated in the Zn·Ph covered steel substrate, adhered to the PPS during bond failure. Therefore, failure must have occurred through the Zn·Ph layer and not at the PPS/Zn·Ph interface.

A dramatic change in composition was apparent on both interfacial sides after cathodic delamination. As seen in Table 7, significant reductions in F, O, Fe, and Zn occurred, and Na was detected. The removal of P and Zn may have been due to the dissolution of Zn·Ph layers caused by the attack of the alkali solution generated by the oxygen reduction reaction at the site of the defect. Since the evolved OH^- ions ionically react with Na^+ dissociated from NaCl, the incorporation of Na relates directly to the penetration of NaOH yielded by this charge balance into the failure zones. Such alkali dissolution of the Zn·Ph layers was reflected by an increase in concentration of S and C atoms in the PPS. But an important question still remained to be answered. Why was the rate of elimination of Fe-related compounds considerably higher than that of the Zn·Ph? To answer this question, we inspected the high-resolution P_{2p} , $\text{Zn}_{2p_{3/2}}$, $\text{Fe}_{2p_{3/2}}$, and S_{2p} spectra of the cathodically delaminated PPS side and the PPS failure surface that was made by pulling the PPS film from the Zn·Ph before the cathodic tests. Figure 12 illustrates the resultant P_{2p} and $\text{Zn}_{2p_{3/2}}$ regions of these samples. The control sample (before cathodic test) denoted as d, had a main line at 134.2 eV for the P_{2p} and at 1023.3 eV for the $\text{Zn}_{2p_{3/2}}$

spectra. These reflect the P and Zn atoms in Zn·Ph^[5]. Peak features and intensities similar to those of the control were observed for both the P_{2p} and the Zn_{2p3/2} regions of the sample (e) after the cathodic tests. In the Fe_{2p3/2} region (Figure 13), the control sample (d) displayed a strong signal at the BE position of 710.7 eV. This corresponds to the formation of Fe₂O₃^[15]. Since an electrochemical reaction between the steel and Zn·Ph solution at an early stage of Zn·Ph precipitation leads to the liberation of free Fe ions from the steel surface^[26], it was not surprising that Fe₂O₃ was formed by the oxidation of free Fe present in the Zn·Ph layers during the Zn₃(PO₄)₂·2H₂O - α-Zn₃(PO₄)₂ phase conversion in air at 350°C before the PPS coating was deposited. In fact, we observed color changes in the Zn·Ph coatings which ranged from a dark gray at 100°C to a light brown at 350°C. A striking decrease in the Fe_{2p3/2} signal intensity was observed from the cathodically delaminated PPS interface (e) (the reason will be discussed later). The S_{2p} region for the control (d) (see Figure 13) revealed two resolvable components at 163.7 and 162.1 eV. The former peak is attributable to the S in the PPS, and the latter belongs to the S in the FeS^[17]. This information seemed to suggest that the SO₂ gas emitted from the PPS in the vicinity of the Zn·Ph layer preferentially reacted with Fe₂O₃ in the Zn·Ph layers, rather than with the α- and γ-Zn₃(PO₄)₂ phases. To confirm this, anhydrous Zn·Ph coatings were exposed in SO₂ gas at 350°C (flow rate ≈ 200 cc/min) for up to 120 min. The chemical compositions of the exposed coating surfaces were investigated by XPS, and then the internally generated P_{2p}, S_{2p}, Fe_{2p}, and Zn_{2p3/2} peak areas were used to calculate the atomic percent ratios. Figure 14 shows the variation in P/Zn, S/Zn, and Fe/Zn ratios as a function of exposure time. The data indicate that the S/Zn ratio increased with exposure time and the Fe/Zn ratio decreased. In contrast, the P/Zn ratio remained relatively constant. Thus, these data strongly support the idea that SO₂ was taken up by the Fe₂O₃ present in the Zn·Ph layers.

Returning to the S_{2p} spectrum in Figure 13, significant changes in spectral features occurred as the cathodic reaction was initiated at the defect. In particular, the S_{2p} signal at the cathodically delaminated PPS side (e) was characterized by the appearance of new peaks at 161.4, 166.3, and 170.0 eV. The first was the most intense. Considering that there was so little residual Fe atom at the delaminated PPS side, these new lines did not reflect the formation of Fe-related sulfur compounds. However, since a large amount of Na remained on the delaminated PPS interface, these lines possibly could be

assigned to Na-related sulfur compounds derived from the cathodic reaction. Assuming that these predicted assignments are correct, other authors^[19] have suggested that the predominate line at 161.4 eV is due to the S in sodium sulphide (Na_2S) as the major by-product of the cathodic reaction. The other lines at 166.3 and 170.0 eV were ascribed to sodium sulphite (Na_2SO_3) and sulphate (Na_2SO_4), respectively.

The striking reduction in the $\text{Fe}_{2p_{3/2}}$ signal (see Figure 13-e) for the cathodically delaminated PPS side was interpreted as follows; the Fe_2O_3 in the Zn·Ph layer reacted with PPS to form FeS, one of several S-related iron reaction compounds. However, it was very difficult to distinguish the photoelectron line of FeS from the Fe_2O_3 line in the $\text{Fe}_{2p_{3/2}}$ region, because the signal originating from Fe in FeS was at a BE position only -0.3 eV lower than that of Fe_2O_3 . Nevertheless, the decreased $\text{Fe}_{2p_{3/2}}$ signal indicated the loss of a great deal of FeS caused by NaOH-catalyzed hydrolysis.

The morphology and elemental distribution on the cathodically failed Zn·Ph side was investigated using SEM and EDX (Figure 15). As seen in the bottom left photograph, SEM topography reveals the existence of two distinctive areas; site A represents an area approximately 1000 μm in diameter surrounding the defect, while the other, site B, is at the edge of the delaminated PPS. The C area in the top photograph, which is an enlargement of site A, discloses the presence of the PPS adhering locally to the substrate. As is evident from the EDX elemental data from this region, a small part of the PPS film that remained on the substrate contained not only S, but also other elements such as Na, Fe, and Zn. The EDX spectrum of area D in the same photograph, indicates the presence of only Fe, and relates to the steel substrate. These findings strongly suggest that almost all of the crystalline conversion coating surrounding the defect was dissolved in the NaOH solution resulting from the cathodic reaction occurring beneath the PPS film. The right-bottom SEM microstructure (an enlargement of site B) is an image of the morphology of a normal Zn·Ph crystal coating, which had not been attacked by NaOH.

A certain amount of the p(AA) polyelectrolyte that was included in the zinc phosphate conversion coating solution is present at the outermost surface sites of the Zn·Ph layers^[27]. Therefore, it was important to determine if interactions between p(AA) and PPS occurred. In an attempt to obtain this information, samples were prepared in the following way. First, steel strips

were dipped for 5 min into a 1.0% p(AA) aqueous solution. The steel was dried in an oven at 350°C for 1 hr to transform the p(AA) macromolecule from the poly(acid), having COOH pendent groups, to the poly(acid)anhydride having and COOH groups^[28]. A PPS slurry was then deposited on the poly(acid)anhydride macromolecule film surfaces, followed by curing in air at 350°C. Finally, the PPS site removed from the poly(acid)anhydride-primed steel was inspected by XPS. Figure 16 shows the XPS spectra for the C_{1s} region of the bulk PPS film (f) and for the interfacial PPS site (g). For the bulk PPS, the single peak at 285.0 eV revealed the aromatic hydrocarbon in PPS. In comparison with the symmetry of the curve for bulk PPS, the curve for samples from the interfacial PPS site had an asymmetric tailing toward the higher BE side. This tail, which separates from the primary peak of aromatic hydrocarbon at 285.0 eV, contained at least two resolvable peaks. Based upon published data^[29], the lines at 288.1 and 289.3 eV represent the carbon in the carboxyl (C=O) group and the carboxylic acid (COOH) group, respectively, thereby suggesting that bond failure occurred through mixed layers of PPS and poly(acid)anhydride. Although there was no evidence about the interfacial bond structure and the chemical or physical interactions, it appears that the poly(acid)anhydride macromolecule had a strong affinity for PPS.

The rough surface structure of crystalline Zn·Ph is another factor which contributes to the mechanical anchoring of the PPS polymer. This results from penetration of the melted polymer into the open surface microstructure and microfissures in the Zn·Ph layers. Consequently, the combination of chemical and physical bonds plays a major role in yielding good adhesion at PPS-to-Zn·Ph joints.

Larger-scale durability testing of PPS/Zn·Ph/steel systems was started. For use in these tests, the outside surfaces of 12-mm-diam by 20-cm-long tubing were treated with the PPS/Zn·Ph process. The specimens are being exposed in an autoclave to HCl-acidified steam (pH~2) at a temperature of 200°C. Weight, dimension, and surface appearance changes are being monitored. To date, after exposure for 2 months, no changes in the diameter and weight of the specimens have been detected, and the surface appearance is unchanged from that of the controls. These tests are continuing.

C. PPS/Al Interfaces

Studies of the interactions at PPS/Al interfaces were also performed. A 6061-T6 Al sheet which had the following composition was used in these experiments: 96.3 wt% Al, 0.6 wt% Si, 0.7 wt% Fe, 0.03 wt% Cu, 0.2 wt% Mn, 1.0 wt% Mg, 0.2 wt% Cr, 0.3 wt% Zn, 0.2 wt% Ti, and 0.2 wt% other. The PPS films was applied by dipping the Al sheet into a slurry consisting of 45 wt% PPS and 55 wt% isopropyl alcohol at 25°C. The slurry-coated substrates were then heated in air at 350°C for 2 hr.

Initial analytical studies focused on identification of the interaction products at the interface. The results from XPS analysis of the S_{2p} core level spectra indicated the presence of aluminum sulfate ($Al_2(SO_4)_3$), a hydrolyzable compound. This was verified when samples were exposed for 8 days to a 80°C pH 3 H_2SO_4 solution containing 0.1 M NaCl. In these tests the bond line between the PPS and Al was directly exposed to the acid environment. Complete separation of the PPS film from the substrate occurred due to the formation of $Al_2(OH)_4SO_4 \cdot 7H_2O$, a reaction product yielded by the hydration of $Al_2(SO_4)_3$.

At first, it would appear that the above results are in contradiction with those obtained earlier at Battelle Columbus. In their tests, Al tubes electrostatically coated with PPS by a commercial firm exhibited good durability when exposed to a condensing flue gas environment.^[2] This result verifies the acid resistance of the PPS. Since in the BNL tests, the PPS/Al interface was intentionally exposed to hot acid, thereby simulating a pinhole or a joint, susceptibility of the interface to attack was demonstrated. Since pinholes or cracks in coatings often occur, these results indicate the necessity of surface modification and tailoring of the PPS to avoid direct contact of PPS with Al. These studies will commence next year.

D. PZS/Al Interfaces

Another approach being considered for providing corrosion protection to aluminum and steel substrates is the use of inorganic polymetallosiloxane (PMS) films^[30,31]. These films are produced by the pyrolysis of sol precursor-induced organopolymetallosiloxane xerogels. The chemical components of the precursor solutions consist of monomeric organosilanes, metal alkoxides [$M(OC_3H_7)_4$ where M is Zr, Ti, Ge], methanol, water, and hydrochloric acid.

Studies were started to investigate the characteristics of polyzirconosiloxane (PZS) coating films derived from two-step, acid-base-catalyzed pre-

cursors consisting of N-[3-(triethoxysilyl)propyl]-4,5-dihydroimidazole (TSPI), $\text{Zr}(\text{OC}_3\text{H}_7)_4$, methanol, and water, over a broad pH range of 1.0 to 13.0. To understand the characteristics of the sol precursors and sol-derived coating films, the work was focused on the electrostatic properties of colloidal states as a function of pH, on thermal behavior (changes in molecular structure at temperatures up to 300°C), microstructural images, elemental compositions, water wettability of the xerogel, and on pyrolyzed xerogel films. These data will then be correlated with the effectiveness of the PZS films to provide corrosion protection to aluminum.

N-[3-(triethoxysilyl)propyl]-4,5-dihydroimidazole (TSPI), and zirconium (IV)-isopropoxide [$\text{Zr}(\text{OC}_3\text{H}_7)_4$] were used as network-forming monomeric materials. A film-forming mother-liquor, which served as the precursor solution, was prepared by incorporating a TSPI- $\text{Zr}(\text{OC}_3\text{H}_7)_4$ mixture into a methyl alcohol/water mixture containing HCl as a hydrolysis accelerator. HCl-catalyzed hydrolysis of the alkoxy groups in the TSPI and $\text{Zr}(\text{OC}_3\text{H}_7)_4$ provided a clear colloidal precursor solution. To increase the pH of the acid solution, NaOH was added to the mother-liquors as a condensation promoter. Table 8 shows the compositions of the precursor solutions prepared using the two-step acid-base-catalyzed method, as a function of pH.

The Al was then coated with PZS xerogels using the following sequence. First, the metal surface was wiped with acetone-soaked tissues to remove any gross surface contaminants. The substrate was then dipped into the colloidal precursor solution at ambient temperature. After dipping, the substrate was withdrawn slowly from the soaking bath, and then preheated in an oven for 30 min at 100°C to yield a xerogel coating film. The film was subsequently pyrolyzed for 30 min in air at temperatures of 250°-300°C.

The stability of the sol precursor solutions was determined using a Micrometrics Zeta Potential Analyzer. Important physico-chemical factors for the original xerogel and pyrolyzed xerogel films such as thermal decomposition, microstructure, elemental components, and chemical conformation and profiles, were obtained using TGA, DTA, IR, XRD, SEM, EDX and AES. The wettability by water of the film surfaces formed at temperatures up to 300°C was determined by measuring the contact angles. Electrochemical corrosion tests were also conducted.

As the initial phase of this work, studies were performed to determine the best conditions for producing the sol precursor solutions. Measurements

of the Zeta potential (z-p) (the electric potential at the boundary between the particle surface, charged by electrochemical adsorption of atmospheric ions, and the surrounding electrolyte medium) were used in these determinations. Figure 17 shows the effect of pH on the z-p values for the precursor solutions. It was known from earlier BNL studies^[30] that the addition of HCl to the solution promotes the hydrolysis of both the monomeric TSPI and $\text{Zr}(\text{OC}_3\text{H}_7)_4$; then, the monomeric species containing hydroxyl groups is produced. Such a hydrolysis-induced monomeric species is slowly converted into a polymeric cluster by alcohol- or water-producing condensation reactions between the hydrolysates. The particle size of these clusters in an aqueous solution may range from ≈ 1 to ≈ 20 nm.

Referring to Figure 17, at pH 1.1 the protons, H^+ , in the solution attack the negative hydroxyl groups on the cluster particles. Consequently, the overall net effective charge on the polydispersities measured +25.7 mV. When NaOH was incorporated into this acid precursor solution, the presence of OH^- led to a charge reversal. As shown, the z-p value decreased with increased pH of the solutions. The isoelectric point (IEP), where there is no net charge (zero mV of z-p) on the particle surfaces, occurred around pH 9.5. With further increase in pH, the z-p charge became negative. Beyond a pH of 11.5, the surface charge shifts to near zero potential in the negative regions.

To better understand these data, the microstructure of xerogel films deposited on the Al substrates was observed with SEM. The films were prepared in a vacuum oven at 70°C. The surface images of films from sols with pHs ranging from 1.1 to 11.5, are shown in Figures 18 and 19. The SEM micrograph (Figure, 18a) of the pH 1.1 sol-derived xerogel displays the continuous features of a smooth transparent film. This suggests that inter-cluster crosslinking leads to the formation of transparent xerogels. As seen in Figure 18b, an increase in the pH from 1.1 to 2.6 resulted in a change in morphology. Two different cluster species, a randomly distributed branch-type polymer, and a transparent-type polymer, are apparent. With a sol of pH 8.6, which is near the IEP, the microtexture of the film (Figure 19c) disclosed a compacted version of highly branched clusters which completely covered the Al substrate. There were no transparent-type clusters present. This change implies that, under basic conditions, the condensation reaction is much faster, and quickly consumes newly generated monomeric species. Such

progression of condensation on the peripheral sites of growing branches leads to the formation of strong interclusters, in terms of the fractal polymeric clusters. Thus, use of a combination of acid and base catalysts promotes decoupling between hydrolysis and condensation. However, the incorporation of an excessive amount of NaOH which gives a very high rate of condensation, resulted in the formation of an entirely different xerogel. At pH 11.5, the SEM image (Figure 19d) showed that the film had a large number of microcracks. We believe that highly progressive condensation leads to bond breakage and reformation of the primary building polymer conformation caused by the deprotonation of hydroxylated cluster species. These results verified that the chemical nature of the sol strongly depends on the pH of the solution. A stable sol, with a substantially larger polymeric cluster, can be prepared in near zero z-p regions on the positive side.

Before surveying the properties of pyrolyzed PZS films deposited on Al substrates, we investigated the thermal behavior of Zr-incorporated organosilanes derived from sols with different pHs, using TGA-DTA. Figure 20 illustrates TGA and DTA curves which reveal the decomposition characteristics during pyrolysis of samples of 150°C-preheated xerogel powders. All of these samples displayed a slight weight loss in the initial temperature range of 30° to 100°C. This weight loss, which is associated with the endothermic peak at 70°C, may reflect the liberation of moisture chemisorbed onto the dried xerogels. The curves indicated that the amount of moisture liberated decreased with increasing pH of the sol. This suggests that the highly condensed xerogels formed by adding a NaOH catalyst are not susceptible to moisture attack. The TGA curve for the sol-derived xerogel samples at pH 1.1 indicated that there are three decomposition states; the first begins at the onset temperature (T_{d1}) near 250°C, the second occurs between $\approx 380^\circ$ and $\approx 470^\circ$ C, and the third from $\approx 500^\circ$ to $\approx 610^\circ$ C. The first and second decompositions, reflecting the DTA endothermic peaks at 320° and 420°C, respectively, are due to the removal of hydrocarbon species from the xerogels. The third, corresponding to the DTA peak at 550°C, may be caused by the elimination of excess carbon species. Beyond the pyrolyzing temperatures of $\approx 610^\circ$ C, there was little weight loss with temperature. Compared to the TGA curve for the pH 1.1 sample, the curves for the NaOH-incorporated samples change shape. There are three notable differences: 1) an increase in the pH of the sol lowers the onset of thermal decomposition temperature in the third stage, 2) the

intensity of the DTA peak at 420°C, corresponding to the second decomposition, decreases significantly, and 3) the total weight loss of samples at 610°C decreases with increasing pH. These findings imply that NaOH-catalyzed condensation plays an important role in forming xerogels that contain low concentrations of removable carbonaceous groups and moisture, and in promoting the conversion of organic-inorganic mixed phases into an inorganic phase at a relatively low temperature.

The above information was considered when xerogel films were deposited on Al substrates. Films dried at 100°C had a thickness as measured with a surface profile system, that ranged from 0.6 to 1.2 μm . The pyrolytic changes and rearrangement in conformation of 100°C-sintered film samples at 300°C were investigated with specular reflectance IR. Figure 21 shows the IR absorption spectra over the wavenumber region of 1350 to 700 cm^{-1} for such films from sols with pHs up to 12.8. The spectrum of the pH 1.1 film (a) had six pronounced bands. As described previously^[30], HCl-catalyzed hydrolysis of TSPI promotes the cleavage of the N-CH₂ linkage. Breakage of this bond then leads to the formation of the imidazoline derivative and organosilanol compounds containing Cl-substituted end groups. Thus, the band at 1300 cm^{-1} is due to the Zr-O-C linkages formed by the dehydrochlorinating reaction between the Cl-substituted end groups in the organosilanol and the hydroxy groups in the hydrated Zr compounds. In an IR study of alkali silicate glass, several investigators^[32-34] reported that the band near 940 cm^{-1} reveals the stretching vibration of Si-O in the Si-O⁻ M⁺ (M: alkali metals) groups containing non-bridging oxygens. Therefore, the peak at 930 cm^{-1} may be due to the non-bridging Si-O stretching mode in the Si-O⁻ Zr⁺ = groups. The other four bands are assigned to the following absorbing species: the Si-C band stretching in the Si-joined propyl groups at 1190 cm^{-1} ^[35], the Si-O-C stretching in the Si-ethoxide at 1100 cm^{-1} ^[36], and the asymmetric and symmetric stretchings of Si-O-Si linkages at 1030 and 770 cm^{-1} , respectively^[37,38]. The Si-O-Si linkages reflect the formation of polymeric organosiloxane, induced by dehydrating-polycondensation reactions between the neighboring silanol functions. As reported by some investigators^[39-41], the dehydrating condensation reactions between the hydrous zirconias (Zr-OH) containing non-bridging hydroxo groups allow the formation of Zr-O-Zr linkages. The absorption band pertinent to this linkage occurs at 710 cm^{-1} . However, no such Zr-O-Zr band was found in this spectrum.

When NaOH was added to the acid-catalyzed sol at 10.4% by weight of total amount of TSPI and $\text{Zr}(\text{OC}_3\text{H}_7)_4$, striking changes occurred in the spectral features. These are shown in Figure 21-b. Compared with the spectrum at pH 1.1: 1) there was a decrease in the intensities at 1300, 1190, 1100, and 770 cm^{-1} , and 2) there was a shift in the Si-O-Si absorption band at 1030 cm^{-1} and the Si-O⁻ Zr⁺ = band at 930 cm^{-1} to 1010 cm^{-1} and 960 cm^{-1} , respectively. Referring to the first change, a further decrease in the intensity of these frequencies was observed as the pH of the sol was increased. The disappearance of Zr-O-C groups at 1300 cm^{-1} can be seen in the spectra (d and e) of films made at pH 11.5 and 12.8. Since the bands around 970 cm^{-1} are attributable to the vibrational mode involving the oxygen-bridging Si-O-metal linkages^[42,43], we believe that the shift in the band to 960 cm^{-1} (the second result), reveals the conversion of the nonbridging Si-O⁻ Zr⁺ groups into bridged Si-O-Zr linkages. The spectrum (c) for the pH 8.6 film showed that the Si-O-Zr band at 960 cm^{-1} shifts further to high frequency sites. Special attention was paid to the changes in intensity of the shifted Si-O-Si and Si-O-Zr bands as a function of the pH value of the sol. Namely, the Si-O-Zr band becomes stronger than that of Si-O-Si, while the intensity of both bands grows markedly with increasing pH.

These IR results strongly suggest that the highly progressive condensation of Zr-incorporated organosilane, brought about by adding a large amount of NaOH catalyst, not only preferentially promotes the formation of Si-O-Zr linkages rather than Si-O-Si linkages in the organopolyzirconosiloxane structures, but also leads to the formation of 100°C-volatilizabile by-products such as alcohol and water. The latter is reflected directly in the TGA-DTA data; the weight loss of 150°C-treated high pH xerogels is much lower than that of low pH xerogels.

Figure 22 shows the IR spectral features of 300°C-pyrolyzed xerogel films. The spectral structures of the pH 1.1 film (a), differ from those of the 100°C-preheated sample in the following ways: 1) the elimination of the peaks at frequencies of 1300 and 1190 cm^{-1} which originate from the Zr-O-C and Si-C bands, respectively, 2) a shift in the absorption of the Si-O-C band, while its peak intensity becomes much weaker, and 3) a shift in the Si-O⁻ Zr⁺ = band from 930 to 970 cm^{-1} . The first two results are indicative of the removal of many carbonaceous groups from the polymeric organozirconosiloxane network. Such pyrolytic phenomena will lead to the third result, namely, the

conversion of non-bridging Si-O⁻ to bridging Si-O-Zr from the PZS network structure at 300°C. For all of the NaOH catalyst-induced films, spectral features resembling those for the 100°C-dried films can be seen in the frequency ranges of 1100 to 900 cm⁻¹. The peak absorbance of the Si-O-Zr band at 970 cm⁻¹ grows conspicuously with an increase in concentration of NaOH, suggesting that the extent of densification of Si-O-Zr linkages in the formed PZS films is strongly related to the pH of the sol. On the other hand, the signal intensity of the Si-O-Si band at 1010 cm⁻¹ declines with an increase in pH.

Figure 23 shows SEM micrographs for various 100°C-sintered films after pyrolysis for 30 min at 300°C. Although uniform-continuous coating films were produced from the 100°C-sintered pH 1.1 xerogel, (see Figure 18-a), pyrolysis at 300°C led to the development and propagation of microcracks and local separation of the film from the substrate. The major cause for this failure was assumed to be the pyrolytic liberation of a relatively large amount of carbonaceous species from the sintered films. This induces large stress cracks caused by the high degree of shrinkage in the film layers. Surface microstructures similar to those of the 100°C-dried films were observed for films produced at pHs ranging from 2.2 to 8.6. In considering the ability of these coatings to provide corrosion protection, the dense microstructure of fractal clusters linked together (c and d) that was seen in films derived from sols at pH 7.1 and 8.6, is of particular interest. There was no evidence of film damage, nor of local separation of the film from the substrate. In addition, there was no evidence of porosity created by the packing of these fractal clusters, which suggests that they are space-filling. In contrast, an undesirable porous film which had many crater-like pits, was fabricated from the sol at pH 12.8 (see Figure 23). The degree of densification of the Si-O-Si and Si-O-Zr linkages in the xerogel structures seem to have a strong influence on the film-forming performance of the pyrolyzed PZS xerogels. Extremely dense Si-O-Zr linkages resulted in poor cluster films. Therefore, the proper proportions of Si-O-Si and Si-O-Zr are important factors in producing good films. These can be produced using pH 7.1 and 8.6 sols.

Figure 24 gives the EDX spectra for 300°C-pyrolyzed film surfaces at pH 1.1, 2.6, and 8.6. The spectrum identified as (a) which is for a pH 1.1 film, had three prominent lines which correspond to Si, Zr, and Cl. The Si and Zr elements relate to the PZS, while the Cl originated from the HCl used as a hydrolysis promoter for the alkoxy groups in the TSPI and Zr(OC₃H₇)₄. When

the pH of this HCl catalyst-induced sol was adjusted to 2.6 by adding NaOH, the spectral structure (b) was characterized by a large increase in the signal intensity of Cl, and the immergence of Na. Further addition of NaOH to the sol system [Spectrum (c)] resulted in increased intensification of both lines. Thus, acceleration of the rate of the condensation reaction by the addition of NaOH not only increases the densification of Si-O-Zr linkages, but also promotes the formation of Na-related Cl compounds as by-products in the PZS layers.

To identify the phase of such a by-product, the same samples used in the EDX inspections were examined by XRD over the diffraction range 0.509 to 0.154 nm. These results are shown in Figure 25. For the pH 1.1 film [Pattern (a)], no peaks were detected, thereby indicating that the PZS was essentially amorphous. In contrast, reflections at 0.326, 0.282, 0.199, and 0.163 nm were observed in the film produced from the pH 2.6 sol [Pattern (b)]. These spacings clearly reveal the formation of halite (crystalline NaCl)^[44]. Increasing the pH to 8.6 (c) resulted in further intensification of these spacings. Therefore, the addition of NaOH to the HCl-catalyzed sol systems leads to the formation of well-crystallized halite particles in the amorphous PZS layers. Since NaCl is an electrolyte species which promotes the corrosion of metals, the presence of NaCl in the films is undesirable. Fortunately, it can readily be eliminated by rinsing the film with the water. This was shown by rinsing a pH 8.6 film with tap water. The subsequent EDX spectrum coupled with a SEM micrograph revealed no Na and only a weak Cl line. In addition, there were no specific changes in the morphology and topography of the film. These results are shown in Figure 26.

To further demonstrate that the NaCl by-product can be removed from the PZS layers, the depth-elemental composition profile in water-rinsed pH 8.6 film layers and in PZS/Al interfacial regions was determined using AES in conjunction with Ar ion sputter-etching. The sputter rate for the depth profiling was ~30 nm/min. Figure 27 depicts the changes in auger peak heights of representative elements such as O, Si, Zr, Cl, and Al versus sputter time for a pH 8.6 film deposited on Al. The peak heights of three major elements, O, Si, and Zr which reflect the PZS film, were gradually reduced as the sputtering time increased. After 27 min, the Si- and Zr-related auger peaks had completely disappeared, while the height of the O signal levelled off. The signal of Al, which is associated with the Al substrate, emerged at a depth of

~630 nm from the surface and increased rapidly with sputtering time until it stabilized after 27 min. The stabilization of the O signal and the elimination of Si and Zr atoms suggest that the presence of Al and O elements at depths >810 nm is due mainly to aluminum oxide phases on the surface of the Al substrate. Thus, the depth ranging from ~630 to ~810 nm seems to represent a PZS/ Al_2O_3 mixed layer in the interfacial zone. The Cl at the surface of the film (zero sputter time) had the lowest peak, corresponding to a minor atomic presence. The height of the peak decreased with sputter times and then disappeared at a depth of ~540 nm. This indicates that there was no Cl in the PZS layers adjacent to the Al substrate.

In making water-impermeable xerogel films, the magnitude of wettability of the coating's surface by water is one of the most important factors governing good protective performance. Therefore, the water-wettability of xerogel film surfaces was estimated from the average value of the advancing contact angle on these surfaces. Figure 28 shows a plot of the contact angles as a function of the film-treating temperature for a pH 8.6 film. Since a high contact angle correlates with a low rate of wetting, the data show that film surfaces treated at high temperature are less wettable. As the film was exposed to high temperatures, the original hydrophilic xerogel surfaces were converted to hydrophobic surfaces. The results suggest that PZS films having minimum water-wetting characteristics can be prepared by pyrolysis at temperatures of $\geq 250^\circ\text{C}$.

All of the above data were correlated with the corrosion protection provided by pyrogenic PZS cluster coatings on Al. The corrosion data were obtained from the polarization curves for PZS-coated Al samples exposed to an aerated 0.5 M sodium chloride solution at 25°C . The typical cathodic-anodic polarization curves exhibited a short Tafel region in the cathodic polarization, but no Tafel region was found at the anodic sites. To evaluate the protective performance of coatings, the corrosion current, I_{corr} , values were measured by extrapolation of the cathodic Tafel slope. Figure 29 illustrates the variation in the I_{corr} value for Al substrates as a function of the treatment temperature for several sol-derived PZS coating films. The protective ability of the coatings depends primarily on the pH value of the sol precursors and the treatment temperature of the films. The I_{corr} value for the coatings preheated at 100°C ranged from 1.2 to 1.9 μA , too high to predict good corrosion protection. The major reason for the poor protection is the

hydrophilic nature of the coatings. All of these films dissolved after they were immersed in water at 25°C for 10 hr. Lower current densities were measured for all but the pH 12.8 films treated at 200°C. As discussed earlier, the films formed in sol with a high pH (≥ 11.5) developed numerous stress cracks, probably caused by the formation of highly condensed polymeric structures. Thus, the I_{corr} value for the pH 12.8 coatings remained essentially constant within the range from 100° to 300°C. For the other coatings, increasing the treatment temperature to 250°C acted to further reduce the I_{corr} . Above this temperature, there was only a slight decrease. Therefore, films treated at temperatures $\geq 250^\circ\text{C}$ have the maximum ability to protect Al substrates. In contrast, the I_{corr} of pH 1.1 films tended to increase with increased temperature above 200°C. This can be associated with failure of the film caused by high shrinkage that is related to the liberation of many carbonaceous groups at elevated temperatures. The lowest I_{corr} value of 0.5×10^{-1} , corresponding to the best protection, was measured on the 300°C-treated pH 8.6 films. This value was approximately one order of magnitude less than for the 300°C-treated film at pH 1.1. The ability of 300°C-treated films to protect Al was rated in the following order: pH 8.6 > 7.1 > 2.6 > 12.8 > 1.1. This finding strongly suggested that a dense PZS fractal cluster coating containing a proper proportion of Si-O-Si to Si-O-Zr linkages provides an effective corrosion barrier for Al substrates.

VI. MAJOR ACCOMPLISHMENTS

Elucidation of some of the fundamental interactions that take place at PPS/steel, PPS/Zn·Ph/steel, PPS/Al and PZS/Al substrate interfaces upon exposure to harsh acidic and alkaline environments has been accomplished. These data indicate that thin inorganic and organic polymer coatings have high potentials for use as low-cost corrosion resistant materials in condensing flue gas applications.

VII. MAJOR PROBLEMS ENCOUNTERED

To date, no major problems have been encountered. The work is on schedule and within the spending rate projections.

VIII. CONCLUSIONS

This R&D effort is being focused to provide information regarding corrosion resistance, heat transfer, material cost, fabrication method and cost, and product reliability since each of these is important in the final design and production of a heat exchanger. Results to date indicate that organic and inorganic-type polymer coating systems applied to low cost metals such as mild steel and aluminum provide good corrosion protection.

Polymeric coatings on heat exchangers and other types of chemical process equipment are used commercially on a routine basis, thereby suggesting that their use can be cost effective. Polyphenylene sulfide (PPS) and other types of polyaryl-type polymers such as polyphenylethersulfone (PES) and polyphenyl ether ether ketone (PEEK) were selected for study in this program due to their high melting points ($>295^{\circ}\text{C}$) and acid resistance. All have common chemical features consisting of aromatic backbone chains coupled with oxygen, ketones, and/or sulphur. They are commercially available and can be applied as coatings using standard spray, dip and fluidized bed processes. When the polymers are mixed with fillers, extrudable composite tubing can be produced.

Although the unit mass cost of high performance organic and pre-ceramic coating materials is high and the heat transfer properties poor, the thin (micron order) coating sections required and the relative ease of application using a dip and bake process yield preliminary coating costs of $<10\text{¢/ft}^2$. The thin section and the ability to vary the wetting characteristics of the coating also minimize heat transfer losses. Other advantages accrued by the use of thin coatings are increased flexibility and reduced thermal stresses.

Thin coatings also have the potential for being porous or containing pinholes due to inadequate distribution of the film. Optimization of the corrosion protective ability with respect to thickness, application method and cost is therefore essential. The ability to reproduce the results on a larger-scale must also be demonstrated.

Composites consisting of high performance polymers used in conjunction with high thermal conductivity fillers also offer the potential to significantly reduce the cost of heat exchangers relative to those constructed from high alloy steels or bulk plastics. A thermal conductivity approaching that of stainless steel is attainable and concerns regarding pinholes in thin coatings are eliminated. Although fabrication costs will probably be greater than

those for bulk polymers, processes such as spin casting, extrusion and injection molding can be utilized.

Experimental work for the program was initiated on October 1, 1990. To date, four polymer/metal systems have been investigated. Based upon the studies conducted to date, the following conclusions can be made.

When high-temperature performance PPS polymer coatings are applied directly to cold-rolled steel surfaces, the chemical reaction at 350°C between the Fe_2O_3 at the outermost surface of the steel and the PPS in air results in the formation of FeSO_4 at the critical interfacial zones. Although the intermediate FeSO_4 layers, as interfacial reaction products, play an important role in developing bond strength at the PPS/steel joint, alkali-catalyzed hydrolysis of FeSO_4 caused by the cathodic reaction, $\text{H}_2\text{O} + 1/2\text{O}_2 + 2\text{e}^- = 2\text{OH}^-$, at any defects in the coating film, will cause catastrophic cathodic delamination of the PPS film from the steel. Therefore, to avoid the direct contact of PPS with steel, a p(AA)-modified Zn·Ph conversion coating should be deposited on the steel surfaces. The chemical resistance of this BNL-developed conversion coating is greater than that resulting from magnesium or iron phosphate systems and gives better adhesion to polymer topcoats. Before applying the PPS, the $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ which is the major phase in the Zn·Ph layers can be converted into an $\alpha\text{-Zn}_3(\text{PO}_4)_3$ phase by thermal dehydration at 350°C. This thermal treatment also promotes the transformation of the poly(acid) structure within the p(AA) into a poly(acid)anhydride, and the oxidation of free Fe atoms dissociated from the steel surfaces during the precipitation of the crystalline Zn·Ph coating. It was also determined that SO_2 emitted from the PPS at the PPS-to-Zn·Ph boundary regions preferentially reacts with oxidized Fe compounds, rather than with Zn and P atoms in the Zn·Ph crystals. Such a gas-solid interaction between SO_2 and the oxidized Fe compound at 350°C causes the formation of a FeS reaction product. In addition, two other interactions have been observed: one is a polymer-to-polymer reaction between the PPS and the poly(acid)anhydride existing at the outer surface of the Zn·Ph layers; the other is the physical interlocking associated with the mechanical anchoring of the PPS polymer. This results from the penetration of melted polymer into the open surface microstructure of the Zn·Ph layers. These physico-chemical factors contribute to the development of adhesion force at the PPS/Zn·Ph interfaces, and are responsible for the high lap-shear bond strength of phosphated metal/PPS/phosphated metal specimens.

Once a cathodic reaction occurs at a defect in the PPS/Zn·Ph system, the action of NaOH derived from the cathodic reaction results in the dissolution and hydrolysis of the anhydrous Zn·Ph and FeS interaction product. Such an alkali-induced dissociation results in the formation of Na-related sulfur compounds, such as Na-sulphide, Na-sulphite and Na-sulphate. However, the rate of cathodic delamination of PPS in the PPS/Zn·Ph system is considerably lower than that in the PPS/steel system.

Adhesive bonds in the PPS/ Zn·Ph systems display outstanding durability against attack by hot H_2SO_4 solutions containing NaCl. In contrast, the bonds of PPS/steel systems failed after exposure for only 8 days to this hot acid solution. The major reason for this failure is the $\text{FeSO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3$ phase transformation in the intermediate layers. The formation of $\text{Fe}_2(\text{SO}_4)_3$ may be deduced from the acid-catalyzed oxidation of the FeSO_4 reaction product formed at the PPS/steel interfaces.

PPS and PZS coatings were applied to unmodified 6061-T6 aluminum surfaces. With the former, a hydrolyzable compound aluminum sulfate was formed at the PPS/Al interface. Upon exposure of these specimens to a 80°C pH 3 H_2SO_4 solution containing 0.1M NaCl, complete delamination of the films occurred within 8 days. Failure was due to the hydration of the $\text{Al}_2(\text{SO}_4)_3$ to yield $\text{Al}_2(\text{OH})_4\text{SO}_4 \cdot 7\text{H}_2\text{O}$. Surface modification of the Al prior to the application of the PPS appears necessary.

Thin (≈ 1 micron) PZS coatings appear to provide good corrosion protection to Al. These dense and hydrophobic coatings can be formed by hydrolysis-polycondensation-pyrolysis synthesis of acid-base catalyzed sol precursors. When amorphous PZSs were applied to Al as protective coatings against NaCl-induced corrosion, the most effective film was derived from a sol having a pH near the isoelectric point in the positive zeta potential region. The following four factors play important roles in producing protective PZS coating films: 1) a proper rate of condensation, 2) a moderate ratio of Si-O-Si to Si-O-Zr linkages in the PZS network, 3) hydrophobic characteristics, and 4) a specific microstructural geometry, in which large fractal clusters are linked together. Xerogel films produced from sols of pH 8.6 and subsequently pyrolyzed at 250°C gave the best corrosion protection.

IX. REFERENCES

1. Proc. 1987 International Symposium on Condensing Heat Exchangers, Battelle Columbus Laboratories, BNL 52069 and GRI-87/0091.2, Vols. 1 and 2, April 1987.
2. Agrawal, A. K. and Hindin, B. Evaluation of alternative materials for condensing heat exchangers, Final Report, August 1989 - August 1990, Battelle Columbus Division, GRI-90/0219, September 24, 1990.
3. Morra, B. S. and Plucinsky, S. R. High temperature engineering plastics for use in condensing heat exchangers, Proc. 1987 International Symposium on Condensing Heat Exchangers, Battelle Columbus Laboratories, BNL 52068 and GRI-87/0091.2, 235-252, April 1987.
4. Sugama, T., Kukacka, L. E., Carciello, N. R., and Warren, J. B. Physico-chemical factors affecting hydrothermal resistance and bonding of polymeric composites to steel surfaces, BNL 37376, Nov. 1985.
5. Sugama, T., Kukacka, L. E., Carciello, N., and Warren, J. B. Use of polyacrylic acid electrolytes diffused in zinc phosphate conversion coatings for the corrosion protection of steel, J. of Coatings Technology, Vol. 61, No. 771, 43-57, Apr. 1989.
6. Sugama, T., Kukacka, L. E., and Carciello, N. Polytitanosiloxane coatings derived from $Ti(OC_2H_5)_4$ -modified organosiloxane precursors, Intl. J. Progress in Organic Coatings, 18, (1990) pp. 173-196.
7. Fontana, J. J., Reams, W., and Cheng, H. C. Potential polymer concrete heat exchanger tubes for corrosive environments, BNL 28945, Proc. 5th International Congress on Polymers in Concrete, Brighton Polytechnic, Brighton, U.K., Sept. 1987.
8. Kaeding, A. O. Polymer concrete lined pipe for use in geothermal applications, Proc. Geothermal Engineering and Materials Program Conference, U.S. DOE, San Diego, 107-112, Oct. 1982.
9. Farnsworth, C. A. Materials and design options for avoiding corrosion in condensing appliance heat exchangers and vent systems, Proc. 1987 International Symposium on Condensing Heat Exchangers, Battelle Columbus Laboratories, BNL 52068 and GRI-87/0091.2, 115-126, April 1987.
10. Lenz, R. W., Handlovity, C. E. and Smith, H. A. Phenylene sulfide polymers. III. The synthesis of linear polyphenylene sulfide. J. Polym. Sci. 58, 351-367 (1962).
11. Port, A. B. and Still, R. H. Synthesis and characterization of poly(phenylene sulfide) poly(2-methylphenylene sulfide), and poly(2,6-dimethylphenylene sulfide). J. Appl. Polym. Sci. 58, 1145-1164 (1979).
12. Lovinger, A. J., Davis, D. D. and Padden, F. J., Jr. Kinetic analysis of the crystallization of poly(phenylene sulfide) polymer. 26, 1595-1604 (1985).

13. Bolger, J. C. In Adhesion Aspects of Polymeric Coatings, K. L. Mittal, Editor, pp. 3-18, Plenum Press, New York, 1983.
14. Riga, J., Boutique, J. P., Piereaux, J. J., and Verbist, J. J. In Physico-chemical Aspects of Polymer Surfaces, K. L. Mittal, Editor, pp. 45-52, Plenum Press, New York, 1983.
15. McIntyre, N. S. and Zetaruk, D. G. X-ray photoelectron spectroscopic studies of iron oxides. *Anal. Chem.* 49, 1521-1529 (1977).
16. Gaarenstroom, S. W. and Winograd, N. Initial and final state effects in the ESCA spectra of cadmium and silver oxides. *J. Chem. Phys.* 67, 3500-3506 (1977).
17. Binder, H. Application of x-ray photoelectron spectroscopy to the elucidation of the bonding in iron-sulfur compounds. *Z. Naturforsch., Teil B* 28, 255-262 (1973).
18. Carver, J. C., Schweitzer, G. K. and Carlson, T. A. Use of x-ray photoelectron spectroscopy to study bonding in chromium, manganese, iron, and cobalt compounds. *J. Chem. Phys.* 57, 973-982 (1972).
19. Lindberg, B. J., Hamrin, K., Johansson, G., et al. Molecular spectroscopy by means of ESCA [electron spectroscopy for chemical analysis] II. Sulfur compounds. Correlation of electron binding energy with structure. *Phys. Scr.*, 1, 286-298 (1970).
20. Tanabe, K., Hattori, H. and Yamaguchi, T. Surface properties of solid superacids. *Critical Rev. Surface Chem.*, 1, 1-25 (1990).
21. Sneed, M. C. and Maynard, J. L. General inorganic chemistry. D. Van Nostrand Company, Inc., New York 1952.
22. Moody, B. J. Comparative inorganic chemistry. Edward Arnold Publishers, Ltd. London, 1965.
23. Shalvoy, R. B., Fisher, G. B., and Stiles, P. J. X-ray photoemission studies of the valence bands of nine [group] IV-VI compounds. *Phys. Rev.* B15, 2021-2024 (1977).
24. Leidheiser, H. and Wang, W. Corrosion control by organic coatings. NACE, Houston, 70-77 (1981).
25. Sugama, T. and Pak, J. *Adv. Mater. Mfg. Pro.*, 6, 227 (1991).
26. Sugama, T., Kukacka, L. E., Carciello, N., and Warren, J. B. *J. Mater. Sci.*, 22, 722 (1987).
27. Sugama, T., Kukacka, L. E., Carciello, N., and Warren, J. B. *J. Mater. Sci.*, 23, 101 (1988).
28. Sugama, T., Kukacka, L. E., Clayton, C. R., and Hua, H. C. *J. Adhesion Sci. Tech.*, 1, 265 (1987).

29. Briggs, D. and Seah, M. P. Practical surface analysis by auger and x-ray photoelectron spectroscopy. John Wiley, New York, 385, 1985.
30. Sugama, T., Kukacka, L. E., and Carciello, N. Prog. Org. Coat., 11, 173 (1990).
31. Sugama, T., Carciello, N., and Taylor, C. J. Non-Cryst. Solids, (in press).
32. Su, G. J., Borelli, N. F., and Miller, A. R. Phy. Chem. Glasses, 3, 167 (1962).
33. Gan, F., Huang, G., and S. Chen. J. Non-Cryst. Solids, 52, 203 (1982).
34. Uchino, T., Sakka, T., and Iwasaki, M. J. Am. Ceram. Sci., 74, 306 (1991).
35. Smith, A. L. Spectochim. Acta., 16, 87 (1960).
36. Bellamy, L. J. The infra-red spectra of complex molecules. Chapman and Hall, London (1975).
37. R. Hanna, J. Am. Ceram. Soc., 48, 595 (1965).
38. Bansal, N. P. J. Am. Ceram. Soc., 71, 666 (1988).
39. Haberkro, K. Ceramurgia Int., 5, 148 (1979).
40. Kendall, K., Alford, N. M., and Birchall, J. D. Proc. Br. Ceram. Soc., 37, 255 (1986).
41. Johes, S. L. and Norman C. J. J. Am. Ceram. Soc., 71, c-190 (1988).
42. Best, M. F. and Condrate Sr., R. A. J. Mater. Sci. Letter, 4, 994 (1985).
43. Lee, S. W. and Condrate Sr., R. A. J. Mater. Sci., 23, 2951 (1988).
44. Joint Committee on Powder Diffraction Standards, Card 5-628.

Table 1. XPS Elemental Analysis of Bulk PPS and Substrates as Reference Surfaces.

Coating and Substrate*	Atomic Concentration, %							
	C	S	O	Mn	Fe	P	Cr	Zn
PPS	82.5	15.5	2.0	-	-	-	-	-
CRS	25.8	-	59.9	1.7	12.5	-	-	-
SS	58.3	-	34.4	-	5.5	-	1.8	-
G-S	30.4	-	50.3	-	-	9.1	6.7	3.6

* PPS: Polyphenylene Sulfide
 CRS: 1010 Cold-Rolled Steel
 SS: 304 Stainless Steel
 G-S: G-90 Galvanized Steel

Table 2. Chemical Composition of Both Interfacial Failure Sides for N₂- and O₂-cured PPS/CRS Joint Systems

Heating Environment	Failed Side	Atomic Concentration, %				
		S	C	O	Mn	Fe
in N ₂	PPS	7.4	42.5	41.5	-	8.6
in N ₂	CRS	4.3	40.8	43.9	0.3	10.7
in O ₂	PPS	3.5	42.1	44.0	-	10.4
in O ₂	CRS	-	31.3	55.5	0.7	12.6

Table 3. Elemental Composition of Interfacial PPS and SS Surfaces at PPS/SS Joints in N₂ and O₂

Heating Environment	Failed Side	Atomic Concentration, %			
		S	C	O	Fe
in N ₂	PPS	12.7	83.9	3.4	-
in N ₂	SS	4.4	82.3	12.7	0.5
in O ₂	PPS	13.3	81.0	5.6	0.1
in O ₂	SS	14.3	24.4	56.5	4.8

Table 4. Atomic Concentration of N₂- and O₂-Treated PPS/G-S Interfaces

Heating Environment	Failed Side	Atomic Concentration, %					
		P	S	C	O	Cr	Zn
in N ₂	PPS	9.3	8.3	51.0	24.9	1.1	5.4
in N ₂	G-S	10.5	7.5	48.0	26.0	1.9	6.2
in O ₂	PPS	13.6	3.2	36.0	37.0	2.3	7.8
in O ₂	G-S	16.0	3.8	35.7	33.8	2.3	8.5

Table 5. Atomic Concentration of Failed PPS and Steel Sides Before and After Exposure for 8 Days to 80°C-H₂SO₄ Solution

<u>Exposure to H₂SO₄</u>	<u>Failed Sides</u>	<u>Atomic Concentration, %</u>					
		<u>S</u>	<u>C</u>	<u>O</u>	<u>Mn</u>	<u>Fe</u>	<u>Cl</u>
Before	PPS	3.5	42.1	44.0	-	10.4	-
Before	G-S	-	31.3	55.5	0.7	12.6	-
After	PPS	6.7	20.9	63.0	-	7.8	1.6
After	G-S	3.1	18.4	65.0	-	11.2	2.3

Table 6. Chemical Composition of Both Interfacial Failure Sides Before and After Cathodic Delamination Tests for PPS/Steel Joint Systems

<u>Cathodic test</u>	<u>Failed Sides</u>	<u>Atomic Concentration, %</u>					
		<u>S</u>	<u>C</u>	<u>O</u>	<u>Mn</u>	<u>Fe</u>	<u>Na</u>
Before	PPS	3.5	42.1	44.0	-	10.4	-
Before	Steel	-	31.3	55.5	0.7	12.6	-
After	PPS	10.7	80.9	6.1	-	1.5	0.8
After	Steel	1.3	23.3	59.6	1.3	13.3	1.2

Table 7. Chemical Composition of Both Interfacial Failure Sides Before and After Cathodic Delamination Tests for PPS/Zn·Ph Joint Systems

<u>Cathodic test</u>	<u>Failed side</u>	<u>Atomic Concentration, %</u>						
		<u>P</u>	<u>S</u>	<u>C</u>	<u>O</u>	<u>Fe</u>	<u>Zn</u>	<u>Na</u>
Before	PPS	8.5	2.5	32.0	47.1	6.1	3.8	-
Before	Zn·Ph	5.3	-	35.9	47.7	8.1	3.0	-
After	PPS	3.4	4.1	56.2	26.9	0.4	2.1	6.9
After	Zn·Ph	2.1	1.5	56.8	31.5	0.9	2.5	4.7

Table 8. Compositions of Sol Precursor Solutions for a pH Range of 1.1 to 12.8

<u>pH</u>	<u>TSPI</u> <u>wt%</u>	<u>Zr(OC₃H₇)₄</u> <u>wt%</u>	<u>CH₃OH</u> <u>wt%</u>	<u>Water</u> <u>wt%</u>	<u>HCl/TSPI +</u> <u>Zr(OC₃H₇)₄</u>	<u>NaOH/TSPI +</u> <u>Zr(OC₃H₇)₄</u>
1.1	7.7	5.1	7.7	79.5	50.0	0.0
2.6	7.7	5.1	7.7	79.5	50.0	10.4
7.1	7.7	5.1	7.7	79.5	50.0	14.0
8.6	7.7	5.1	7.7	79.5	50.0	18.0
11.5	7.7	5.1	7.7	79.5	50.0	26.0
12.8	7.7	5.1	7.7	79.5	50.0	39.0

Figure Captions

- Figure 1. Lap shear bond strength at metal-to-metal PPS adhesive joints after exposure in N_2 and O_2 at $350^\circ C$.
- Figure 2. XPS high-resolution spectra in S_{2p} , $Fe_{2p3/2}$ and $Zn_{2p3/2}$ regions for reference polyphenylene sulfide (PPS), cold-rolled steel (CRS), stainless steel (SS) and galvanized steel (G-S) surfaces.
- Figure 3. S_{2p} spectra at failed interfaces of PPS/CRS joint system prepared in N_2 and O_2 gases at $350^\circ C$.
- Figure 4. S_{2p} region at interfacial failure locus of PPS/SS joint system.
- Figure 5. S_{2p} spectra at failure locus in PPS/G-S joint system.
- Figure 6. Lap-shear bond strength vs. exposure time to a $80^\circ C$ pH3 H_2SO_4 solution containing 0.1M NaCl.
- Figure 7. S_{2p} region for PPS (h) and steel (i) interfaces separated by the attack of hot acid solution on the PPS/steel joint.
- Figure 8. Schematic diagram of cathodic delamination test.
- Figure 9. S_{2p} core level spectra for the PPS side (a) removed from the steel before cathodic delamination tests, and the delaminated PPS (b) and steel (c) sides after cathodic tests.
- Figure 10. XRD tracings for original Zn·Ph samples (a), and $350^\circ C$ -dehydrated Zn·Ph samples (b).
- Figure 11. The cathodic delamination of PPS films from steel and Zn·Ph-deposited steel substrates in 1 M NaCl.

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BINDING ENERGY, eV

Figure 12. P_{2p} and Zn_{2p3/2} regions for the interfacial PPS sides before cathodic treatment (d) and at the cathodically delaminated PPS interface (e)

Figure 13. Fe_{2p_{3/2}} and S_{2p} regions for interfacial PPS sides before cathodic test (d) and at the cathodically delaminated PPS interface (e).

Figure 14. Changes in P/Zn, S/Zn, and Fe/Zn atomic ratios as a function of exposure time to SO_2 .

Figure 15. SEM microprobe data and EDX spectra of the cathodically delaminated area (A) near a defect and at the delaminated front (B) of anhydrous Zn·Ph.

Figure 16. C_{1s} spectra for bulk PPS (f) and PPS interface (g) removed from poly(acid)anhydride-primed steel.

Figure 17. Changes in zeta potential of sol precursors as a function of pH.

Figure 18. SEM micrographs for pH (a) 1.1 sol- and (b) 2.6 sol-derived xero-
gel films deposited on aluminum surfaces.

Figure 19. SEM micrographs for pH (c) 8.6 sol- and (d) 11.5 sol-derived xerogel films deposited on aluminum surfaces.

Figure 20. TGA and DTA curves for the pyrolysis of xerogels heated in air at a rate of 10°C/min.

Figure 21. IR absorption spectra for 100°C-sintered xerogels at pH (a) 1.1, (b) 2.6, (c) 8.6, (d) 11.5, and (e) 12.8.

Figure 22. IR spectra for 300°C-pyrolyzed xerogels at pH (a) 1.1, (b) 2.6, (c) 8.6, (d) 11.5, and (e) 12.8.

Figure 23. SEM micrographs for 300°C-pyrolyzed xerogels at pH (a) 1.1, (b) 2.6, (c) 7.1, (d) 8.6, and (e) 12.8.

Figure 24. EDX spectra for 300°C-pyrolyzed xerogel film surfaces at pH (a) 1.1, (b) 2.6, and (c) 8.6.

Figure 25. XRD patterns for 300°C-pyrolyzed xerogels at pH (a) 1.1, (b) 2.6, and (c) 8.6.

Figure 26. SEM-EDX inspection of 300°C-pyrolyzed pH 8.6 film surface after rinsing with water.

Figure 27. AES depth-profile of pyrolyzed PZS-coated aluminum after rinsing with water.

Figure 28. Effect of temperature on the water-wettability of xerogel film surfaces

Figure 29. Changes in the corrosion current, I_{corr} , of PZS xerogel-coated aluminum substrates as a function of coating treatment temperature; pH 1.1 (○), 2.6 (Δ), 7.1 (□), 8.6 (●), and 12.8 (x).

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