

**Advanced Zinc Phosphate Conversion and Pre-Ceramic Polymetallosiloxane
Coatings For Corrosion Protection of Steel and Aluminum, and
Characteristics of Polyphenyletheretherketone-Based Materials**

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| 13. ABSTRACT (Maximum 200 words) The characteristics of anhydrous zinc phosphate (Zn·Ph) coatings deposited by immersing the steel in transition Co, Ni, and Mn cation-incorporated phosphating solutions were investigated. Two important features for the anhydrous 340°C-heated Zn·Ph were addressed. One was to determine if the electron trapping behavior of Co ²⁺ and Ni ²⁺ ions adsorbed in the crystal lattices acts to inhibit the cathodic reaction on the Zn·Ph, and the second was to determine the less susceptibility of the α -Zn ₃ (PO ₄) ₂ phase to alkali-induced dissolution. The factors governing the film-forming performance of pre-ceramic polymetallosiloxane (PMS) coatings for aluminum (Al) substrate surfaces were investigated. Four factors were important in obtaining a good film: 1) the formation of organopolymetallosiloxane at sintering temperatures of 150°C; 2) the pyrolytic conversion at 350°C into an amorphous PMS network structure in which the Si-O-M linkage were moderately enhanced; 3) the non-crystalline phases; and 4) the formation of interfacial oxane bond between PMS and Al oxide. The formation of well-crystallized polyphenyletheretherketone (PEEK) in the vicinity of silica aggregates was found in the melted body made in N ₂ . Such a PEEK crystalline structure contributed significantly to the thermal and hydrothermal stabilities of mortar specimens at temperatures up to 200°C, and the resistance in 5 wt% H ₂ SO ₄ solution at 80°C. | | | |
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STATEMENT OF WORK

Under U.S. Army Research Office (ARO) sponsorship, on Contract Numbers, MIPR-AR0102-89, 103-90, 119-91 and 157-92, Brookhaven National Laboratory (BNL) performed research on three topics:

- 1) Advanced zinc phosphate conversion coatings,
- 2) Synthesis and characteristics of pre-ceramic polymetallosiloxane coating films, and
- 3) Crystalline polyphenyletheretherketone (PEEK) - based materials.

Major research activities within each of these topics are described below.

1. Advanced Zinc Phosphate Conversion Coatings

The major phase in the insoluble zinc phosphate (Zn·Ph) conversion coatings, which is responsible for improved corrosion protection, was identified to be the same $Zn_3(PO_4)_2 \cdot 2H_2O$, as that used as a starting material. From the viewpoint of crystal molecular structure, because Zn·Ph layers contain a certain amount of crystallized water, it should be considered that when thermal barrier organic topcoat systems, such as polyimide [1,2], polybenzimidazoles [2], polyquinoxalines [3,4], and polyphenylene sulphide [4], are applied directly to the Zn·Ph surface, high-temperature treatment of the topcoats to form solid polymer films will lead to interfacial disbondment and separation brought about by the dehydration of the Zn·Ph. This failure is associated with the formation of weak boundary layers, resulting in poor corrosion protection. It was very important, therefore, to gain fundamental knowledge regarding the thermal degradation and phase transformation of Zn·Ph at an elevated temperature, before studying the interfacial chemical nature between the high-temperature performance polymers and the crystalline Zn·Ph. On the other hand, during the corrosion of iron and steel in a near neutral aqueous environment, the cathodic half reaction in terms of the oxygen reduction reaction, is $H_2O + 1/2 O_2 + 2e^- = 2 OH^-$. A shortcoming of Zn·Ph coatings as a barrier to the corrosion of steel is that the hydroxyl ions generated by this cathodic reaction [5] induce dissolution of the coating layers. A lower susceptibility of Zn·Ph to alkali dissolution also minimizes cathodic delamination rates for polymeric topcoat films. Thus, it was very important in assessing anticorrosive coatings to estimate the extent of alkali dissolution of Zn·Ph.

The ionic and/or elemental cobalt and nickel atoms are well-known inhibitors of the cathodic reaction of electrogalvanized steel [6-9]. The mechanism of this inhibition of corrosion was described by Leidheiser and Suzuki [10] as being due to the electron trapping reactions, M^{2+} (M: Co and Ni) + $2e^- = M^0$, of such atoms doped in the zinc oxide lattice. The M^{2+} ions favorably trap the electrons evolved from the anodic reaction, $Zn^0 - 2e^- \longrightarrow Zn^{2+}$, occurring at the oxide/solution interface, thereby inhibiting the cathodic reaction.

Accordingly, the emphasis of our present study was directed towards developing and characterizing advanced hydrous and anhydrous Zn•Ph containing the Co and Ni atoms, and poly(acrylic)acid, p(AA), which is a polyelectrolyte macromolecule species. The advanced Zn•Ph coatings will inhibit oxygen reduction reactions and minimize the rate of cathodic delamination of high-temperature performance polymer topcoats from phosphated steels.

2. Synthesis of Pre-Ceramic Polymetallosiloxane Coating Films

Ceramic coatings have not yet been widely used on aluminum and magnesium alloys, and on other low melting-point metal substrates because of two main reasons. First, coatings must adhere well and have an appropriate expansion coefficient, especially during temperature cycling, otherwise the coating will separate from the substrate. Second, many ceramic coatings must be applied and processed at high temperature ($>1000^{\circ}\text{C}$), using expensive and time-consuming methods, such as chemical vapor deposition.

To solve these problems with conventional ceramic coatings, our work was focused upon the synthesis of pre-ceramic inorganic polymetallosiloxane (PMS) polymers, and upon the characteristics of the synthesized PMS as corrosion-protective coatings on aluminum substrates.

The use of metal alkoxides, $\text{M}(\text{OR})_4$ (where M is Ti, Zr, Ge, Al, B, La, and Sn, R is CH_3 , C_2H_5 , C_3H_7 , or C_4H_9), as a means of enhancing the network connectivity and, hence, the extent of three-dimensional crosslinking of polymeric organosilanes synthesized using sol-gel techniques in terms of hydrolysis-polycondensation processes, was investigated previously [11, 12]. These authors reported that the incorporation of $\text{M}(\text{OR})_4$ into the organosilane system improved mechanical properties such as the modulus of elasticity and tensile strength of the organosiloxane polymer. Huang et al. also reported that the addition of excessive amounts of $\text{M}(\text{OR})_4$ to the systems results in large reductions in the elongation at the failure point of the polymers [13]. All of these studies were performed at temperatures up to 220°C .

An inorganic polysilane formed by a sol-gel polycondensation process involving tetraethylorthosilicate, $\text{Si}(\text{OC}_2\text{H}_5)_4$, is presently used as a binder in inorganic zinc-rich primers, which act to inhibit the corrosion of metals [14]. The major characteristics of these cured inorganic zinc primer films are their excellent adhesion to metallic substrates, thermal stability, resistance to ultraviolet light and weathering, and abrasion. As a result, they appear promising for use as reliable underlying structures to which organic topcoats can be applied.

On the basis of the above information, our attention was focused on the characteristics of polymeric materials synthesized through hydrolysis-condensation reactions of $\text{M}(\text{OR})_4$ -incorporated organosilane monomeric mixtures over the temperature range $100\text{--}500^{\circ}\text{C}$. When film fabrication temperatures $\geq 300^{\circ}\text{C}$ are considered, it can be assumed that a large number of carbon-containing groups will be eliminated pyrolytically from the polymer network structures as a result of elevated temperature. Hence, attention was given to the pyrolytic changes in the conformation of M compound-modified organosilane polymers. Such conformational changes and their processes, as a function of temperature,

may be different, depending on the species of organosilane and the proportions of organosilane to $M(OR)_4$ used as original starting materials.

To obtain such information, we examined three topics. First, emphasis was placed on the pyrolytic conformational changes and the mechanisms of Ti compound-modified organosilane polymers formed at various $Ti(OR)_4$ to organosilane monomer ratios. In this study, the 3-glycidoxypropyltrimethoxysilane (GPS) examined by previous investigators [11,12] was used. The observed conformational changes were correlated with alterations in the surface morphology, changes in surface chemical composition and chemical states of the Ti compound-modified GPS coating films overlayed on aluminum substrates at temperatures up to 500°C. The ability of the coatings formed at temperatures ranging from 100°C to 500°C to inhibit the pitting corrosion of aluminum was studied secondly. The third research topic focused on the use of other metal alkoxide species, such as $Al(OC_3H_7)_3$, and $Zr(OC_3H_7)_4$. In addition, the fabrication of thin films (thickness $<1\mu m$), which may form microcrack-free coatings, because of lower rates of volatility and pyrolysis, was also considered. Finally, based upon fundamental knowledge obtained from the above studies, efforts were then focused on the fabrication of good coating films and the evaluation of their corrosion protective performance.

3. Crystalline Polyphenyletheretherketone (PEEK) - Based Materials

The melt crystallized polyaryl polymers, such as polyphenylenesulphide (PPS), $\left(-\text{C}_6\text{H}_4-\text{S}\right)_n$, polyphenyletheretherketone (PEEK), $\left(-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{O}\right)_n$ and polyphenyletherketone (PEK), $\left(-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{O}\right)_n$, have common chemical features consisting of aromatic backbone chains coupled with oxygen, ketone, and/or sulphur. When these linear polymers are left in an oven at a temperature above their melting point of $> 280^\circ\text{C}$, chain extension of the main phenyl groups caused by melting leads to molecular orientation, which is reflected in the crystallization of the polymers during cooling from the melting temperature to a lower temperature [15-17]. Such crystallization behavior of the polyaryls gives them specific desirable characteristics as adhesives, such as high temperature stability, high radiation, chemical, and hydrothermal resistance, and good mechanical and dielectric properties. Thus, polyaryls have become of increasing interest for applications in coatings, as adhesives, and in composites.

Our particular interest was to investigate the thermal, hydrothermal, and chemical durabilities of PEEK polymer mortar specimens, which were prepared by the melting-cooling processes of PEEK powder-sand mixtures. In addition, the thermal characteristics, crystalline behavior, and change in chemical structure of the PEEK neat cements under air or N_2 environments were also explored.

SUMMARY OF RESULTS

1. Advanced Zinc Phosphate Conversion Coatings

Advanced Zn·Ph conversion coatings can be prepared by immersing steel in Co^{2+} and Ni^{2+} ion-incorporated p(AA)-zinc phosphate solution systems. The formation of M^{2+} (M: Co and Ni)-p(AA) salt complexes containing $-\text{COO}^- \text{M}^{2+} -\text{OOC}-$ groups played an important role in accelerating and promoting the growth and development of Zn·Ph crystal layers over the steel, and also introduced amorphous Fe-rich phosphate conversion layers in the vicinity of Fe_2O_3 substrates. The electron trapping behavior of the M^{2+} ions dissociated from the complex formations and M hydroxides in the NaCl solution inhibited cathodic reactions, thereby resulting in an extended lifetime for the Zn·Ph, which serves to provide corrosion protection for steel. In the final stages of the conversion process, the crystal phase of Ni system-derived conversion coatings consisted of zinc orthophosphate dihydrate, $[\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}]$ 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 uniform coverage of $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ -hopeite interlocked crystals over the steel may reduce the rate of corrosion.

In thermal dehydration processes at 340°C , a hopeite $\rightarrow \gamma\text{-Zn}_3(\text{PO}_4)_2$ phase transition occurs. In contrast, the $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ was preferentially converted into the $\alpha\text{-Zn}_3(\text{PO}_4)_2$ phase which has a alkali dissolution rate considerably lower than that of the γ -phase. This results in a minimized cathodic delamination rate of polymeric films from α -phase steel substrates.

When high-temperature performance PPS polymer coatings were directly applied to cold-rolled steel surfaces, the chemical reaction at 350°C between the Fe_2O_3 at the outermost surfaces of the steel and the PPS in air led to 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, the 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, caused 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 was deposited on the steel surfaces. Before applying the PPS, the $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ as a major phase of the Zn·Ph layers was converted into an $\alpha\text{-Zn}_3(\text{PO}_4)_3$ phase by thermal dehydration at 350°C . This thermal treatment also promoted the transformation of the poly(acid) structure within the p(AA) into the poly(acid)anhydride, and the oxidation of free Fe atoms dissociated from the steel surfaces during the precipitation of the crystalline Zn·Ph coating. We found that SO_2 emitted from the PPS at the PPS-to-Zn·Ph boundary regions preferentially reacts with the 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 caused the formation of a FeS reaction product. In addition, the two different interactions were recognized: one was the polymer-to-polymer reaction between the PPS and the poly(acid)anhydride existing at the outer surface of the Zn·Ph layers; the other was the mechanical interlocking associated with the mechanical anchoring of the PPS polymer, which resulted from the penetration of the melted polymer into the open surface microstructure of the Zn·Ph layers. These physico-chemical factors,

contributing to the development of adhesion force at the PPS/Zn-Ph interfaces, were essentially responsible for a high lap-shear bond strength on the phosphated metal-to-phosphated metal PPS 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 resulted in the formation of the Na-related sulfur compounds, such as Na-sulphide, Na-sulphite, and Na-sulphate. However, the rate of cathodic delamination of PPS for the PPS/Zn-Ph system was considerably lower than that for the PPS/steel system.

Based upon this information, additional work to continue its development is needed. Topics requiring additional work are as follows: 1) steel surface preparation requirements for achieving a rapid deposition of Zn-Ph crystals, 2) the application of Zn-Ph to galvanized steel surfaces, and 3) an evaluation of other high-temperature performance polymers such as polyimide, polybenzimidazole and polyphenyletheretherketone, as a topcoating material for Zn-Ph.

2. Synthesis of Pre-Ceramic Polymetallosiloxane Coating Films

Inorganic amorphous polymetallosiloxane, PMS, can be synthesized through hydrolysis-polycondensation-pyrolysis reactions of sol-precursor solution systems consisting of N-[3-(triethoxysilyl) propyl]-4,5-dihydroimidazole (TSPI) and M(OC₃H₇)_n (M: Zr, Ti and Al, n: 3 or 4) as a film-forming reagent, HCl as a hydrolysis catalyst, and CH₃OH and water as a liquor medium. During this study of corrosion-protective thin films for low melting point aluminum substrates, the following seven items could be conclusively generalized as the major physico-chemical factors governing the film-forming behavior of PMS under the sol precursor (25°C) → sintering (150°C) → annealing (350°C) processes:

- 1) During the sol-film forming stage, adding HCl to the mixtures of TSPI and M(OC₃H₇)_n induces the formation of hydroxylated metals, the Cl-substituted end groups in the monomeric organosilane, and the separation of imidazole derivatives from TSPI.
- 2) In the sintering process of sol films at 150°C, the formation of metal oxide polyorganosiloxane bond formed by the dechlorinating reaction between the Cl attached to propyl carbon in organosilane and the proton in the hydroxylated Zr or Ti compounds, played an important role in weight loss of the film.
- 3) Referring to 2), the Al hydroxide, derived from Al(OC₃H₇)₃ in which the trivalent ion is the principal oxidation state, preferentially reacts with hydroxylated organosilane to form the Al-O-Si linkage at a low temperature. However, this linkage was broken when the sintered film was annealed at 350°C, thereby creating large stress cracks and a high weight loss of the film.

- 4) The pyrolysis of Ti and Zr oxides-incorporated polyorganosiloxane compounds led to the formation of Ti and Zr oxides-crosslinked with polysiloxane, while also eliminating carbonaceous groups and Cl compounds from the sintered materials. These crosslinked network structures served to minimize the development of stress cracks in the films pyrolyzed at 350°C.
- 5) Although a certain amount of crystalline anatase particles were present in the amorphous polytitanosiloxane (PTS) coatings, the moderate crosslinking effects of Ti oxides and the densification of the M-O-Si linkage provided the most effective coating film in this study.
- 6) The identification of covalent oxane bonds at the interfaces between the PTS and the alkali-etched aluminum substrate illustrates the possibility of strong adhesion forces.
- 7) Referring to 4), 5), and 6), the integrated assignments of these factors were correlated directly to good corrosion resistance of aluminum alloys in NaCl solutions.

All the information described above was obtained from experiments with the sol precursor solution in the presence of acid catalysts. As described by several investigators [18,19], the microstructure of the film can be altered by varying the rate of polymerization of sol particles; namely, the extent of growth of the polymeric sol in an aqueous medium depended primarily on the pH of the precursor solution. When acid-type catalysts were added to the solution, the sol consisted of entangled linear polymers. By contrast, a highly condensed sol consisting of randomly branched chains was prepared by incorporating base-type catalysts. Xerogel films derived from the acidic sol precursor system had a continuous, dense microstructure, while the base-type system results in the formation of globular structures consisting of aggregations of randomly grown individual clusters. Therefore, additional work will focus on an investigation of the characteristics of fractal PMS cluster coating films derived from two-step, acid-base-catalyzed precursors consisting of N-[3-(triethoxysilyl)propyl]-4,5-dihydroimidazole (TSPI), M(OR)_n, methanol, and water, over a broad pH range of 1.0 to 13.0.

3. Crystalline Polyphenyletheretherketone (PEEK)-Based Materials

When melt crystallized polyphenyletheretherketone (PEEK) thermoplastic polymer was used as a high-temperature performance cementitious material, the degree of crystallinity of PEEK was dependent upon gaseous environment present at the polymer melting temperature of > 340°C. Namely, a well-formed PEEK crystal neat cement was assembled by melting-cooling processes in N₂ gas, whereas the oxygen-catalyzed deformation of PEEK structures in air led to a low rate of crystallinity, reflecting a poor thermal stability of cement. With regard to the PEEK mortar specimens made by the same process of the packed PEEK powder-silica sand mixtures at temperatures ranging from 400°C to 25°C, the microstructure of PEEK developed in the vicinity to the SiO₂ sand surfaces in N₂ was characterized by the growth of the crystals possessing transcrystalline textures. The creation of such spherulites at the interfaces

may be due to the nucleation of crystalline PEEK by the SiO_2 . No spherulitic growths were found at the PEEK- SiO_2 interfaces prepared in air. As a result of the formation of well-crystallized PEEK, mortar specimens not only have excellent thermal and hydrothermal stabilities at temperatures up to 200°C, but also maintain strength when exposed in 5 wt% H_2SO_4 at 80°C.

Considering that PEEK is currently utilized as a binder in high performance fiber-reinforced polymer composites, additional work to formulate composite systems will be directed towards, 1) crystallinity-related studies, 2) phase compositions, 3) adhesive mechanisms, and 4) microstructure developments, within PEEK layers adjacent to the fibers.

LIST OF PROGRAM PRESENTATIONS, PUBLICATIONS, AND PATENTS

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T. Sugama, Polyacrylic Acid-Modified Zinc Phosphate Conversion Coatings for Corrosion Protection of Steel. Proceedings of the 1989 Tri-Service Conference on Corrosion, Atlantic City, New Jersey, October 17-19, 1989.

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T. Sugama, Polyacid Macromolecule Primers. United States Patent Number 4,889,718 on Dec. 26, 1989.

T. Sugama, Solid-Gel Precursor Solutions and Methods for the Fabrication of Polymetallosiloxane Coating Films. United States Patent Number 5,110,863 on May 5, 1992.

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