BNL--42547

DE90 000533

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January 1989

Prepared for presentation at the
Tri-Service Corrosion Conference
Showboat Casino Hotel
Atlantic City, New Jersey
October 17 through 19, 1989

PROCESS SCIENCES DIVISION
DEPARTMENT OF APPLIED SCIENCE
BROOKHAVEN NATIONAL LABORATORY
ASSOCIATED UNIVERSITIES, INC.

This work was performed under the auspices of the
U.S. Department of Energy, under contract No. DE-AC02-76CH00016
and supported by the U.S. Army Research Office Program MIPR-ARO-102-89

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POLYACRYLIC ACID-MODIFIED ZINC PHOSPHATE CONVERSION COATINGS FOR CORROSION PROTECTION OF STEEL

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ABSTRACT

Polyacrylic acid, p(AA), electrolyte macromolecules diffused into crystalline zinc phosphate (Zn•Ph) conversion coatings that are precipitated onto cold-rolled steel by dissolution-recrystallization processes, enhance the corrosion protection of steel. One of the specific subserviences was that, when the NaOH-dissolution of Zn•Ph is considered, the Zn-OOC electrostatic bonds at p(AA)-Zn•Ph interfaces are transformed into $Na^{+-}OOC$ ionic bonds which associate with the salt complexed macromolecules. Another is the intermolecular chemical reactions between p(AA) and polymeric topcoats. These contributions relate directly to a lower cathodic delamination rate.

INTRODUCTION

Insoluble crystalline zinc phosphate (Zn•Ph) conversion coatings can be produced on steel surfaces by immersing the surface-cleaned steel substrate into a phosphating solution containing three components, zinc orthophosphate dihydrate [$Zn_3(PO_4)_2 \cdot 2H_2O$], H_3PO_4, and water. The major phase in the conversion coating derived from this simple phosphating solution is the same zinc phosphate dihydrate as that used in the converting solution. This suggests that the conversion to the Zn•Ph occurs through a dissolution-recrystallization process of the original $Zn_3(PO_4)_2 \cdot 2H_2O$ powders. As a result, all of the conversion coatings which are discussed in this paper were prepared using the above process.

When cold-rolled steel surfaces are treated with zinc phosphating solutions containing polyelectrolyte macromolecules having proton-donating type pendant groups such as carboxylic acid or sulfonic acid, several corrosion protective benefits are accrued. The positive surface sites of phosphate crystal embryos at the beginning of the precipitation of Zn•Ph conversion coatings on the steel surface are strongly chemisorbed by the anionically charged segments of the polyelectrolytes.[1-3] This segmental chemisorption of polyanions either on newly precipitated nuclei or on growth sites during the primary crystallization processes, not only acts to array a uniformly packed fine crystal morphology brought about by the suppression and delay of the crystal growth, but also significantly improves the stiffness and ductility characteristics of the normally brittle Zn•Ph layer. Enhancement of adhesion with subsequent polymeric finishers is also obtained. The latter relates directly with the chemical bonds formed at the interface between the functional organic species such as ionic carboxylate and carboxylic acid groups existing at the outer-most surface sites of the conversion coating and the polymeric topcoats.

On the other hand, Leidheiser, et al.[4] have reported that cathodic delamination of polymeric coatings from zinc phosphated steel surfaces is due mainly to alkaline dissolution of the phosphate coating. This is caused by the hydroxyl ions generated by oxygen reduction reactions, $H_2O + 1/2\ O_2 + 2\ e^- = 2\ OH^-$, and the migration of alkali metal cations through the topcoat to the reaction zone for charge balance. Thus, it has been demonstrated that the sodium hydroxide solution dissociates a larger amount of zinc and phosphate ions from the Zn•Ph coating surfaces. Since the OH^- ions which cause delamination at paint/Zn•Ph interfaces form at pores and defects in the Zn•Ph layers, the formation of highly dense, thick, and low porosity conversion coatings should yield inherently slow oxygen reduction kinetics.

Therefore, studies were conducted to explore the effects of polyacrylic acid [p(AA)] polyelectrolyte macromolecules when they are internally diffused throughout the crystalline Zn•Ph, and on the degree of the alkaline dissolution of coatings. Cathodic delamination studies for polyester-modified polyurethane (PU)-coated Zn•Ph specimens were also performed to determine the role of the intermolecular chemical reaction at PU modified Zn•Ph interfaces in reducing the delamination rates of the PU topcoat from the Zn•Ph.

RESULTS AND DISCUSSION

In order to investigate the ability of p(AA)-chemisorbed conversion coatings to provide corrosion protection to steel, p(AA) macromolecules at concentrations of up to 5 wt% were incorporated into a convertible solution consisting of 1.3 wt% $Zn_3(PO_4)_2 \cdot 2H_2O$, 2.7 wt% H_3PO_4 and 96.0 wt% water. Figure 1 shows SEM microtexture views and associated EDX data for the unmodified, and 1 and 2% p(AA)-modified conversion coatings. It is evident from comparisons of the topographical features of the crystals precipitated on the steel surfaces, that the addition of p(AA) serves to decrease the crystal size. This is due primarily to the chemisorption of p(AA) on the precipitated crystal nuclei faces at the beginning of recrystallization processes, thereby suppressing the crystal growth.[3] The accompanying EDX data indicate that the Fe/Zn ratios for the conversion coatings increase with increased p(AA) concentration. Since the only source of Fe is the steel, the extent of suppression of crystal growth by the p(AA) relates directly to the precipitation rate of iron-rich phosphate compounds. At a 5% p(AA) concentration, a further increase in the Fe/Zn ratio was obtained (not shown in figure). The surface morphological image shows two discriminable crystal phases: one is that of a reticular crystal network and the other is the plate-like crystal network. From the EDX quantitative evaluation, the former is associated with the Fe-rich phosphate crystalline coatings and the latter is from the Zn-rich phosphate compounds. The identification of these different phosphate phases was made using x-ray powder diffraction (XRD) with CuK radiation at 50 KV and 16 mA.

As a result, for the 2% p(AA) samples, all of prominent spacing lines in the XRD pattern ascribe to zinc phosphate dihydrate [$Zn_3(PO_4)_2 \cdot 2H_2O$], which is representative of the recrystallization of the starting material dissolved in the phosphating solution.[5] In contrast, the XRD pattern for the 5.0% p(AA) sample has two new spacings at 0.311 and 0.437 nm. These spacings reveal the presence of strengite ($FePO_4 \cdot 2H_2O$).[6] Therefore, the Fe-rich reticular and Zn-rich plate-like crystals which were observed by SEM-EDX analyses, are associated with the formation of $FePO_4 \cdot 2H_2O$ and $Zn_3(PO_4)_2 \cdot 2H_2O$ phases, respectively.

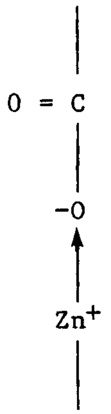
This results in the production of thinner conversion coatings containing a high proportion of ferric phosphate compounds. Thus, the coating thickness and iron content appears to depend on the amount of p(AA). Experimentally, the measured thicknesses for coatings containing 0, 1, 2 and 5% p(AA) were approximately 30, 28, 25 and 20 μm, respectively.

Efforts were made to determine how the proportions of Fe existing in the conversion layers participate in the corrosion protection process. To obtain this information, the polarization behavior of p(AA)-modified conversion specimens in an aerated 0.5M NaCl solution was determined, and the resultant polarization curves were correlated as a function of EDX Fe/Zn ratios for various p(AA) concentrations. These results are given in Figure 2. A comparison of the cathodic polarization areas from the unmodified Zn•Ph and p(AA)-modified Zn•Ph specimens indicates two noteworthy features: (1) the short-term steady-state current value for the modified specimens is lower than that for the unmodified one in the potential region between -1.0 and -1.1 v, and (2) the incorporation of 5% p(AA) resulted in a shift in corrosion potential to a more negative site and an increase in current density at the potential axis. The lower current density for the modified specimens (result No.1 above) compared to that of the specimen without p(AA), is attributed to a low hydrogen reduction as well as to a less active surface. This confirms that the oxygen reduction reaction is inhibited by the p(AA) macromolecule chemisorbed on the crystal faces. With regards to the second observation, the introduction of 5% p(AA) into the conversion layer seemed to reduce the corrosion-resistive effectiveness. From this observation and the previously discussed SEM-EDX data, it can be concluded that the presence of agglomerated strengite in the $Zn_3(PO_4)_2 \cdot 2H_2O$ layer results in an increase in intrinsic phosphate porosity, thereby giving poor corrosion protection.

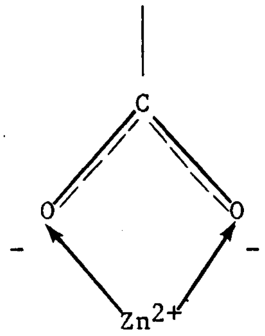
Another important goal of our work was to obtain knowledge regarding possible interactions between p(AA) and the crystal conversion coating, and then to understand how the interfacial reaction products act to increase the corrosion resistance of Zn•Ph-coated steel. The former was investigated by means of XPS, and it was observed that even when a high concentration of 5% p(AA) was used, the p(AA) film deposited at the outermost surface sites was thin enough to see the photoemission signal from the underlying Zn- and Fe- phosphate compounds. The binding energy (BE) scale in the XPS spectra was calibrated with the C_{1s} of the principal hydrocarbon, "CH_n", peak fixed at 285.0 eV as an internal reference standard.

The C_{1s} core level photoemission spectra for bulk p(AA), and 1% p(AA)- and 5% p(AA)- modified conversion coating surfaces are shown in Figure 3. The C_{1s} region of the bulk p(AA) (Figure 3-a) has two main peaks; 285.0 eV corresponds to the hydrocarbons in the main chain and 288.9 eV ascribes to the carbon originating from the carboxylic acid, COOH, in the p(AA). The spectrum for the 5% p(AA)-modified coating (Figure 3-b) shows a shift in the peak to a lower BE site and the appearance of a new peak at 287.2 eV, as compared to that of the bulk p(AA). The new peak emerging at about 1.7 eV lower BE from the COOH peak, is located between a carbonyl carbon, C=O, at approximately 288.0 eV and a carbon-oxygen single bond at approximately 286.5 eV.[7] For samples containing 1% p(AA) (Figure 3-c), a further shift in the COOH peak toward lower BE was observed.

Figure 4 shows typical 2p doublet separation spectra for the Zn2p3/2 and 2p1/2 lines from unmodified and modified conversion coatings. The distance separating the 2p3/2 and the 2p1/2 energies for both the unmodified and modified coatings is in the range of 23.7 to 23.5 eV. This means that the presence of p(AA) in the conversion coatings does not change the separation distance. Therefore, these peaks appear to be assigned to zinc originating from the zinc phosphate dihydrate crystal. The main difference between these spectra is the shift of the 2p3/2 and 2p1/2 peaks to higher energy sites when the p(AA) content is reduced. For 5% and 1% p(AA) concentrations, the values of 1022.5 eV (Figure 4-e) and 1022.9 eV (Figure 4-f) for the 2p3/2 core level correspond to increases of 0.1 and 0.5 eV, respectively, compared to unmodified coatings. The reason for the increased Zn2p peak energy, the decrease in BE of the COOH carbon, and the new peak at 287.2 eV for the C_{1s} region, may be charge transfer from the Zn in the crystal coating to the electron accepting oxygen portion in the functional pendent group of p(AA). In fact, the O_{1s} core level (not shown) at the p(AA)/Zn•Ph interfaces indicated the presence of a strong peak at 531.4 eV which ascribes to the formation of COO-metal complexes. Two possible Zn-O bond formations for carboxylate-linked Zn complexes yielded through a mechanism involving charge transfer reactions at p(AA)-Zn•Ph interfaces are discussed below.



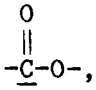
(I)



(II)

One of the complex formations is a zinc-oxygen-carbon (Zn-O-C) bond structure (I) which is produced by the reaction of an oxygen atom in the carboxylic anion with a Zn atom. The other (II) may be formed by a charge transferring interaction between both oxygens in the carboxylate group and the Zn atom. The latter formation relates to the assignment of the new line at 287.2 eV which is situated between the C=O and the C-O bond peaks. It was found that the interfacial reaction products at the p(AA) - Zn•Ph interfaces are Zn-O-C complexes containing an electrostatic bond yielded through the charge transferring reaction.

The studies were extended further to investigate the influence of these interfacial complex products upon the alkali-dissolution of the conversion coatings. Table 1 indicates the changes in the EDX intensity ratios of P/Zn and Fe/Zn, and E_{corr}, as a function of p(AA) for phosphated steel specimens after exposure to a 0.1M NaOH solution for 1 hr at 25°C. As seen in the table, the P/Zn ratios for all exposed specimens are significantly lower than those for the unexposed specimens. All of the Fe/Zn ratios increased. The former suggests the dissociation of a greater amount of phosphate brought about by the alkaline dissolution of Zn•Ph. Thus, this seems to imply that interfacial reaction products composed of Zn-O-C complexes do not significantly inhibit the alkali-dissolution of conversion coatings. However, the differences in Fe/Zn ratios compared with those from the unexposed samples decreased significantly with increased p(AA) concentrations, thereby suggesting that p(AA) macromolecules diffused electrostatically onto Zn•Ph crystal faces act to decrease the rate of ferrous ion dissociation from the steel.

The E_{corr} values for specimens after exposure to NaOH were determined from the polarization curves in aerated 0.5M NaCl solutions. To investigate the variation in Na atom percentages as a function of p(AA), the surfaces of the exposed specimens were also examined using XPS. As noted in Table 1, the E_{corr} values for all the exposed specimens containing p(AA) shifted to less negative positions, as compared to those for the unexposed ones. The largest shift was observed for specimens modified with 5% p(AA). Figure 5 gives comparisons between the C_{1s} spectrum features of 1% p(AA)-modified Zn•Ph before (Figure 5-j) and after (Figure 5-k) exposure to NaOH solutions. The most striking features in the spectrum of the exposed samples were the shift in the carboxyl carbon,  $-\underline{\overset{\overset{O}{\|}}{C}}-O-$, peak to a higher BE site, and a decrease in intensity of the peak at 287.2 eV, while maintaining the same position of hydrocarbons at 285.0 eV. In conjunction with the increase of 0.3 eV in the BE of carboxyl carbon, there was a corresponding decrease in the BE in the Zn2p3/2 region for the sample subjected to NaOH exposure (see Figure 6-m), as compared with that of the unexposed sample (Figure 6-l). The excitation of the new line at 1020.4 eV for the exposed samples is assigned to the formation of new Zn-based compounds brought about by the alkali-dissolution of the conversion coating. This seems to suggest that during the exposure to the NaOH solution, Na ions act to promote the breakage of the Zn-OOC electrostatic bonds. The breakage may be related to an elemental substitution of Zn for Na. However, the corresponding Na_{1s} core level spectra have not yet been clearly resolved because of a very noisy exciting peak feature.

On the basis of the above information, the following statements can be made regarding the function of p(AA) in reducing the dissociation of Fe and improving the protection of the conversion coatings when subjected to NaOH. When the p(AA)-modified conversion coatings come in contact with a NaOH solution, the reactive Na^+ ion will break the Zn-OOC electrostatic bonds in the interfacial reaction products to form a $-COO^- Na^+$ salt complex which contains an ionic bond. This transformation from a Zn-O electrostatic bond to a Na-O ionic bond can be expressed as follows:

$$\text{-COO-Zn- +2NaOH} \longrightarrow \text{-COO}^- \text{ Na}^+ + \text{NaO-Zn-} + H_2O$$

It can therefore be assumed that the precipitation of a salt complexed macromolecule formed by an ionic reaction between the carboxylic anion and the Na^+ cation during the progression of the alkaline dissolution of the conversion layers can serve as a barrier to the ferrous ion dissociation from the steel. This reflects on the corrosion resistance of the steel.

The effect of p(AA) macromolecules existing at the outermost surface sites of the modified Zn•Ph coatings on the resistance to the cathodic delamination of the polymeric topcoat from the Zn•Ph, was also investigated. In these studies, a polyester-modified polyurethane (PU) topcoat was applied to modified Zn•Ph specimens. The cathodic delamination tests for the PU-coated Zn•Ph specimens were conducted in an air covered 0.5M NaCl solution using an applied potential of -1.5 volts vs SCE for up to 6 days. A defect was made using a drill bit with a diameter of approximately 1 mm. After exposure, the specimens were removed from the cell and allowed to dry. The PU coating was removed by cutting, and a delaminated region which appeared as a light gray area adjacent to the defect, was detected. These test results are reported in Table 2. The PU to-blank steel joint systems exhibited considerable delamination of the PU after exposure for only one day. In contrast, the presence of a conversion coating as an intermediate layer in the PU/steel joint system significantly reduced the rate of cathodic delamination. Further improvement was obtained using the p(AA)-modified conversion coating systems. As seen in table, the delamination rates for the 6 day-exposed specimens decrease with increased p(AA) concentrations ranging from 1 to 5%.

In the PU/p(AA)-modified coating joint systems, the major reason for reducing the rate of delamination is the intermolecular chemical reactions between the carboxylic acid groups of p(AA) existing at the outermost surface sites of the conversion coating and the isocyanate groups of PU. The interfacial reaction product formed through the interaction mechanism given below could result in a lower susceptibility to hydrolysis of the particular isocyanate which is essentially hyrolyzed to substitute the primary amine in the presence of NaOH.[8,9]

$$\text{-R-NCO + HOOC-R-} \longrightarrow \text{-R-NH-CO-O-CO-R-} \longrightarrow \text{-R-NH-CO-R-} + CO_2$$

The above statements suggest that the initial failure in this joint system occurs at the conversion coating/steel interface, in contrast with the PU/conversion coating interfacial regions for the PU-unmodified coating joint systems.

CONCLUSIONS

The following generalizations can be drawn from our results.

1. The precipitation of a dense crystalline conversion coating on cold-rolled steel by a dissolution-recrystallization process using zinc orthophosphate dihydrate as a starting material, considerably reduced the corrosion rate of steel in an aerated NaCl solution.

2. When modified with p(AA) electrolyte macromolecules, the conversion coatings yield low hydrogen evolution as well as a less active surface.

3. The precipitation of a large amount of strengite, $FePO_4 \cdot 2H_2O$, formed by adding an excessive amount of p(AA), seems to result in a less effective protective coating.

4. The interfacial reaction products at the p(AA)-zinc phosphate interfaces, were identified to be Zn-OOC complexes yielded by a charge transfer reaction between Zn atoms in the crystalline conversion coating and the electron accepting oxygen portions of the p(AA).

5. The resultant Zn-O electrostatic interfacial bond had no significant effect on the rate of alkaline dissolution of conversion coatings subjected to NaOH exposure, because of the breakage of the Zn-O bond by the attack of reactive Na^+.

6. The formation of $-COO^- Na^+$ salt complexed macromolecules precipitated by transformation of Zn-O electrostatic bonds into Na-O ionic bonds are subservient to the corrosion resistance of steel.

7. The intermolecular chemical reaction between the carboxylic groups of the p(AA) existing at the outermost surface sites of the conversion coating and the isocyanate groups in polyurethane topcoats led to a lower rate of cathodic delamination of the polyurethane film from the substrate. Thus, the beginning of the delamination failure occurs through the conversion coating/steel interface, as compared to that at the polyurethane/conversion coating interface in the polyurethane unmodified coating joint system.

REFERENCES

1. Sugama, T., Kukacka, L.E., Carciello, N., and Warren, B., "Polyacrylic Acid Macromolecule - Complexed Zinc Phosphate Crystal Conversion Coatings," J. Appl. Polymer Sci., 30, 4357 (1985).

2. Sugama, T., Kukacka, L.E., Carciello, N., and Warren, B., "Factors Affecting Improvement in the Flexural Modulus of Polyacrylic Acid-Modified Crystalline Films," J. Appl. Polymer Sci., 32, 3469 (1986).

3. Sugama, T., Kukacka, L.E., Carciello, N., and Warren, B., "Chemisorption Mechanism and Effect of Polyacrylic Acid on the Improvement in Bond Durability of Zinc Phosphate-to-Polymer Adhesive Joints," J. Mater. Sci., 22, 722 (1987).

4. Sommer, A. J. and Leidheiser, H. Jr., "Effect of Alkali Metal Hydroxides on the Dissolution Behavior of a Zinc Phosphate Conversion Coating on Steel and Pertinence to Cathodic Delamination," Corrosion, 43, 661 (1987).

5. Joint Committee on Powder Diffraction Standards, Card 30-1491.

6. Joint Committee on Powder Diffraction Standards, Card 33-667.

7. Bartha, J.W., Hahn, P.O., LeGoues, F., and Ho, P.S., "Photoemission Spectroscopy Study of Aluminum - Polyimide Interface," J. Vac. Sci. Technol., 3, 1390 (1985).

8. Sugama, T., Kukacka, L.E., Clayton, C.R., and Hua, H.C., "Effects of Polyacrylic Acid Primers on Adhesion and Durability of FPL-Etched Aluminum/Polyurethane Systems," J. Adhesion Sci. Tech. 1, 265 (1987).

9. Arnold, R.G., Nelson, J.A., and Verbanc, J.J., "Chemistry of Organic Isocyanates," p. 13. E.I. duPont de Nemours, Wilmington, DE (1956).

Table 1. Variations in P/Zn and Fe/Zn Intensity Count Ratios and Corrosion Potential Values, E_{corr}, as a Function of p(AA) Concentration for Phosphated Steel Specimens After Exposure to 0.1M NaOH Solution.

PAA,	Before Exposure			After Exposure		
%	P/Zn	Fe/Zn	E_{corr}, Volt	P/Zn (Difference*)	Fe/Zn (Difference)	E_{corr}, Volt
0	0.55	0.49	-0.592	0.26 (-52.7%)	0.72 (+46.9%)	-0.620
1	0.54	0.56	-0.595	0.24 (-55.6%)	0.75 (+33.9%)	-0.540
2	0.57	0.60	-0.610	0.23 (-59.7%)	0.79 (+31.7%)	-0.521
5	0.55	0.74	-0.651	0.25 (-54.6%)	0.89 (+20.3%)	-0.480

*Difference compared with that of unexposed specimen; difference, % = [(ratio of exposed specimen - ratio of unexposed specimen)/ratio of unexposed one] x 100.

Table 2. Comparison Between the Delaminated Areas of Polyurethane-Coated Steel, Unmodified Zn•Ph, and p(AA)-Modified Zn•Ph Panels Exposed to 0.5M NaCl Solution.

p(AA), %	Delaminated Area, mm^2		
	1 Day	3 Day	6 Day
PU/Steel Joint	113	1256	---
0	0.8	4.9	19.6
1	0.2	2.5	10.8
2	0.2	0.9	7.1
5	0.2	0.9	4.9

P(AA): 0%

Element	Intensity Counts/100 sec.	Intensity ratio/Zn
Fe	18134	0.49
Zn	36843	1.00
P	20107	0.55

P(AA): 1.0%

Element	Intensity Counts/100 sec.	Intensity ratio/Zn
Fe	19068	0.56
Zn	34050	1.00
P	18387	0.54

P(AA): 2.0%

Element	Intensity Counts/100 sec.	Intensity ratio/Zn
Fe	18368	0.60
Zn	30611	1.00
P	17295	0.57

Figure 1. SEM photographs and associated EDX data for unmodified and p(AA)-modified conversion coatings.

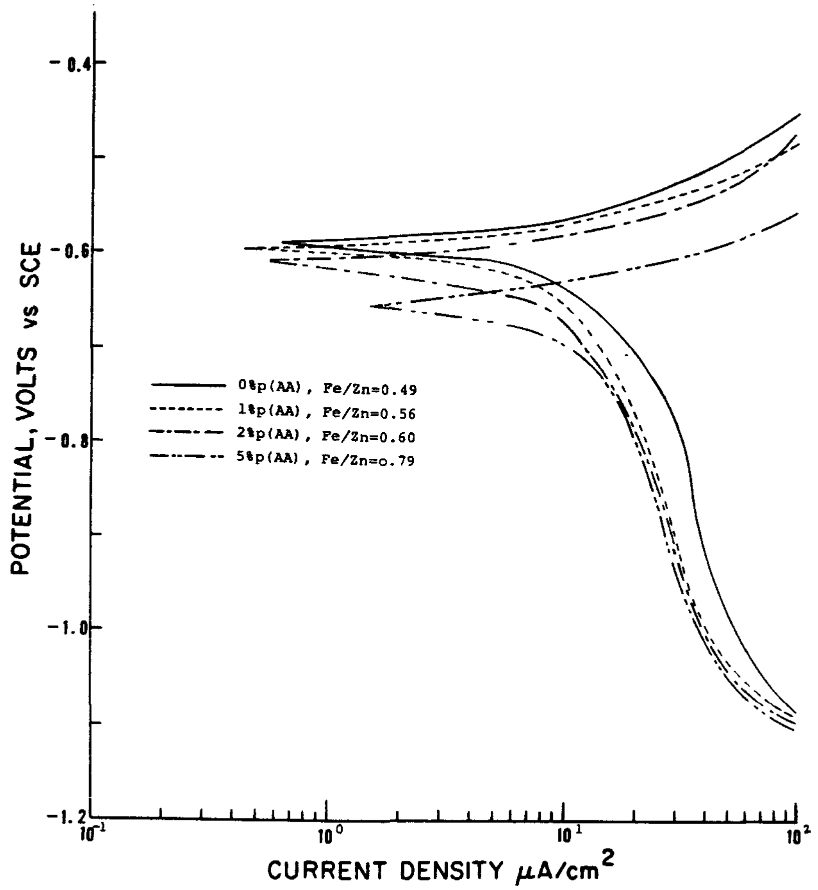


Figure 2. Polarization curves for zinc phosphated steel specimens containing p(AA) concentrations of up to 5% in aerated 0.5M NaCl solutions.

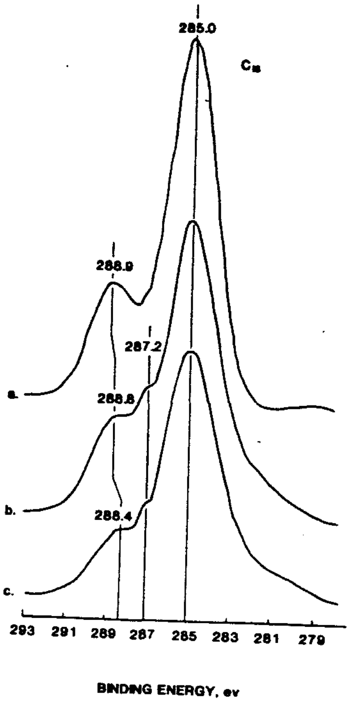


Figure 3. C_{1s} spectra for bulk p(AA) (a), 5% p(AA)-Zn•Ph interface, (b) and 1% p(AA)-Zn.Ph interface (c).

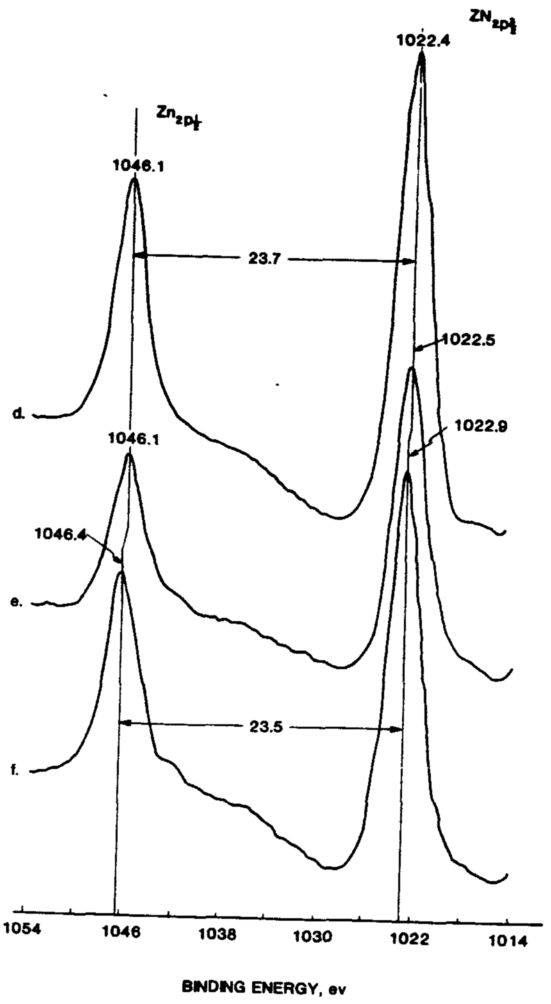


Figure 4. Zn2p separation spectra for unmodified Zn•Ph (d), 5% p(AA)-modified (e) and 1% p(AA)-modified Zn•Ph (f).

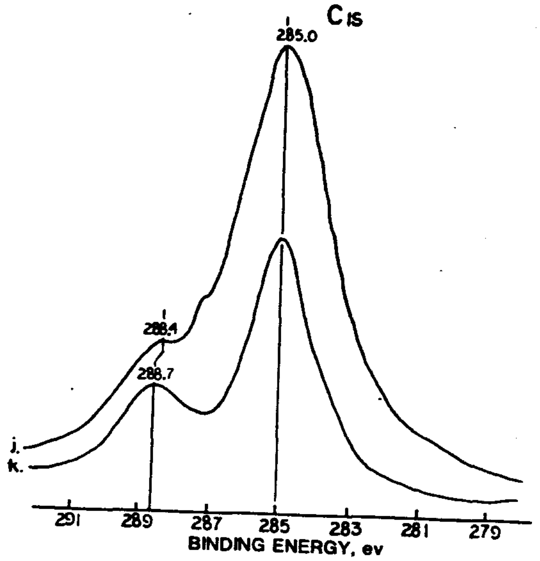


Figure 5. C_{1s} spectra for 1% p(AA)-modified Zn•Ph before (j) and after (k) exposure in 0.1M NaOH solution.

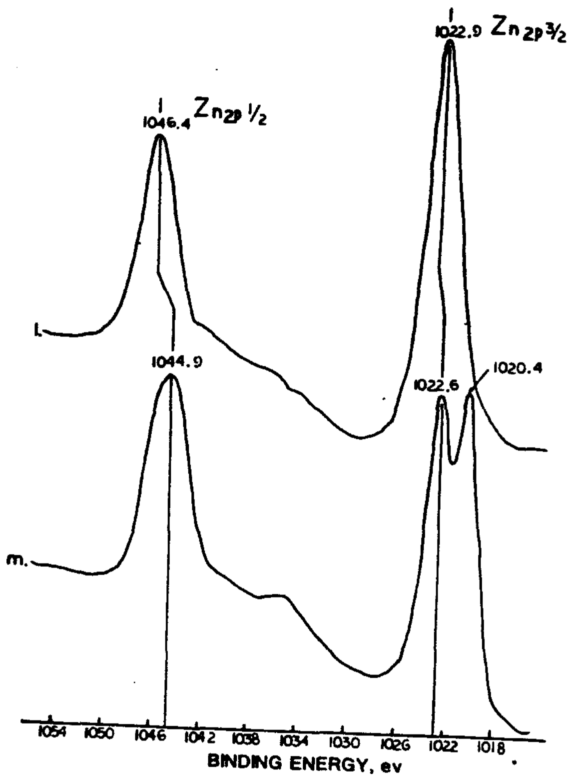


Figure 6. Zn2p regions for unexposed (l) and NaOH - exposed p(AA)-Zn•Ph (m).