

# **Alternative to Chrome Etching Processes for Metals**

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<p>Several industries, including the National Center for Manufacturing Science, have initiated programs for chrome abatement. The programs, however, generally focus on chrome reduction by use of existing technologies and do not address the elimination of chrome in pretreatment processes by new technology development. It is proposed to evaluate polymeric coupling agents as replacements for chromium pretreatment processes on aluminum and steel.</p> <p>Polymeric coupling agents offer a practical alternative and improvements to chrome etching pretreatments presently utilized on aluminum and steel. Polymeric coupling agents are molecules that have the ability to chemically react with both the metal substrate and wide variety of polymer top coats, thus forming a "bridge" between them. The coupling agents can be tailored to specific systems, depending on the functionalities of the polymer top coat and the reactivity of the metal substrate. Bond failure caused by environmental factors (humidity, etc.) can be greatly reduced. In addition, polymeric coupling agents are able to distribute mechanical and thermal stresses near the metal interface thereby reducing internal stress concentrations that result in bond failure.</p> <p>A copolymer has been polymerized containing both b-diketone and epoxy functional groups. This copolymer is being evaluated as a potential polymeric coupling agent for bonding polymers to aluminum. X-ray Photoelectron Spectroscopy indicates interaction of the coupling agent with the aluminum oxide surface. Etched coupling agent treated joints exhibited improved joint strengths after immersion in water. Coupling agent treated aluminum substrates displayed improved corrosion resistance after ASTM B117 salt spray chamber exposure as compared to untreated controls.</p> <p>Quinone-amine polyurethanes (QAPs) are being evaluated as potential polymeric coupling agents for the steel-epoxy system. Infrared Spectroscopy and X-ray Photoelectron Spectroscopy indicate chemical interactions of the coupling agent with both the steel and epoxy surfaces. Quinone-amine treated steel substrates exhibited increased joint shear strengths as compared to untreated controls. Increases in both hot water stability and corrosion resistance were also observed for coupling agent treated substrates. X-ray Photoelectron Spectroscopy and Scanning Electron Microscopy investigations suggest that failure is occurring within the epoxy layer.</p>					
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## **Foreword**

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**E. Timothy Oppelt, Director  
National Risk Management Research Laboratory**

## **Abstract**

Several industries, including the National Center for Manufacturing Science have initiated programs for chrome abatement. The programs, however, generally focus on chrome reduction by use of existing technologies and do not address the elimination of chrome in pretreatment processes by new technology development. It is proposed to evaluate polymeric coupling agents as replacements for chromium pretreatment processes on aluminum and steel.

Polymeric coupling agents offer a practical alternative and improvements to chrome etching pretreatments presently utilized on aluminum and steel. Polymeric coupling agents are molecules which have the ability to chemically react with both the metal substrate and wide variety of polymer top coats, thus forming a "bridge" between them. The coupling agents can be tailored to specific systems, depending on the functionalities of the polymer top coat and the reactivity of the metal substrate. Bond failure caused by environmental factors (humidity, etc.) can be greatly reduced. In addition, polymeric coupling agents are able to distribute mechanical and thermal stresses near the metal interface thereby reducing internal stress concentrations which result in bond failure.

A copolymer has been polymerized containing both b-diketone and epoxy functional groups. This copolymer is being evaluated as a potential polymeric coupling agent for bonding polymers to aluminum. X-ray Photoelectron Spectroscopy indicates interaction of the coupling agent with the aluminum oxide surface. Etched coupling agent treated joints exhibited improved joint strengths after immersion in water. Coupling agent treated aluminum substrates displayed improved corrosion resistance after ASTM B117 salt spray chamber exposure as compared to untreated controls.

Quinone-amine polyurethanes (QAPs) are being evaluated as potential polymeric coupling agents for the steel-epoxy system. Infrared Spectroscopy and X-ray Photoelectron Spectroscopy indicate chemical interactions of the coupling agent with both the steel and epoxy surfaces. Quinone-amine treated steel substrates exhibited increased joint shear strengths as compared to untreated controls. Increases in both hot water stability and corrosion resistance were also observed for coupling agent treated substrates. X-ray Photoelectron Spectroscopy and Scanning Electron Microscopy investigations suggest that failure is occurring within the epoxy layer.

This report was submitted in fulfillment of Cooperative Agreement No. CR821875 by the University of Connecticut. This report covers a period of time from October 1993 to October of 1995.

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## Chapter 1

### Introduction

The National Center for Manufacturing Sciences and many industrial companies have initiated major programs concerning chrome abatement. Such programs, however, are generally limited to reducing the quantity of chromium compounds utilized annually in existing products and technologies and do not address the elimination of chrome use through new, longer term technology development [1]. Acidic chromium oxide, chromic acid or dichromate salts are widely utilized in etching or sealing pretreatment of aluminum and steel parts prior to bonding to adhesives or application of various organic coatings, for the purpose of promoting durable adhesion. A list of applications for chrome in surface etching, preparation, and cleansing baths is shown below [2 and 3].

- **Chromic acid deoxidizing/desmutting** - chromic acid is used to remove the natural metal oxide and other surface contaminants to prepare a surface for plating, painting, or other surface treatment.
- **Chromic acid etch** - chromic acid roughens surfaces to improve coating adhesion.
- **Chromic acid anodize** - anodizing is a process for treating aluminum to give a highly corrosion-resistant coating that offers an excellent surface for bonding and painting. Anodizing uses electrochemical methods to form a thin aluminum oxide layer that contains chromium ions.
- **Sealing** - Sodium dichromate as a sealant enhances fatigue properties by anodizing and by depositing oxydichromate onto the anodized layers.
- **Chemical film** - chromate solutions can be used to chemically deposit a thin film to prepare metal surfaces for subsequent coating application.

The key factor in these processes for promotion of durable adhesion is hexavalent chromium ions, which are water soluble and very toxic to most species of aquatic life as well as to humans and animals [4-6]. Present chemical processes to remove chromium from effluent baths include reduction of the hexavalent chromium to the trivalent form by sodium sulfite, followed by precipitation, electroplating, ion exchange or electrowinning, or reverse osmosis [7]. Precipitated chromium compounds are then disposed of in landfills with possible legal ramifications, or recycled at high cost. Concentrated solutions may be reused or recycled.

Although optimization of standard technologies can result in a reduction of the quantity of toxic chromium compounds utilized in industrial pretreatment processes, it is only through the elimination of chromium pretreatment processes that contamination will be completely avoided. Elimination of chromium pretreatment processes requires the development of new technologies, through fundamental research, that yield coating bond strengths and bond durabilities comparable to those of chrome pretreated surfaces, without the use of chromium compounds. The objective of this research was to investigate polymeric coupling agents as potential replacements for chromium compound pretreatments.

Use of polymeric coupling agents offers a practical alternative and improvement to the chrome pre-treatments presently utilized on aluminum and steel [8-13]. From the environmental aspect, the elimination of the chrome etching

process would greatly reduce a source of toxic hexavalent chromium. Polymeric coupling agents are typically applied from solutions of less than 0.1 wt% coupling agent, thus significantly limiting quantities for disposal. Solution compositions will be dependent upon the coupling agent under study, however a major focus during coupling agent development will be low toxicity. In addition, the polymeric coupling agent solutions will likely be recyclable.

Polymer coupling agents offer a wide range of advantages in addition to the environmental issue. Of primary interest is that coupling agents can be optimized for a specific metal/polymer system, reacting with the functionalities of the metal and polymer substrate which are to be bonded. In addition, the functionalities and their relative concentrations on the coupling agent backbone can be tailored to improve environmental resistance to bond failure. For example, the coupling agent can be made hydrophobic to enhance corrosion resistance. The porous nature of the oxidized aluminum surface facilitates both mechanical interlocking and chemical (ionic or covalent) bonding to active surface moieties. Another advantage of polymeric coupling agents is that they are able to absorb and distribute mechanical and thermal stresses within the bond, thereby reducing internal stress concentrations which result in bond failure.

In contrast to "primers", coupling agents form true, verifiable chemical (ionic or covalent) bonds to both the metal oxide and the polymer substrate, whereas primers typically enhance wetting or other physical surface interactions. In addition, a true coupling agent is optimal at a thickness of 150Å. Primers are typically applied in layers on the order of microns in thickness [8].

Scientific evaluation of organic coupling agents on metals, other than silanes and titanates, has been very limited. Silanes and titanates have been discussed in a review by Comyn [13]; while evidence of chemical attachment of these two agents has been found, the improvement in mechanical properties of adhesive joints relative to controls is not substantial in many instances, especially when water is present.

The objective of this research was to develop and/or identify suitable polymeric coupling agents for bonding polymers to aluminum and steel, thus eliminating the use of the environmentally unfriendly chromium pretreatments and ultimately yielding bond strengths and bond durability equal or superior to current levels.

## Coupling Agent Selection

### Aluminum

Investigations of a  $\beta$ -diketone functionalized copolymer as a potential polymeric coupling agent are presently in progress.  $\beta$ -diketones have been shown to form stable chelates with a variety of metals and metal oxides [14 and 15]. These metal  $\beta$ -diketonates behave as inner complexes, showing predominantly covalent behavior [15]. Figure 1 shows the general structure of an oxygen-bonded  $\beta$ -diketone. Low molecular weight  $\beta$ -diketones have also been shown to exhibit corrosion resistance and improve coating adhesion on aluminum substrates [14].

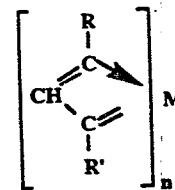


Figure 1. General structure of an oxygen-bonded  $\beta$ -diketone.

## *Steel*

Quinone-amine polymers have been shown to adhere strongly to metals and alloys and greatly improve corrosion resistance of iron particles [16]. The corrosion resistance has been attributed to the presence of functional groups that can function as moisture resistant adhesion promoters [16-18]. A significant example is that they have been shown to displace water from wet, rusty steel surfaces [18]. Figure 2 shows the

chemical structures of the components of the copolymer. By altering the relative ratios of the components in the copolymerization we are able to vary the amount of soft segment, diol, in the copolymer, thus enabling us to produce an entire range of coupling agents with varying degrees of molecular flexibility. Reactivity of the QAPs with the organic top coat is under investigation.

## Chapter 2

### Conclusions

#### Aluminum

A copolymer has been polymerized containing both  $\beta$ -diketone and epoxy functional groups. This copolymer is being evaluated as a potential polymeric coupling agent for bonding polymers to aluminum. X-ray Photoelectron Spectroscopy indicates interaction of the coupling agent with the aluminum oxide surface. Etched coupling agent treated joints exhibited improved joint strengths after 3 and 5 days immersion in 57° C water. Coupling agent treated aluminum substrates displayed improved corrosion resistance after 24 hours in an ASTM B117 salt spray chamber as compared to untreated controls.

Coupling agent treated aluminum substrates will be sent to Astroseal Products Manufacturing Co., Inc., Old Saybrook, CT and ALCOA, Alcoa, PA for evaluation during the first quarter of 1996. Both companies have expressed interest in sample evaluation and assistance with commercialization of viable products and technologies.

The results of this research were presented at four national conferences: Annual Adhesion Society Meeting, February 17-21, 1995, Hilton Head, SC; SAMPE's 27th International Technical Conference, October 7-12, 1995, Albuquerque, NM; AIChE Annual Meeting, November 12-17, 1995, Miami, FL; and the Annual Adhesion Society Meeting, February 18-22, 1996, Myrtle Beach, SC.

#### Steel

Quinone-amine polyurethanes (QAPs) are being evaluated as potential polymeric coupling agents for the steel-epoxy system. Infrared Spectroscopy and X-ray Photoelectron Spectroscopy indicate chemical interactions of the coupling agent with both the steel and epoxy surfaces. Quinone-amine treated steel substrates exhibited increased dry joint shear strengths as compared to untreated controls. The increase in joint strength is directly related to both the amount of quinone-amine moieties in the coupling agent and the concentration of the coupling agent solution. Increases in both hot water stability and corrosion resistance were also observed for coupling agent treated substrates. X-ray Photoelectron Spectroscopy and Scanning Electron Microscopy investigations suggest that failure is occurring within the epoxy layer. Preliminary investigation of  $\beta$ -diketone, silane and thiol functionalized polymers indicate good promise for use as coupling agents for the steel-epoxy system.

Samples have been sent to Inland Steel, East Chicago, IL, United Technologies, East Hartford, CT, and Hamilton Standard, Windsor Locks, CT, for evaluation. These companies have also expressed interest in sample evaluation and assistance with commercialization of viable products and technologies.

These results have been presented at a poster session in the 18th Annual Adhesion Society Meeting, February 19-

22, 1995 at Hilton Head, SC and in a talk at the Society of  
Plastics Engineers Meeting (ANTEC 95), May 7-11, 1995 in  
Boston, MA. The final results will also be presented in a talk  
at the 19th Annual Adhesion Society Meeting, February 1996  
at Myrtle Beach, SC.

## **Chapter 3**

### **Recommendations**

Coupling agent treated steel and aluminum substrates exhibited both increased joint strengths and improved corrosion resistance as compared to untreated controls. In addition, spectroscopic analysis indicates chemical interaction between the coupling agents with both the metal and polymer substrates. As a method of direct comparison, similar joint strength and corrosion resistance evaluations must be performed on chromium pretreated substrates. Further work is

required in the area of optimizing the coupling agent treatment process. Development on the quinone-amine coupling agent system for steel should continue in direct conjunction with industrial partners in order to insure optimization proceeds in a direction toward potential commercialization. The aluminum coupling agent system requires additional research in the area of coupling agent development as well as process optimization.

## Chapter 4

### Experimental

#### Aluminum

Synthesis of 7-octen-2,4-dione was performed via Claisen condensation of ethyl acetate and 5-hexen-2-one. To a suspension of 0.1 mole of sodium methoxide (Fisher) in 85 ml of tetrahydrofuran was added dropwise 0.1 mole of 5-hexen-2-one (Aldrich), with stirring. Upon addition, the mixture was allowed to continue stirring 15 minutes at room temperature. This was followed by the dropwise addition of 0.1 mole ethyl acetate (Aldrich). The reaction vessel was fitted with a condenser and heated at reflux for 24 hours. The tetrahydrofuran was removed via rotary evaporator. The remaining residue was dissolved in distilled water and the excess reagents were removed by ether extraction. The  $\beta$ -diketone was released from its sodium complex by adjusting the pH to 5 with a 10% solution of hydrochloric acid. The  $\beta$ -diketone was separated via extraction with ether. Evaporation of the ether revealed a red-brown liquid. The product was confirmed by infrared, positive test with iron (III), and the green copper chelate formation.

The 2-(methacryloyloxy)ethyl acetoacetate copolymer was formed via radical polymerization of 0.10 mole 2-(methacryloyloxy)ethyl acetoacetate (Aldrich), MAEAA, with  $0.37 \times 10^{-1}$  mole glycidyl methacrylate (Acros) in 50 ml of acetone at 68° C for five hours.  $0.34 \times 10^{-3}$  moles of benzoyl peroxide (Aldrich) were utilized as the initiator. The copolymer was precipitated in methanol. Solution NMR of the copolymer suggests copolymerization is in a ratio of 2 epoxy groups to 1 MAEAA group. The presence of the  $\beta$ -

diketone was verified by formation of the solid green copper chelate of the copolymer.

Two pretreatment processes were employed prior to coupling agent application, degreasing and an etch. The degreasing process consisted of immersion in methanol for 30 minutes, wiping with a lint-free methanol soaked cloth, and air drying. Samples subjected to the etch pretreatment were immersed in a 5% sodium hydroxide solution, at 90° C for 1 minute, rinsed in distilled water, and desmuted. Desmuting was accomplished via immersion in a 20% nitric acid solution at room temperature for 5 minutes followed by a distilled water rinse and air drying.

X-ray Photoelectron Spectroscopy (XPS) experiments were conducted on a 5300 Series Perkin-Elmer XPS. All data was collected at a pressure less than  $2 \times 10^{-8}$  torr, 15.0 kV, and 600 watts. Curve fitting was performed on high resolution spectra collected with a pass energy of 8.45 eV.

Modified torsional shear joints, Figure 2, were utilized to evaluate the joint strength and durability. Joint halves were pretreated and air dried [19]. If the joints were to receive the coupling agent treatment it was then applied.  $44\text{mg} \pm 1$  of epoxy resin (Epon 828 and 4,4'-methylenedianiline, 28phr) was applied to the raised annulus of the torsional joint, the joint halves bonded together and the entire joint cured at 120°C for one hour and 150°C for two

hours. Joint durability studies were conducted by immersing cured joints into 57°C water for varying lengths of time (days) and measuring the joint strength after removal from the water.

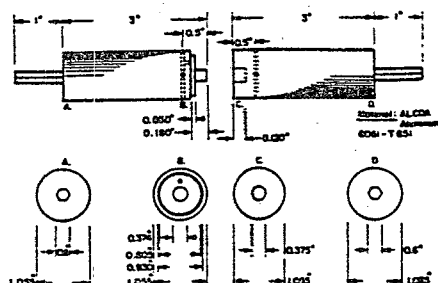
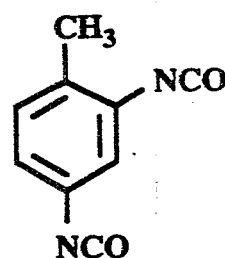


Figure 2. Modified torsional shear joint [19].

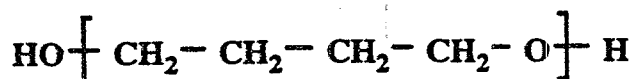
## Steel

Three quinone-amine polyurethanes (QAPs), a low molecular weight  $\beta$ -diketone (Benzoyl acetone), 2 Silanes (3-glycidoxypopyltrimethoxysilane and 3-aminopropyl-triethoxysilane) and PETM (Pentaerythritol tetramercaptopropionate) have been used as coupling agents for the epoxy-steel system. The low molecular weight  $\beta$ -diketone and the silanes were purchased from the Aldrich Chemical company. The silanes were purified prior to use. PETM was purchased from Pfaltz and Bauer Inc.

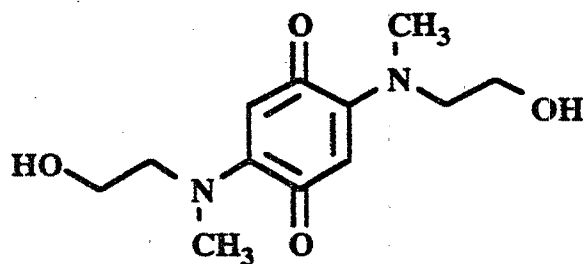
The QAPs compounds were synthesized by Dr. Nikles's group at the CMIT, Univ. of Alabama, by a two step process. The first step gives a prepolymer with a hard block, to which a soft segment diol is reacted subsequently to give the block-copolymer. The QAPs contain 40%, 20% and 30% of the amine-quinone monomer (AQM-1) and stoichiometric amounts of TDI and Tetrathane 650 (Polytetrahydrofuran of mol. wt. 650) (Figure 3).



(a)



(b)



(c)

Figure 3. Chemical structures of the components of the quinone-amine copolymer: a) toluene diisocyanate, b) tetrathane, c) amine-quinone monomer 1.

The hard segment content of these segmented polyurethanes were 67%, 34% and 51% respectively. The AQM was made from 1,4-benzoquinone and 2-(N-methylamino) ethanol. A low-molecular weight amine quinone monomer (AQM-2) was made to aid in surface studies. The polymers have been characterized by IR spectroscopy, thermal analyses (TGA and DSC) and GPC.



The conditions for the surface preparation of the joints were optimized. The following surface treatment was found to be the best for the steel joints. The joints were immersed in a 3% citric acid aqueous solution with the pH of the solution adjusted to the value of 7 using ammonium hydroxide. This solution was maintained at a temperature of 70° C. After ten minutes, the joints were immersed in distilled water to remove the excess of the acid followed by an immersion in methanol to remove the excess of water. Next, the joints were immersed in a dilute solution of the coupling agent in the appropriate solvent. The solvents used were THF for the QAP, methanol-water for the silanes (fresh solutions), and methanol for the low molecular weight  $\beta$ -diketone and the PETM. The excess coupling agent was washed off with solvent and the surface dried. A stoichiometric amount of Epon 828® epoxy resin and a methylene dianiline (MDA) curing agent were mixed, and a calculated quantity of this resin was applied to each joint. The joints were subjected to a cure cycle of 120°C for 1 hour followed by 150°C cure for 2 hours. Finally, the joints were cooled in air.

The surface of steel coupons were analyzed after the application of the QAP or the low molecular weight  $\beta$ -diketone using IR Reflectance Microscopy, ATR-IR (Attenuated Total Reflectance Infrared Spectroscopy). IR was used in the transmittance mode to study the interaction of QAP with the Epoxy.

X-ray Photoelectron Spectroscopy (XPS) experiments were conducted on a 5300 Series Perkin-Elmer XPS. All data was collected at a pressure less than  $2 \times 10^{-8}$  torr, 15.0 kV, and 600 watts. Curve fitting was performed on high resolution spectra collected with a pass energy of 8.95 eV. XPS (X-ray Photoelectron Spectroscopy) studies were done on the bare metal surface and the QAP coupling agent

treated surfaces. The spectra were obtained after treatment of the steel coupons with the QAPs and washing off the excess coupling agent using pure solvent.

The locus of failure analysis was done by analyzing fracture surfaces (broken in pure shear) of steel-epoxy lap shear joints made with the QAPs as the coupling agents. XPS and Scanning Electron Microscopy (SEM) were used in tandem to analyze these fracture surfaces.

The corrosion resistance of steel coupons coated with the coupling agent followed by epoxy resin were evaluated in accordance to ASTM B117 standard test method of salt spray (fog) testing using a lab scale salt spray apparatus. The samples were held in a mist of salt water for a period of 10 days and analyzed qualitatively.

## Chapter 5

### Results and Discussion

#### Aluminum

##### 7-octen-2,4-dione Synthesis

We have successfully synthesized a polymerizable  $\beta$ -diketone, 7-octen-2,4-dione, Figure 4. Preliminary investigation of the interaction of 7-octen-2,4-dione with an aluminum oxide substrate via Reflection-Absorption Infrared Spectroscopy suggests the formation of a chelate between the  $\beta$ -diketone and aluminum in the aluminum oxide layer. Figure 5a is a spectrum of 7-octen-2,4-dione on an aluminum substrate. The peak at  $1703\text{ cm}^{-1}$  corresponds to that of the free ketone and the peak at  $1612\text{ cm}^{-1}$  to the enolic form of the diketone tautomer, Figure 6. The absence of the peak at  $1703\text{ cm}^{-1}$  in Figure 5b, after thorough washing of the substrate, suggests that the only  $\beta$ -diketone that remains on the aluminum substrate after washing is in a 6-membered ring formation or is chelated with aluminum in the oxide layer. Figure 7. Similar results have been reported by Allara for 2,4-pentanedione on aluminum substrates [20].

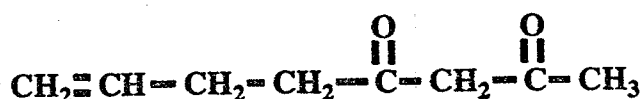


Figure 4 Chemical structure of 7-octen-2,4-dione

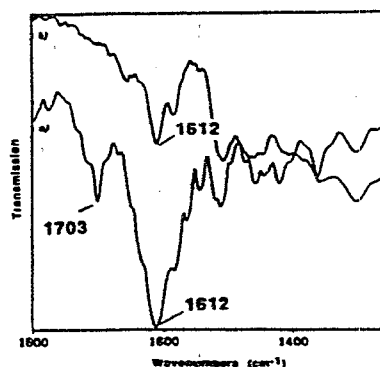


Figure 5. Reflection-Adsorption Infrared spectra of a) a thick layer of 7-octen-2,4-dione on an aluminum substrate, and b) the sample from (a) after thorough rinsing with methanol.

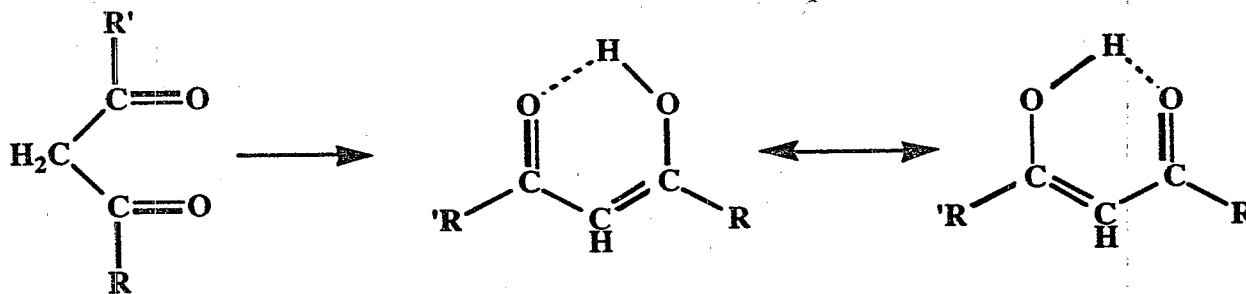
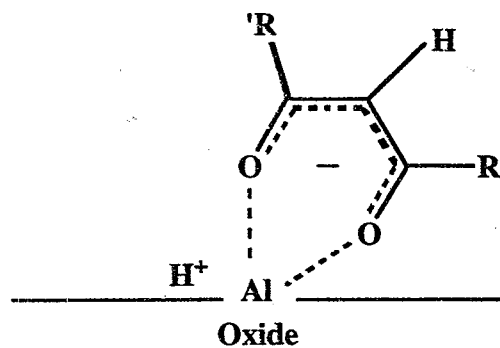


Figure 6. Tautomeric forms of  $\beta$ -diketones.



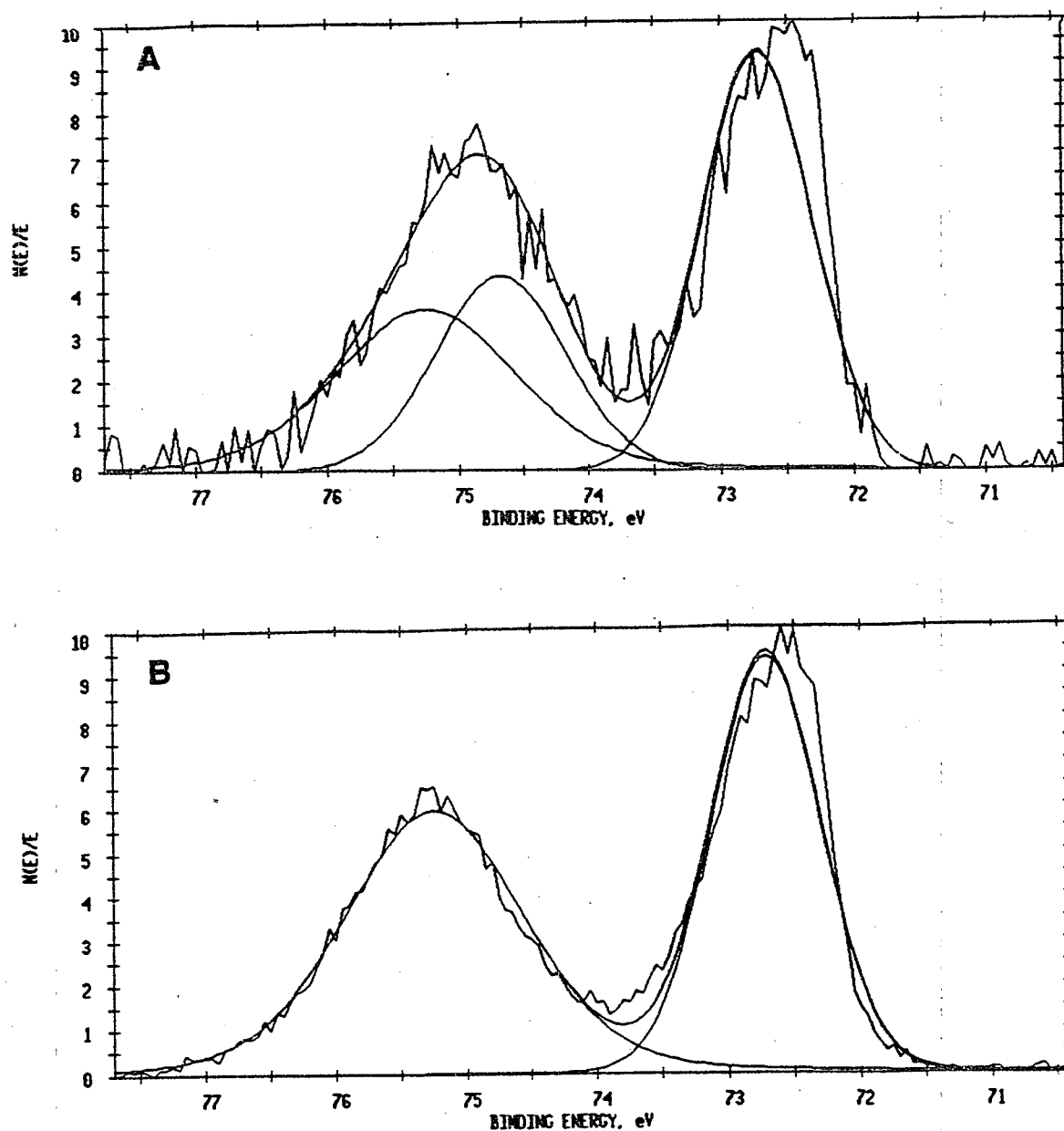
**Figure 7.** Suggested structure of the  $\beta$ -diketone chelate with the aluminum oxide surface [20].

The  $Al2p$  region of the XPS spectrum of an aluminum substrates following treatment with 7-octen-2,4-dione is shown in Figure 8a. The spectrum of the bare aluminum oxide is shown in Figure 8b. The appearance of a second oxide peak at lower binding energies in the  $Al2p$  region of the XPS spectrum of an aluminum substrates following treatment with 7-octen-2,4-dione suggest that either the  $\beta$ -diketone is promoting dissolution of the weak outer

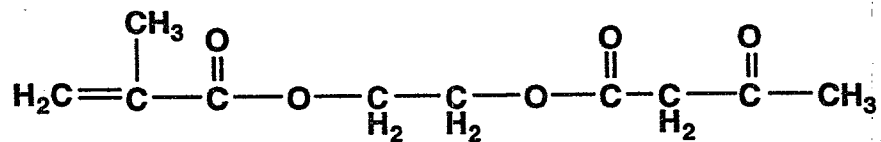
oxide layer while exposing an underlying layer with a different chemical structure or that the second peak may be due to chelate formation of the  $\beta$ -diketone with aluminum in the aluminum oxide layer. Further study is necessary to determine the origin of the second oxide peak.

As stated, our goal was to copolymerize 7-octen-2,4-dione with an epoxy reactive functionalized monomer and to then evaluate the polymer in terms of joint strength and corrosion resistance imparted to coated aluminum substrates. Unfortunately, after extensive experimentation, polymerization proved futile. Polymerization was complicated due to the hydrogen atom in the alpha position to the allyl functionality. This highly reactive hydrogen atom promoted chain transfer, thereby halting polymer growth.

The polymerization difficulty prompted a change in research plans in mid-May 1995. We purchased a commercially available  $\beta$ -diketone, 2-(methacryloyloxy)ethyl acetoacetate (MAEAA), Figure 9. We have successfully homopolymerized and copolymerized MAEAA



**Figure 8.** Al<sub>2</sub>p region of the XPS spectrum of a) an aluminum substrated following treatment with 7-octen-2,4-dione and b) a bare aluminum substrate.



**Figure 9.** Chemical structure of 2-(methacryloyloxy)ether acetoacetate.

## ***Copolymer Synthesis***

The copolymer was formed via radical polymerization of 2-(methacryloyloxy)ethyl acetoacetate, MAEAA, with glycidyl methacrylate in of acetone, as described in the Experimental Section of this report. The copolymer has a Tg of 47° C and a decomposition temperature of 232° C. The chemical interaction of the copolymer with an aluminum oxide substrate was evaluated with X-ray Photoelectron Spectroscopy.

## ***X-ray Photoelectron Spectroscopy***

X-ray Photoelectron Spectroscopy was utilized to investigate the nature of the interaction between the copolymer coupling agent and an aluminum substrate. Etched and degreased samples were prepared as described in the Experimental section of this paper. Verification of the presence of the coupling agent on the substrate surface following coupling agent treatment was accomplished by comparing the Cls regions of the spectra of a solvent cast copolymer film to the spectra of an aluminum substrate following coupling agent treatment. Due to the complexity of the Cls spectrum for the copolymer, limited information regarding the nature of the coupling agent/aluminum substrate interaction was obtained. If chelation of the  $\beta$ -diketone was occurring with aluminum ions in the aluminum oxide layer of the substrate then this would result in an alteration in the electronic environment of the affected aluminum atoms. Thus, the Al2p region of the spectrum was investigated at high resolution. In addition, to eliminate any changes in

binding energies that may be a result of solvent interactions, coupling agent treated substrates were compared to aluminum substrates that were subjected to the same pretreatment process and soaked in pure solvent for 1 hour. Tables 1 and 2 list the binding energies for two sets on samples, etched and degreased, respectively. For the etched samples, there is no effect of the coupling agent on the binding energies of either the oxide or the metallic aluminum species with their binding energies at 75.31 and 72.78 respectively. The degreased samples, however, showed a distinct shift to lower binding energies for the oxide peak as a result of coupling agent treatment. The sample soaked in pure solvent displayed an oxide peak at 75.55 and a metallic aluminum peak at 72.65 eV whereas the coupling agent treated sample had peaks at 74.41 and 72.65 eV respectively. Two explanations are offered for the shift in the binding energy for the oxide peak: 1) the peak is due to chelate formation of the  $\beta$ -diketone with the aluminum atoms in the aluminum oxide layer, or 2) dissolution of the outermost layer of the aluminum oxide occurred during immersion in the coupling agent, exposing an underlying aluminum oxide layer of different chemical composition. Further investigation is necessary to distinguish between these two possible causes for the peak shift. This shift in binding energy has been noted previously for studies of the low molecular weight  $\beta$ -diketone 7-octen-2,4-dione [9]. Reflection-Adsorption Infrared Spectroscopy experiments are currently in progress.

**Table 1.** Binding energies (eV) for etched samples after immersion in pure solvent and coupling agent solution.

NMP eV	NMP / CA eV	Assignment
72.78	72.76	metallic Al
75.31	75.32	Al oxide

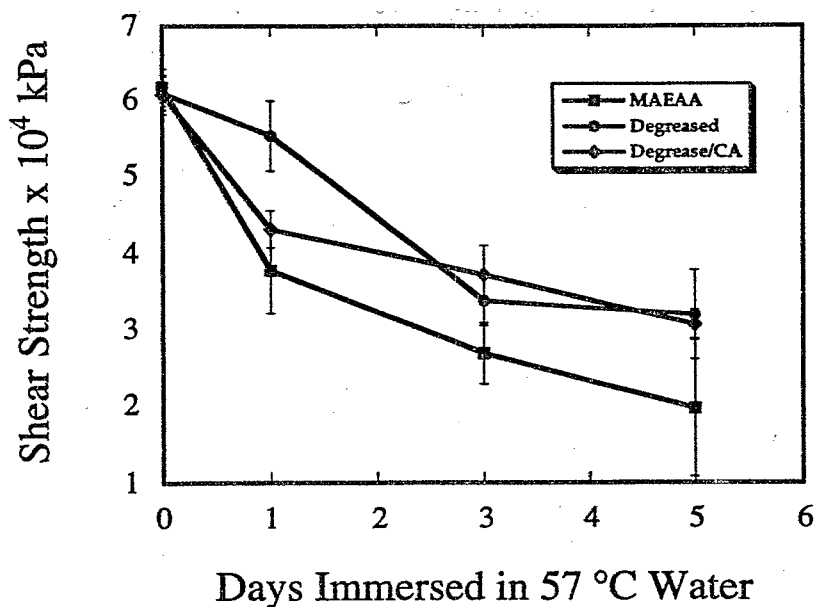
**Table 2.** Binding energies (eV) for degreased samples after immersion in pure solvent and coupling agent solution.

NMP eV	NMP / CA eV	Assignment
72.65	72.65	metallic Al
75.55	74.41	Al oxide

### ***Joint Strength and Durability***

Joint strengths and durabilities for the copolymer treated joints were evaluated via torsional shear experiments [21]. Figure 10 illustrates the joint strengths of degreased copolymer treated torsional shear joints in comparison to untreated controls. Each experimental data point is the average of at least four joints and the error bars are the standard deviation of the data set. Dry joint strengths for the coupling agent treated and untreated joints are comparable. Strengths after one day of immersion in 57° C water revealed a significantly lower joint strength for the coupling agent

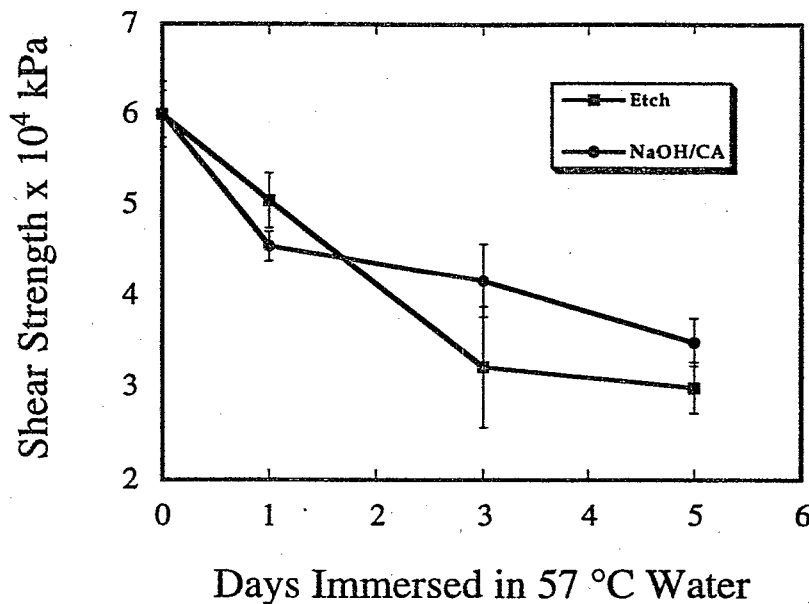
treated joints as compared to the untreated controls. Joint strengths after 3 and 5 days immersion, however, again revealed comparable strengths for both the coupling agent treated and the untreated controls. The initial decrease in joint strength following water immersion is generally attributed to the plasticization of the epoxy due to moisture uptake. The increased rate of joint strength loss over the first one to two days for the coupling agent treated joints suggests that the presence of the coupling agent influences the initial rate of moisture uptake of the resin.



**Figure 10.** Shear strength (kPa) as a function of days immersed in 57° C water for degreased coupling agent treated joints and untreated degreased controls.

Figure 11 illustrates the joint strengths of etched copolymer treated joints as compared to etched untreated controls. Dry joint strengths for the coupling agent treated and untreated joints are comparable. Strengths after one day of immersion in 57° C water revealed a significantly lower joint strength for the coupling agent treated joints as

compared to the untreated controls, similar to that observed for the degreased samples in Figure 10. Joint strengths after 3 and 5 days immersion, however, revealed improved strengths for the coupling agent treated as compared to the untreated controls. Thus at longer immersion times the coupling agent improves joint durability.

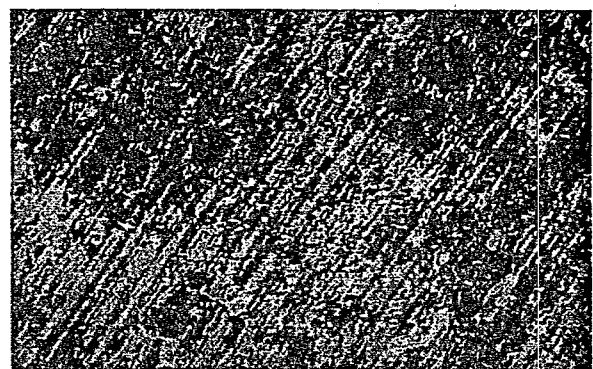


**Figure 11.** Shear strength (kPa) as a function of days immersed in 57° C water for etched coupling agent treated joints and untreated etched controls.

### Corrosion Resistance

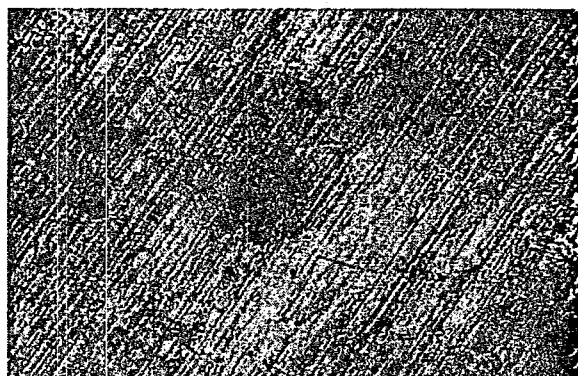
Corrosion resistance of a coupling agent treated substrate was evaluated by visual inspection of two aluminum substrates following exposure to an ASTM B117 salt spray chamber for 24 hours. One substrate was degreased and served as a control sample while the second sample was degreased and treated with the coupling agent. Micrographs (20x magnification) of the two sample surfaces are shown in Figures 12 and 13. The untreated aluminum substrate showed extensive discoloration and pitting. The coupling agent treated sample exhibited significantly less discoloration and pitting as compared to the untreated control. The discoloration and pitting on the treated sample appeared to be concentrated in distinct region suggesting that the coupling agent coating was not uniform over the entire surface. This

incomplete coverage may be due to incomplete cleaning during the degreasing process.



**Figure 12.** Micrograph (20x magnification) of degreased aluminum substrate after 24 hours in an ASTM B117 salt spray chamber.





**Figure 13.** Micrograph (20x magnification) of etched aluminum substrate after 24 hours in an ASTM B117 salt spray chamber.

## Steel

### Joint Strength

The AQM-1 (model compound) and the quinone-amine polyurethanes (QAPs) were found effective in very low concentrations e.g., 0.05%, 0.2% etc. by weight in THF, and caused an increase in the joint strength with increased concentration. The average (sets of seven) measured joint shear strengths of joints made using AQM-model as the coupling agent (CA) are found in Table 3 below.

**Table 3.** Dry shear strength of joints treated with CA1 as compared to untreated controls as a function of coupling agent concentration.

Sample	Shear Strength (psi)
Controls	8760
0.2% CA1	9365
0.4% CA1	9665

The QAPs were found to be effective, even in low solution concentrations, in increasing the joint shear stress of the steel-epoxy joints. Joints showed an increase in strength with increased concentration of the coupling agent solution. The joint shear stresses of the coupling agents (CAs) QAP-1B, -2B and -3B (with tetrahydrofuran as the solvent) treated joints are found in Table 4.

**Table 4.** Joint shear stresses of coupling agent treated steel joints

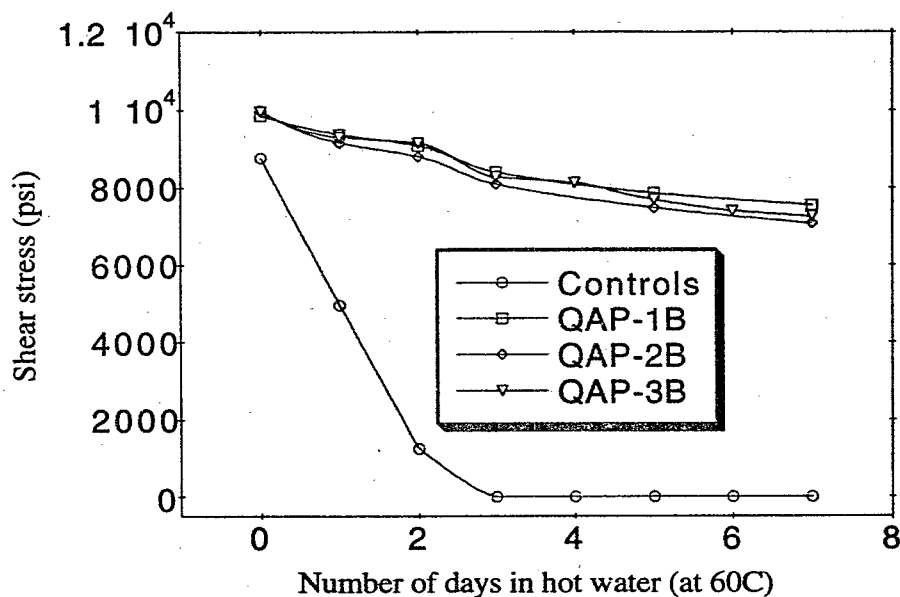
% CA in solution (by wt)	QAP1B as CA (psi)	QAP2B as CA (psi)	QAP3B as CA (psi)
0	8760	8760	8760
0.1	9830	9855	9835
0.2	9855	9995	9955
0.5	9950	10240	10145
1.0	10475	10890	10745

The increase in the dry joint shear strength from the low molecular weight compound (AQM) to the polymeric coupling agents (QAP-1B and QAP-2B) is due to the ability of a polymer to distribute stresses better. In the polymers, the increase in joint shear strength with increase in concentration of the coupling agent used probably indicates the presence of a good amount of entanglement of the coupling agent with the epoxy topcoat.

Among the polymers used, the QAP-2B has a lower melting point and a higher soft segment content and so is

much more flexible than the QAP-3B and -1B copolymers. This, probably leads to much more entanglement of chains at the interface and crack tip energy dissipation when this polymer is used, with consequent improvement in dry joint strength.

Water durability tests also indicated that the QAP coupling agents could be used to make joints that were extremely stable in hot water (60°C). The comparative water stability data for the three QAPs is shown in Figure 14.



**Figure 14.** Water Stability of the quinone-amine polyurethanes.

The QAP-1B outperformed the QAP-3B and QAP-2B (in the same order) in strength retention over longer periods of immersion in hot water. Quinone-amines are known for their hydrophobicity and these polymers are indeed very stable in water. The reason for the initial drop in the shear stress in both the cases may be more to do with the plasticization effects of water on the epoxy and coupling agent than any actual bond rupture across the interface. The higher strength retention of the QAP-1B may be due to its inherent rigidity

which results from its stiffer backbone and higher hard segment content when compared to QAP-3B and QAP-2B. This allows a much lower quantity of water to penetrate, thus reducing the plasticization effect.

Two silanes, 3-glycidoxypropyltrimethoxy-silane (GS) and 3-aminopropyl-triethoxysilane (AS) were evaluated for their effectiveness as coupling agents for steel. A methanol-water solvent system was utilized. The average (sets

of seven) dry joint shear strengths of the silane treated joints are found in Table 5.

**Table 5.** Dry shear strength of joints treated with organosilanes GS and AS as compared to untreated controls.

Sample	Shear Strength (psi)
Controls	8760
0.2% GS treated	9255
0.2% AS treated	9205

The low molecular weight  $\beta$ -diketone (BK) and the PETM treated joints showed improvements in the joint strength compared to the controls. Methanol was used as a solvent in both cases. The average (sets of seven) dry joint shear strengths of the joints are found in Table 6.

**Table 6.** Dry shear strength of joints treated with  $\beta$ -diketone and PETM as compared to untreated controls.

Sample	Shear Strength (psi)
Controls	8760
0.2% BK	9400
0.2% PETM	9325

Of the other compounds used, only the 3-aminopropyltriethoxysilane and benzoyl acetone treated joints were moderately stable in water.

### *Infrared Spectroscopy*

It was seen spectroscopically that the quinone-amine polyurethane coupling agent had chemical interaction with the steel and epoxy surfaces. IR spectroscopy in the reflectance mode was used to investigate the interaction of the coupling agent with steel (shift in the C=C or the carbonyl peak : from 1622 to 1604 wavenumbers in QAP-1B; from 1730 to 1743 wavenumbers in QAP-2B and from 1722 to 1703 wavenumbers in QAP-3B), while the transmission IR mode was used to investigate the interaction of the coupling agent with epoxy (disappearance of the amine peaks at 1633 and 1554 wavenumbers in the spectra of the QAP-1B, after reaction with epoxy). These seem to indicate interactions of the coupling agent with the two surfaces.

### *X-ray Photoelectron Spectroscopy*

XPS studies were done on the bare metal surface and the QAP coupling agent treated surface after washing with copious quantities of solvent. The QAP-1B treated surface showed Iron(II) oxide and benzoquinone like oxygen peaks in addition to a third oxygen peak. The presence of oxygen from the coupling agent indicates that it was not washed off completely from the surface by the solvent. These 3 kinds of oxygen peaks probably indicate the interaction of the oxygen from the quinone moiety with the steel surface. There was only a single nitrogen peak, so the amine moiety is free to react with the epoxide ring of the top coat in the system. A similar behavior was seen with the QAP-2B and -3B as well.

The model compound (AQM-1) showed the presence of 3 types of oxygen peaks as well, confirming the interaction of the quinone moiety with the steel surface. The presence of more than one nitrogen peak in the model compound probably indicates that the nitrogen interacts with the surface as well in this case, the compound probably forming a chelate with the metal. This type of behavior was not observed for the QAPs.

### *Fracture Surface Analysis*

The XPS results of fractured lap shear joints show that the number and type of oxygen and nitrogen peaks of the fractured joints were different from those seen with the coupling agent alone on steel. These additional peaks are expected only if there was the presence of amine cured epoxy on the outer surface of the fractured joints. Both sides of the fractured joint showed the above mentioned behavior. This leads us to believe that the bond could be rupturing in the epoxy layer. This belief is further corroborated by SEM results which show large bundles of epoxy visible in what otherwise looks like exposed metal surface on the fractured

joint. Vast areas of the fracture surface also show coverage by epoxy. Preliminary XPS results obtained after immersing the lap shear joints in hot water also support this belief.

### *Corrosion Resistance*

The qualitative corrosion resistance results of steel coupons coated with the coupling agent followed by epoxy resin, after evaluation in accordance to ASTM B117 standard test method of salt spray (fog) testing using a lab scale salt spray apparatus, are shown in Table 7. The samples were held in a mist of salt water for a period of 10 days

**Table 7.** ASTM B117 Salt spray apparatus corrosion resistance evaluation.

Sample	Streaks/Spots	Result
Steel-epoxy	Completely corroded	Completely corroded
Steel-QAP1B-epoxy	None	Inhibition
Steel-QAP2B-epoxy	Streaks	Retardation
Steel-QAP3B-epoxy	Spots	Better retardation

We are investigating the effects of flexibility and of primary amine groups in the polymer chain on the bonding process by using various other types and percentage compositions of the AQM in the quinone amine polyurethane.

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