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STRUCTURE AND PROPERTIES OF POLYMERS AND ORGANOSILANES  
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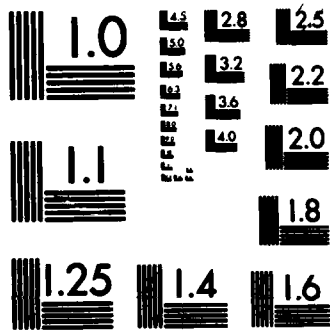
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STRUCTURE AND PROPERTIES OF POLYMERS AND ORGANOSILANES ADSORBED  
ONTO OXIDIZED ALUMINUM AND TITANIUM

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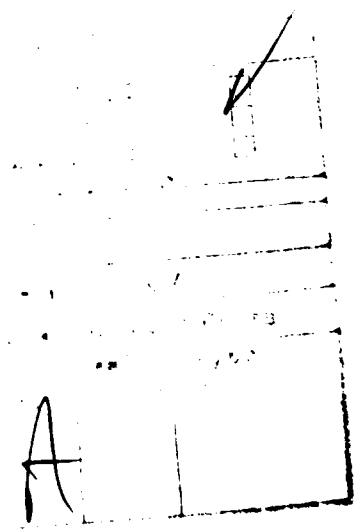
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affected by the substrate or the pH of the  $\gamma$ -APS solutions.  $\gamma$ -APS films were very effective primers for improving the wet strength of titanium/epoxy and iron/epoxy lap joints. However, the properties of the films as primers depended strongly on the substrate and the pH of the solutions. It was concluded that the properties of the films depended more on the orientation of the  $\gamma$ -APS molecules at the oxide surface than on the overall structure of the films. The orientation of the adsorbed  $\gamma$ -APS molecules was determined by the pH of the solutions and by the isoelectric point of the oxides on titanium and iron.

$\gamma$ -APS was also an effective primer for improving the wet strength of aluminum/epoxy adhesive bonds. However, the structure of the films formed by  $\gamma$ -APS adsorbed onto aluminum alloys containing copper was a strong function of pH. At high pH values the oxides on aluminum were etched and aluminosiloxane polymers were adsorbed. At intermediate pH values little etching was observed and siloxane polymers were adsorbed. Such siloxane polymers may function as primers to improve the wet strength of aluminum/epoxy adhesive bonds by inhibiting or retarding hydration of the oxide on aluminum.



## I. Introduction

One of the most important limitations regarding the use of adhesive bonding for joining metals concerns the adverse effects of water. It is well known that in the absence of water, properly prepared adhesive joints are very strong and that failure of such joints is almost invariably cohesive within the adhesive. However, it is also well known that in the presence of moisture even the most carefully prepared adhesive joints weaken and eventually fail near the interface.

The deleterious effects of moisture are not unique to metal-to-metal adhesive joints. A very similar problem is encountered in glass fiber reinforced composites. In that case, the solution to the problem has been to pretreat the glass fibers with dilute aqueous solutions of organosilane "coupling agents" (1). The primary objective of this research is to determine the applicability of organosilanes as "primers" for improving the hydrothermal stability of metal-to-metal adhesive joints.

Several theories have been proposed to describe the mechanisms by which silanes function as coupling agents on glass (1). One of the most widely accepted is the so-called chemical bonding theory (see Figure 1). This theory considers that silane coupling agents function by forming stable covalent bonds with both the substrate and an adhesive applied to the substrate. However, there is little direct evidence to support this theory. An additional objective of this research is to determine the mechanisms by which organosilanes interact with the oxidized surfaces of metals and improve the hydrothermal stability of metal-to-metal adhesive joints.

The usefulness of organofunctional silanes as primers for improving the hydrothermal stability of metal-to-metal adhesive joints was determined by immersing metal/epoxy lap joints in water at 60°C and determining the strength retained as a function of immersion time. The mechanisms by which silanes function as primers were determined using surface analysis techniques such as reflection-absorption infrared spectroscopy (RAIR), ellipsometry, and x-ray photoelectron spectroscopy (XPS) to determine the structure of thin films formed by silanes adsorbed onto metal mirrors from dilute aqueous solutions.

Previous reports have described the molecular structure of thin films of  $\gamma$ -aminopropyltriethoxysilane ( $\gamma$ -APS) adsorbed onto iron, titanium, and aluminum and the properties of such films as primers for improving the wet strength of iron/epoxy, titanium/epoxy, and aluminum/epoxy adhesive joints. This report describes some additional features of the structure of  $\gamma$ -APS primer films on iron, titanium, and aluminum and discusses the mechanisms by which such primer films improve the wet strength of iron/epoxy, titanium/epoxy, and aluminum/epoxy adhesive joints.

## II. Experimental

Sample substrates for surface analysis were prepared by mechanically polishing enameling iron (Armco, Inc.), titanium-6Al, 4V (Timet, Inc.), and 2024-T3 aluminum alloy (Alcoa, Inc.). Films were formed on freshly polished mirrors by immersing the mirrors in 1% aqueous solutions of  $\gamma$ -aminopropyltriethoxysilane ( $\gamma$ -APS, Union Carbide Corp.) for appropriate times, removing the mirrors from the solution, and blowing the excess solution off the mirrors using a strong stream of nitrogen. In some cases hydrochloric acid was added to the  $\gamma$ -APS solutions to lower the pH.

Infrared spectra of films formed by  $\gamma$ -APS adsorbed onto iron, titanium, and aluminum were obtained using a Perkin-Elmer Model 180 infrared spectrophotometer and external reflection accessories from Harrick Scientific Co. XPS spectra were obtained using a Physical Electronics x-ray photoelectron spectrometer and magnesium  $K_{\alpha}$  radiation. Ellipsometry was performed using a Rudolph Research Model 436 ellipsometer.

Lap joints were prepared according to ASTM standard D1002. Metal adherends (1 x 4 x 0.063") were mechanically polished, rinsed repeatedly, and dried. Pairs of adherends were then bonded together using an adhesive consisting of an epoxy resin (Epon 828, Shell Chemical Co.) and 9.4 weight percent of a tertiary amine catalyst (Ancamine K-61B, Pacific Anchor Chemical Co. or Shell Curing Agent D, Shell Chemical Co.). In some cases, the adherends were pretreated with a  $\gamma$ -APS primer as described above. In all cases the lap joints were immersed in water at

60°C. At various intervals, joints were removed from the water, dried, and tested using an Instron Universal Testing Instrument to determine the breaking strength.

### III. Results and Discussion

#### A. Titanium and iron substrates

The structure of primer films formed by  $\gamma$ -APS adsorbed from aqueous solutions onto the oxidized surface of titanium does not vary greatly as a function of pH (2,3). Under most conditions the primer films are composed of siloxane polymers characterized by a strong infrared absorption band near  $1100\text{ cm}^{-1}$  (see Figure 2). Films formed at pH 10.4 contain absorbed carbon dioxide that is bound to the amino groups to form amine bicarbonate salts. The bicarbonate species are characterized by absorption bands near 1570, 1470, and  $1300\text{ cm}^{-1}$  (see Figure 2A). Films formed from solutions acidified to pH 8.5 or 5.5 are characterized by absorption bands near 1600 and  $1500\text{ cm}^{-1}$  that are assigned to the deformation vibrations of protonated (i.e.,  $\text{NH}_3^+$ ) amino groups (see Figures 2B and 2C). Otherwise there is little difference in the structure of primer films formed by  $\gamma$ -APS adsorbed onto the oxidized surface of titanium at different pH values.

The structure of the films formed on iron is very similar (3). Siloxane polymers are formed at all pH values. Films formed at pH 10.4 contain absorbed carbon dioxide that is bound to the amino groups to form amine bicarbonate salts. Films formed from acidified solutions contain protonated amino groups. However, light etching of the oxide has been observed (4) during immersion of iron mirrors in aqueous solutions of  $\gamma$ -APS at pH 10.4 (see Figure 3). As a result, primer films formed on iron by adsorption of  $\gamma$ -APS from aqueous solutions at pH 10.4 probably contain a few iron ions coordinated to amino nitrogen atoms. No

etching of the oxide has been observed during immersion of iron mirrors in acidified aqueous solutions of  $\gamma$ -APS (4) and no etching of the oxide has been observed during immersion of titanium mirrors in aqueous solutions of  $\gamma$ -APS regardless of pH (3).

The results described above indicate that the structure of  $\gamma$ -APS primer films is similar on iron and titanium and does not depend significantly on pH. However, the properties of the primer films do depend on the substrate and on the pH. The breaking strength of iron/epoxy lap joints as a function of immersion time in water at 60°C is shown in Figure 4 (3-5). Joints prepared from unprimed adherends retained only about 25% of their original strength after 60 days immersion. By comparison, joints prepared from adherends primed with aqueous solutions of  $\gamma$ -APS at pH 10.4 retained about 50% of their original strength after similar immersion in water. However, iron/epoxy lap joints prepared from adherends primed at pH 8.0 were the most durable and retained about 75% of their initial strength after 60 days in water at 60°C.

$\gamma$ -APS films were also effective primers for titanium/epoxy lap joints (3,4) but the effect of the pH at which the primer was applied was quite different (see Figure 5). The breaking strength of titanium/epoxy lap joints prepared from unprimed adherends decreased slowly from about 1260 psi to about 960 psi during 60 days immersion in water at 60°C. However, the strength of titanium/epoxy lap joints prepared from adherends primed with  $\gamma$ -APS at either pH 10.4 or pH 8.0 decreased very little during

immersion in water at 60°C and was still about 1750 psi after 60 days.

Considering that the structures of  $\gamma$ -APS films on titanium and iron are very similar but the properties of the films are very different, it seems evident that the properties of the primer films are not related to the overall structure of the films. Instead, it seems likely that the properties of the films are determined by the orientation of the  $\gamma$ -APS molecules at the surface of the oxide.

Hydrolyzed  $\gamma$ -APS contains two functional groups that can be ionized. The amino group can be ionized according to the reaction



and the silanol group can be ionized according to the reaction



The pH values at which these equilibrium reactions are half completed are referred to as the  $\text{pK}_a$  values for the reactions. For ionization of the amino groups on  $\gamma$ -APS (reaction 1), the  $\text{pK}_a$  is about 10.4. For ionization of the silanol groups on hydrolyzed  $\gamma$ -APS (reaction 2), the  $\text{pK}_a$  is about 3.0 (6).

The hydroxyl groups present on the surface of an oxide can also be ionized. At high pH values the reaction



takes place while at low pH values the reaction



is obtained. At some intermediate pH value (called the isoelectric point of the surface-IEPS), the numbers of positive and negative charges on the surface are equal and there is no net charge on the surface. The isoelectric points for the oxidized surfaces of iron and titanium are near 10.0 and 6.0, respectively (6).

Bolger (7) has suggested that an organic compound having ionizable functional groups will be stably adsorbed onto the oxidized surface of a metal during immersion in water if the pH of the water is between the  $\text{pK}_a$  of the ionizable functional group and the isoelectric point of the oxide. Otherwise the organic compound will be displaced from the surface by water.

When  $\gamma$ -APS is adsorbed onto the oxidized surface of iron from an aqueous solution at pH 8.0, the amino groups should be positively charged and the silanol groups should be negatively charged. The  $\gamma$ -APS molecules should be adsorbed through the silanol groups (see Figure 6). Iron/epoxy lap joints prepared from adherends primed with  $\gamma$ -APS at pH 8.0 should be relatively stable during long term exposure to nearly neutral water since the pH of the water (6.2) would be between the isoelectric point of the surface (10.0) and the  $\text{pK}_a$  of the silanol groups (3.0). Reference to Figure 4 indicates that iron/epoxy lap joints

prepared from adherends primed with  $\gamma$ -APS at pH 8.0 are in fact very stable during immersion in water at 60°C.

When  $\gamma$ -APS is adsorbed onto the oxidized surface of iron from an aqueous solution at pH 10.4, all of the silanol groups and about half of the amino groups are ionized. The isoelectric point of iron oxides is close to 10.0. Therefore, the  $\gamma$ -APS primer should be adsorbed onto the oxidized surface through both protonated amino and ionized silanol groups (see Figure 7). During long term exposure to nearly neutral water (pH 6.2), the silanol groups should be stably adsorbed (i.e., pH of water between IEPS of oxide and  $pK_a$  of silanol groups) but the amino groups should be displaced by water. As a result,  $\gamma$ -APS should be less effective as a primer for iron/epoxy adhesive joints when applied to the iron adherends at pH 10.4 and that is observed (see Figure 4).

IEPS for the oxidized surface of titanium is about 6.0. At either pH 10.4 or 8.0,  $\gamma$ -APS should be adsorbed onto the oxidized surface of titanium through the amino groups (see Figure 8). During immersion in water at pH 6.2, the amino groups are just stably adsorbed (i.e., the pH of the water is between the  $pK_a$  of the amino groups and the IEPS).  $\gamma$ -APS should be equally effective as a primer for titanium/epoxy lap joints when applied at either pH 10.4 or 8.0 and that is observed (see Figure 5).

#### B. Aluminum substrates

The behavior of  $\gamma$ -APS on the oxidized surface of 2024 aluminum alloy is very different. As noted above, the air-formed oxides on iron and titanium are relatively stable during

immersion in aqueous solutions of  $\gamma$ -APS. However, the oxidized surface of 2024 aluminum mirrors was rapidly etched during immersion in basic solutions of  $\gamma$ -APS but the rate of etching decreased as the pH of the solutions was decreased (2,8).

Infrared spectra of films formed by  $\gamma$ -APS adsorbed onto aluminum mirrors from aqueous solutions acidified to pH 6.8 were similar to those of thin films formed on iron and titanium mirrors at comparable pH values (see Figure 9A). Such spectra were characterized by infrared bands near 1600 and 1500  $\text{cm}^{-1}$  that were assigned to protonated amino groups and by a strong band near 1120  $\text{cm}^{-1}$  that was assigned to the SiO stretching vibrations of a siloxane polymer (4,8).

RAIR spectra of films formed by  $\gamma$ -APS adsorbed onto aluminum from aqueous solutions at higher pH values were quite different from those of films formed on iron and titanium under similar conditions, reflecting the dissolution of aluminum oxides (see Figures 9B, 9C, and 9D). Films formed by adsorption of  $\gamma$ -APS onto 2024 aluminum mirrors at pH 8.5 also contained protonated amino groups as indicated by absorption bands near 1600 and 1500  $\text{cm}^{-1}$ . However, the siloxane stretching mode was observed near 1080  $\text{cm}^{-1}$ . This mode is usually observed near 1120 or 1130  $\text{cm}^{-1}$  for  $\gamma$ -APS films on aluminum under conditions where little dissolution of the oxide occurs. Therefore, the band near 1080  $\text{cm}^{-1}$  for films formed on aluminum at pH 8.5 may be related to formation of an aluminosiloxane polymer (2,8).

The infrared spectra of films formed on aluminum at pH 10.4 depended strongly on the adsorption time. Films formed during a

one minute adsorption were similar to those formed on iron and titanium at pH 10.4 (see Figure 9C). However, films formed during 15 minutes adsorption at pH 10.4 were characterized by an infrared band near  $1060\text{ cm}^{-1}$  (see Figure 9D), again indicating dissolution of the oxide and the likely formation of an aluminosiloxane polymer (2,8).

As shown in Figure 10, XPS spectra of mechanically polished 2024 aluminum mirrors (4) were characterized by strong bands near 531.1 eV and near 74.0 eV that were assigned to the O(1s) and Al(2p) binding energies of  $\text{Al}_2\text{O}_3$  and by very weak bands near 952.4 and 931.4 eV that were assigned to either metallic copper or Cu(I) ions (2024 aluminum alloy contains about 4.5% copper). XPS spectra of thin films formed by  $\gamma$ -APS adsorbed onto such mirrors for 15 minutes at pH 8.5 were generally similar to spectra of the "bare" mirrors (see Figure 11) but additional bands characteristic of N(1s), Cl(2p), and Si(2p) electrons were observed near 400.2, 199.0, and 101.7 eV, respectively (4). The Si(2p) binding energy was near that expected for a siloxane polymer (9). The N(1s) peak had components near 399.8 and 400.6 eV, indicating the presence of both free and protonated amino groups (9). The presence of both chlorine and protonated amino groups indicates the formation of an amine hydrochloride.

The XPS spectra of thin films formed by  $\gamma$ -APS adsorbed onto 2024 aluminum mirrors for 15 minutes at pH 10.4 (4) were similar to spectra of films formed during 15 minutes at pH 8.5 except for a few features (see Figure 12). The Cl(2p) band was not observed and the N(1s) band had only one component, near 399.8 eV,

indicating free amino groups. The intensity of the copper 2p bands near 952.4 and 931.4 eV increased significantly, indicating etching of the oxide and an accumulation of Cu(I) ions in the  $\gamma$ -APS films.

Some evidence for coordination of Cu(I) ions to amino nitrogen atoms was obtained for films formed by  $\gamma$ -APS adsorbed onto aluminum for 15 minutes at pH 10.4 (4). For such samples, the x-ray induced copper Auger band was split into two components near 339.4 and 336.9 eV (see Figure 13). Very similar results have been obtained for films formed by  $\gamma$ -APS adsorbed onto electropolished copper mirrors from aqueous solutions at pH 10.4 (10). As shown in Figure 14A, the main band in the x-ray induced copper Auger spectra for freshly polished copper mirrors is near 336.4 eV, a value that is characteristic of Cu(I) ions in  $\text{Cu}_2\text{O}$  (9). When a film of  $\gamma$ -APS was adsorbed onto the mirrors from an aqueous solution at pH 10.4, the oxide was etched and Cu(I) ions accumulated in the  $\gamma$ -APS film. A new band was observed near 339.4 eV in the x-ray induced copper Auger spectra (see Figure 14B), indicating that some of the Cu(I) ions in the  $\gamma$ -APS films were in a different bonding structure and were probably coordinated to amino nitrogen atoms (10). Considering that similar splitting of the x-ray induced copper Auger band is observed for  $\gamma$ -APS adsorbed onto 2024 aluminum at pH 10.4, it seems likely that the Cu(I) ions in the films formed on aluminum are also coordinated to amino nitrogen atoms.

The shape of the Al(2p) band was carefully investigated for evidence of the formation of aluminosiloxane polymers during

adsorption of  $\gamma$ -APS onto aluminum mirrors from aqueous solutions at pH 10.4. As shown in Figure 15A, the Al(2p) band for freshly polished 2024 aluminum mirrors consists of a strong component near 74.0 eV and a weak component near 71.2 eV. These bands were assigned to Al(III) ions in  $\text{Al}_2\text{O}_3$  and to metallic aluminum, respectively (9). The Al(2p) band for a thin film formed by  $\gamma$ -APS adsorbed onto an aluminum mirror for 15 minutes from an aqueous solution at pH 10.4 is shown in Figure 15B. The strong component near 74.0 eV was assigned to Al(III) in an oxide-like environment and the weak component near 71.4 eV was assigned to metallic aluminum. However, in this case some structure was observed on the high energy side of the Al(2p) band (see Figure 15B). In order to determine the origin of that structure, the band shown in Figure 15B was deconvoluted into four bands, near 77.9, 76.1, 74.0, and 71.4 eV, as shown in Figure 16. The high energy bands near 77.9 and 76.1 eV may be related to the formation of aluminosiloxane polymers. However, it is more likely that these bands should be assigned to the 3p binding energies of the Cu(I) ions that accumulate in the  $\gamma$ -APS films during adsorption onto 2024 aluminum alloy at pH 10.4.

The shapes of the O(1s) band near 531.1 eV and the Si(2p) band near 101.7 eV were also examined carefully for evidence of the formation of aluminosiloxane polymers. However, no fine structure that could be related to the formation of such polymers was observed. It is evident that formation of aluminosiloxane bonds does not cause large shifts in the Al(2p), Si(2p), or O(1s) binding energies and that detection of such bonds using XPS will

require the use of a high resolution spectrometer and/or careful deconvolution.

Some very interesting results were obtained when inert gas sputtering was used to determine the depth profile of films formed by adsorption of  $\gamma$ -APS for 15 minutes at pH 10.4. The aluminum and oxygen concentrations were relatively low at the surface of the silane films but increased rapidly as a function of sputtering time. The aluminum concentration always increased during sputtering but the oxygen concentration went through a maximum after about 3 minutes (see Figure 17). Assuming that the sputtering rate was approximately  $10\text{\AA}/\text{min}$ , the total thickness of the films (silane plus oxide) was estimated as  $125\text{\AA}$ .

The silicon concentration was relatively high at the surface of the films but decreased rapidly during sputtering. The copper concentration went through two maxima, implying that copper segregated near the free surface of the silane films and near the silane/oxide interface (see Figure 18).

The hydrothermal stability of aluminum/epoxy adhesive joints has been extensively studied. Recently it has been shown that the decrease in strength observed for such joints during exposure to water at elevated temperatures is related to hydration of the oxide (natural or anodic) to form pseudoboehmite, a weak poorly crystallized hydroxide having the approximate composition  $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$  (11). The pseudoboehmite adheres only poorly to the substrate and its formation leads to a rapid degradation of joint strength. We have previously shown that  $\gamma$ -APS films are effective primers for improving the wet strength of

aluminum/epoxy adhesive joints (12) and we were interested in determining the extent to which these primers inhibited hydration of aluminum oxides. Some preliminary results (4) are described below.

Several sample mirrors were prepared by mechanically polishing 2024 aluminum as described previously. Thin films of  $\gamma$ -APS were then applied to half of the mirrors by immersing them in dilute aqueous solutions of  $\gamma$ -APS at pH 7.0. After 15 minutes, the mirrors were withdrawn and the excess solution was blown off with a strong stream of nitrogen. The mirrors were then heated in an oven at 100°C for 20 minutes to thoroughly polymerize the silane films. The remaining (control) mirrors were not treated with  $\gamma$ -APS but they were heated in the same way as the silanated mirrors. All of the mirrors were then immersed in a beaker of distilled, deionized water at 60°C.

At appropriate intervals, pairs of mirrors (silanated and control) were removed from the beaker and dried. The mirrors were then examined with the ellipsometer to determine the ellipsometric parameters  $\Delta$  and  $\psi$  for the hydroxide layers. A computer program was used to determine the thickness of the hydroxide layers assuming that the refractive indices of the hydroxide and substrate were 1.58 and 1.14 (1-4.06i), respectively (13). The results are shown in Figure 19. Hydration of the control mirrors was very slow during the first 7.5 minutes but was rapid for times between 7.5 and 10.0 minutes. Hydroxide layers about 700Å thick were obtained after 10 minutes. Hydration of the silanated mirrors was very slow and little

change in the thickness of the hydroxide was obtained after 10 minutes.

These results indicate that  $\gamma$ -APS films may improve the wet strength of aluminum/epoxy adhesive joints by inhibiting hydration of the oxide. However, as shown above, the adsorption of  $\gamma$ -APS onto 2024 aluminum alloy is a complex function of pH. At intermediate pH values, siloxane polymers containing small numbers of copper ions are adsorbed. At higher pH values rapid etching of the oxide is obtained and aluminosiloxane polymers containing large numbers of copper ions are obtained for all but the shortest adsorption times. Work is in progress to determine which type of  $\gamma$ -APS film most effectively stabilizes the oxidized surface of 2024 alloy. That will enable the optimum pH for applying  $\gamma$ -APS to this alloy to be determined.

#### IV. Conclusions

Thin films formed by  $\gamma$ -aminopropyltriethoxysilane ( $\gamma$ -APS) adsorbed from aqueous solutions onto the oxidized surfaces of metals are very effective, easily applied primers for improving the hydrothermal stability of metal-to-metal adhesive joints. However, the reaction between  $\gamma$ -APS and metal oxides varies considerably depending on the metal. As a result, the optimum conditions for applying the primer also vary.

$\gamma$ -APS is a very effective primer for titanium and iron adherends. The structures of the primer films formed on titanium and iron are similar but their properties are quite different.  $\gamma$ -APS primers are more effective when applied to iron at pH 8.0 than when applied at pH 10.4. However, the primers are equally effective when applied to titanium at pH 8.0 and 10.4. The properties of the primer films on titanium and iron are determined by the orientation of the  $\gamma$ -APS molecules at the primer/oxide rather than by the overall structure of the primer films. The orientation of the  $\gamma$ -APS molecules is determined by the isoelectric point of the oxide and by the pH of the aqueous solution from which the silane is adsorbed.

$\gamma$ -APS films are also effective primers for aluminum adherends. The films probably function by inhibiting or retarding hydration of the oxide. However, the reaction between  $\gamma$ -APS and 2024 aluminum alloy is a strong function of pH. When  $\gamma$ -APS is adsorbed onto 2024 aluminum from nearly neutral aqueous solutions, little etching of the oxide occurs and simply polysiloxane films are formed. However, when  $\gamma$ -APS is adsorbed at

pH 10.4, etching of the oxide occurs and aluminosiloxane polymers are formed. Work is in progress to determine which type of film is the most effective primer.

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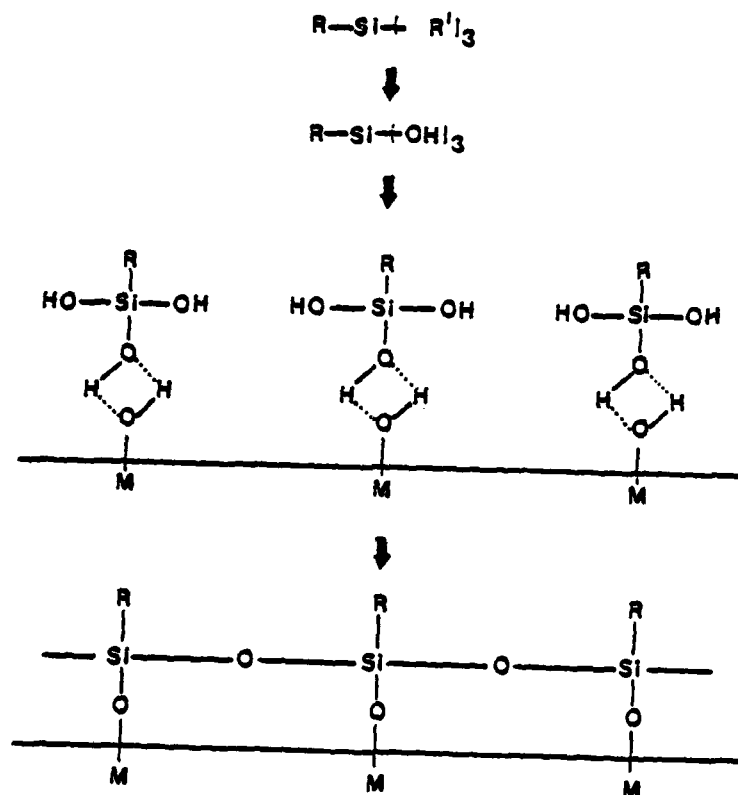


Figure 1. Chemical bonding theory of mechanism by which silane "Coupling agents" function.

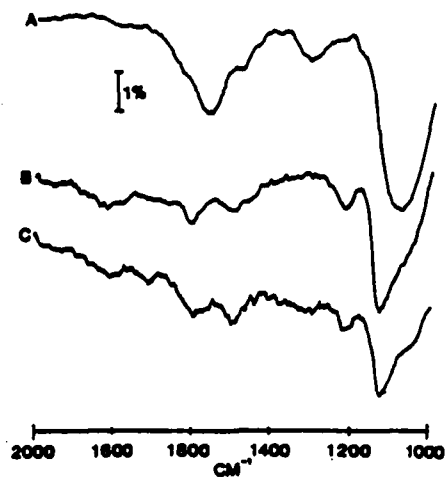


Figure 2. Infrared spectra of thin films formed by  $\gamma$ -APS adsorbed onto titanium mirrors from 1% aqueous solutions at (A) - pH 10.4, (B) - pH 8.5, and (C) - pH 5.5.

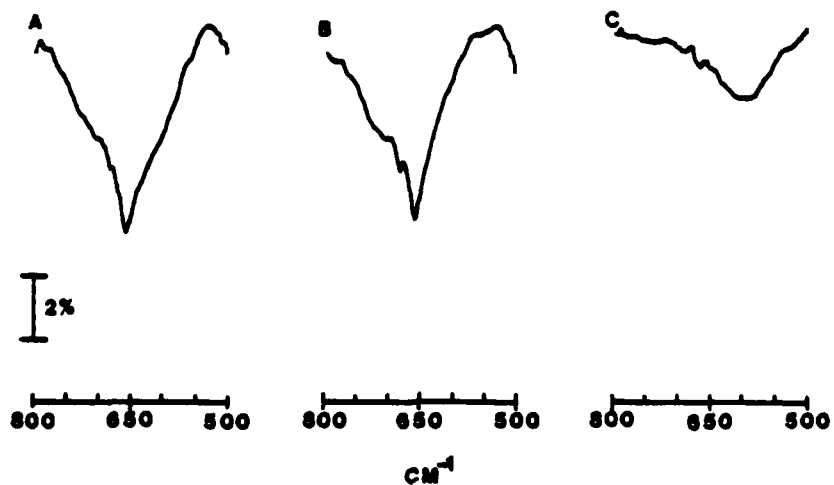


Figure 3. Effect of immersion in 1% aqueous solution of  $\gamma$ -APS at pH 10.4 on infrared spectra of air-formed oxide on iron mirrors: (A) - before immersion, (B) - after immersion, and (C) - difference.

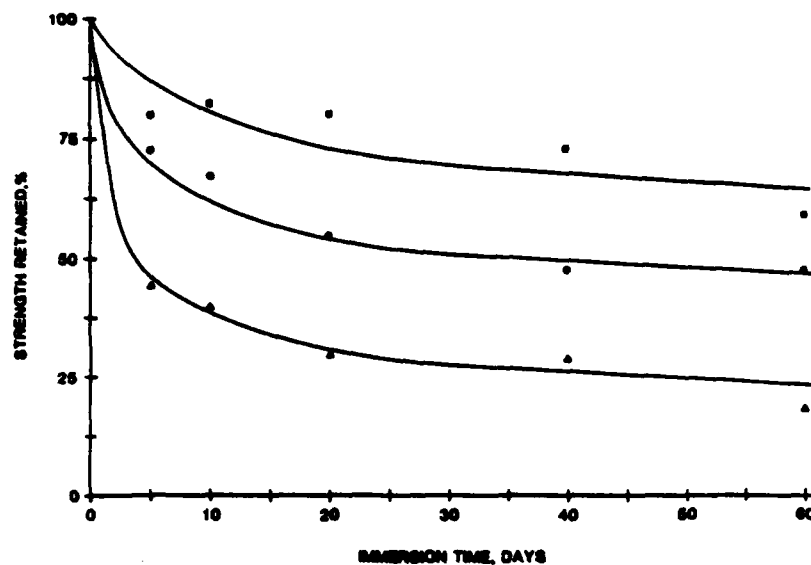


Figure 4. Breaking strength versus immersion time in water at 60°C for iron/epoxy lap joints:  $\Delta$ -no silane primer,  $\circ$ - $\gamma$ -APS primer at pH 10.4, and  $\square$ - $\gamma$ -APS primer at pH 8.0.

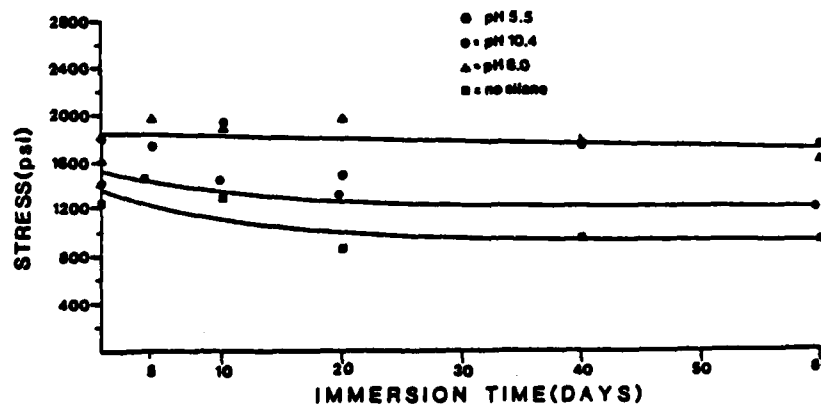
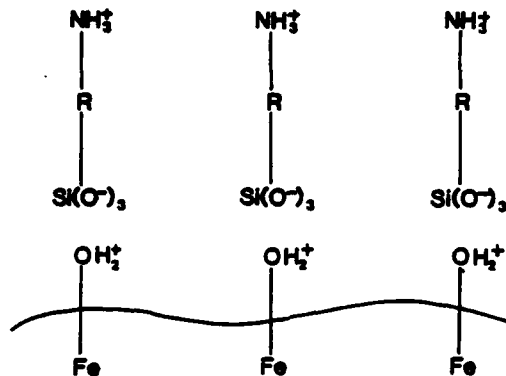


Figure 5. Breaking strength versus immersion time in water at 60°C for titanium/epoxy lap joints:  $\square$ -no silane primer,  $\circ$ - $\gamma$ -APS primer at pH 10.4,  $\Delta$ - $\gamma$ -APS primer at pH 8.0, and  $\odot$ - $\gamma$ -APS primer at pH 5.5.

**IRON**  
**(IEPS = 10.0)**

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$\gamma$ -APS adsorbed at pH 8.0



IN WATER AT pH 6.2:

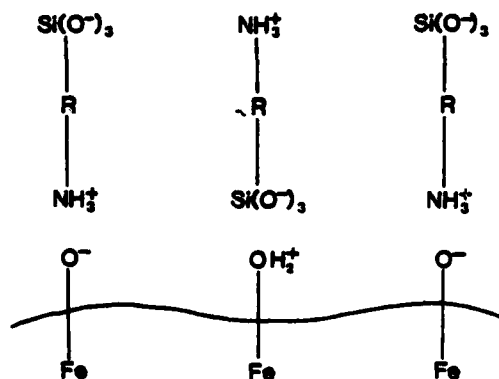
silanol groups stably adsorbed

Figure 6. Schematic representation of the adsorption of  $\gamma$ -APS onto iron from solutions at pH 8.0.

**IRON**  
**(IEPS = 10.0)**

---

$\gamma$ -APS adsorbed at pH 10.4



IN WATER AT pH 6.2:

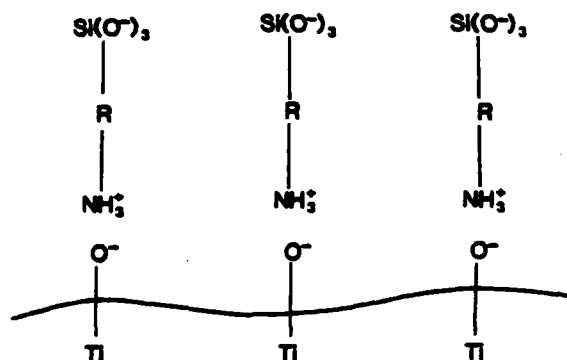
silanol groups stably adsorbed

amino groups not stably adsorbed

Figure 7. Schematic representation of the adsorption of  $\gamma$ -APS onto iron from aqueous solutions at pH 10.4.

**TITANIUM**  
**(IEPS  $\approx$  6.0)**

$\gamma$ -APS adsorbed at pH 8.0 or 10.4



**IN WATER AT pH 6.2:**

**amino groups just stably adsorbed**

Figure 8. Schematic representation of the adsorption of  $\gamma$ -APS onto titanium from aqueous solutions at pH 10.4 or pH 8.0.

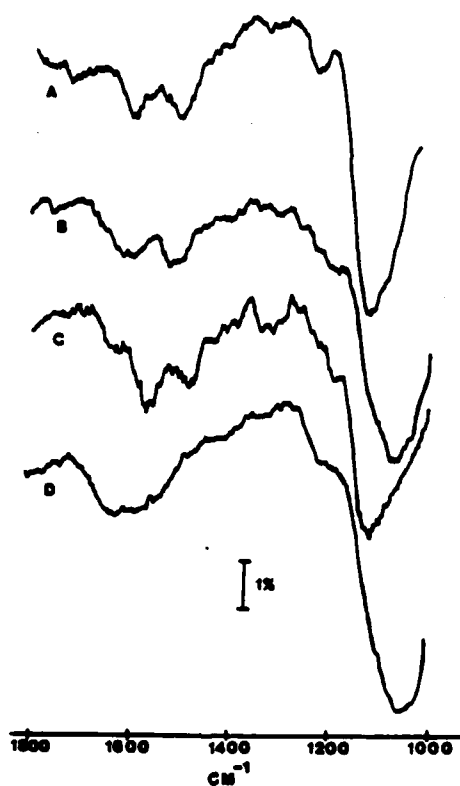


Figure 9. Infrared spectra of thin films formed by  $\gamma$ -APS adsorbed onto aluminum mirrors from 1% aqueous solutions at (A) - pH 6.8, 15 minutes, (B) - pH 8.5, 15 minutes, (C) - pH 10.4, 1 minute, and (D) - pH 10.4, 15 minutes.

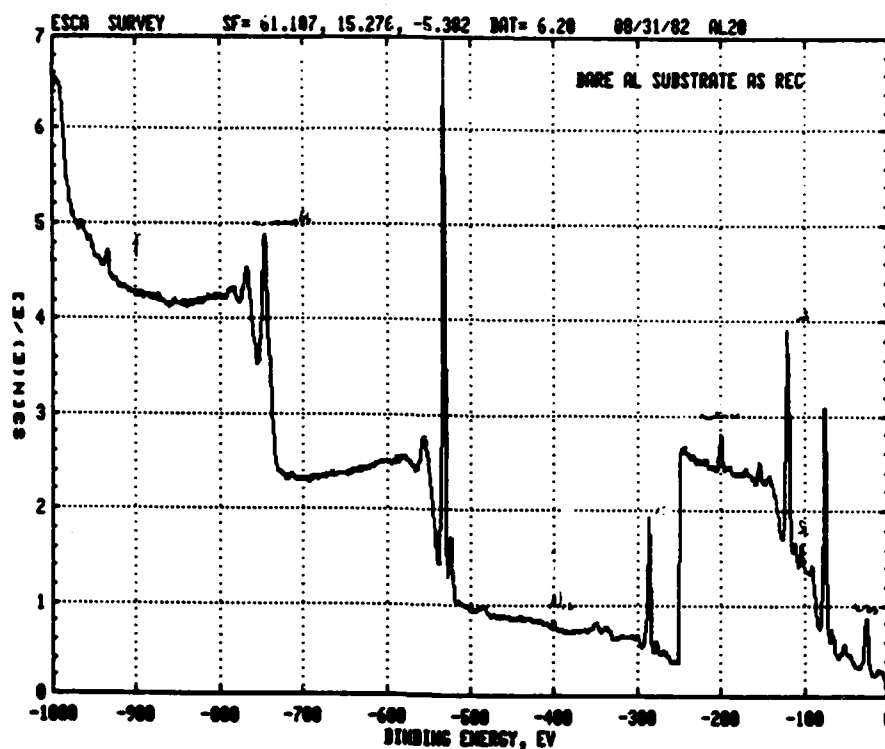


Figure 10. XPS spectrum of 2024 aluminum substrate

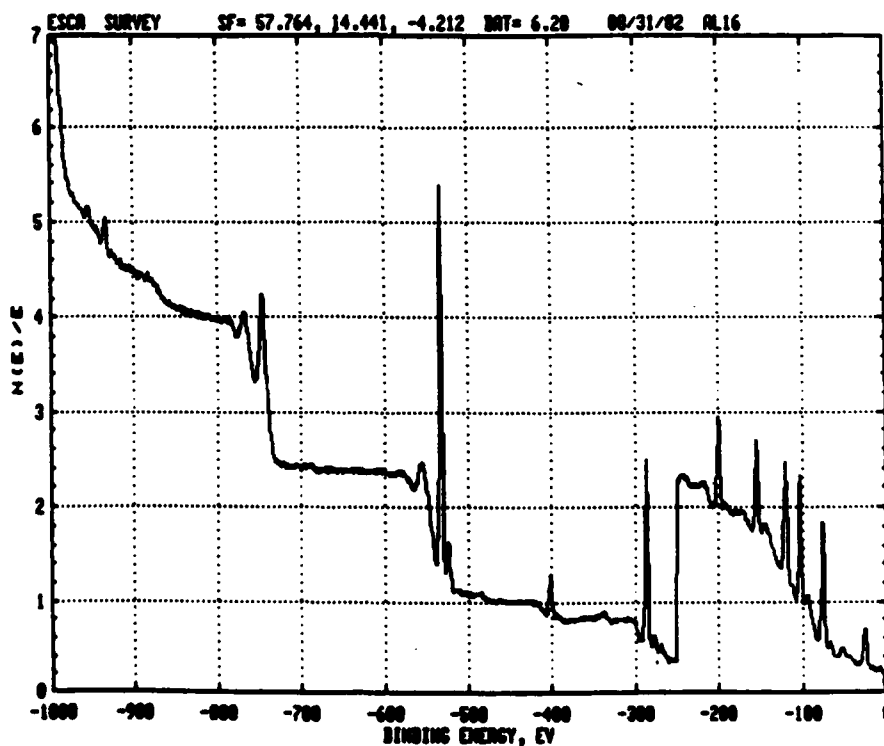


Figure 11. X-ray photoelectron spectra of thin films formed by  $\gamma$ -APS adsorbed onto aluminum mirrors from 1% aqueous solution at pH 8.5 for 15 minutes.

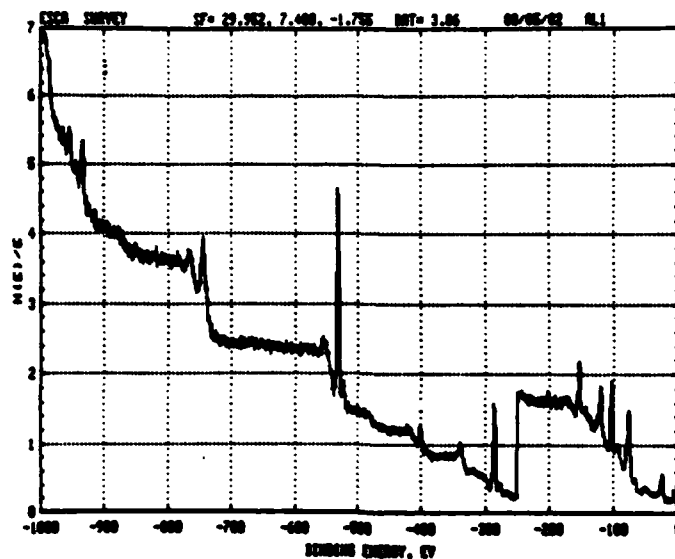


Figure 12. X-ray photoelectron spectra of thin films formed by  $\gamma$ -APS adsorbed onto aluminum mirrors from 1% aqueous solution at pH 10.4 for 15 minutes.

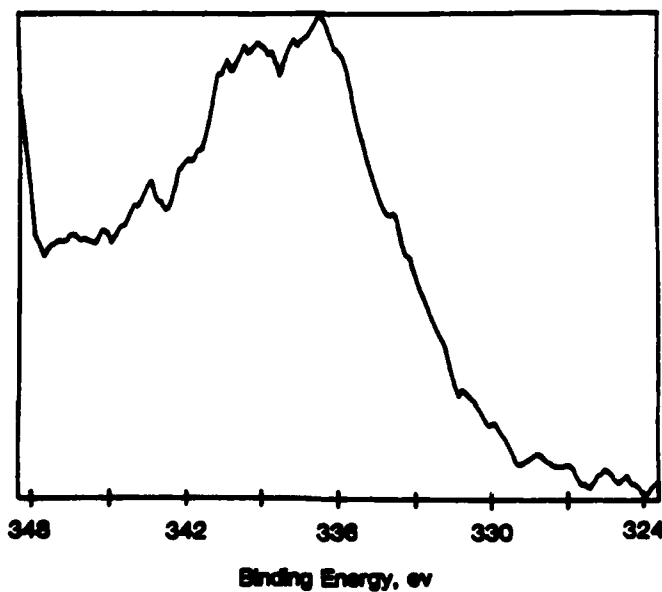


Figure 13. X-ray induced copper Auger spectra for films formed by  $\gamma$ -APS adsorbed onto 2024 aluminum for 15 minutes at pH 10.4.

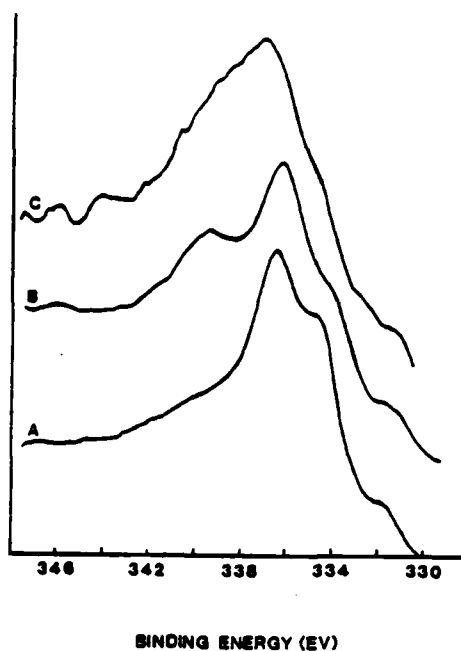


Figure 14. X-ray induced copper Auger spectra for (A) - freshly polished copper mirrors, (B) - polished copper mirror with freshly deposited  $\gamma$ -APS film, and (C) - polished copper mirror with  $\gamma$ -APS film aged in laboratory atmosphere.

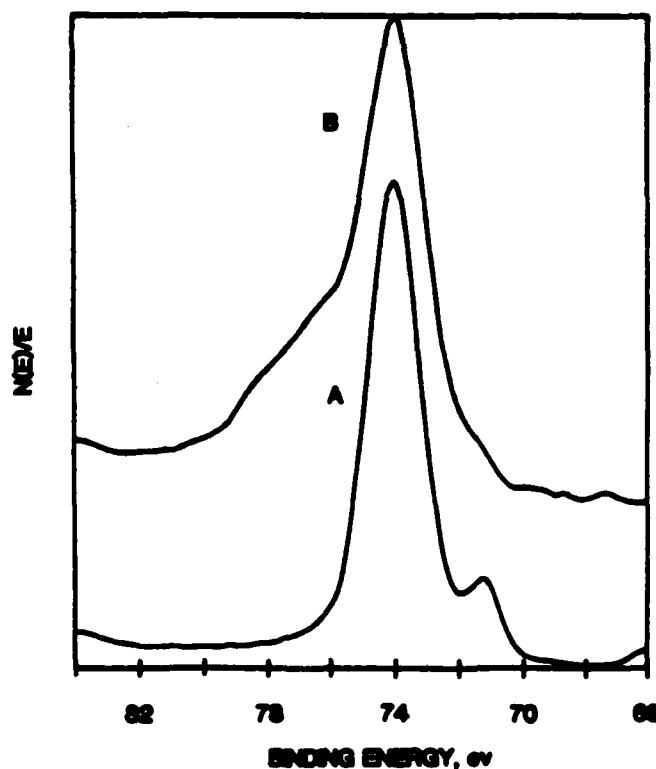


Figure 15. Fine structure of Al(2p) XPS spectra for (A) - freshly polished 2024 aluminum mirrors and (B) - polished mirrors from adsorption of  $\gamma$ -APS for 15 minutes at pH 10.4.

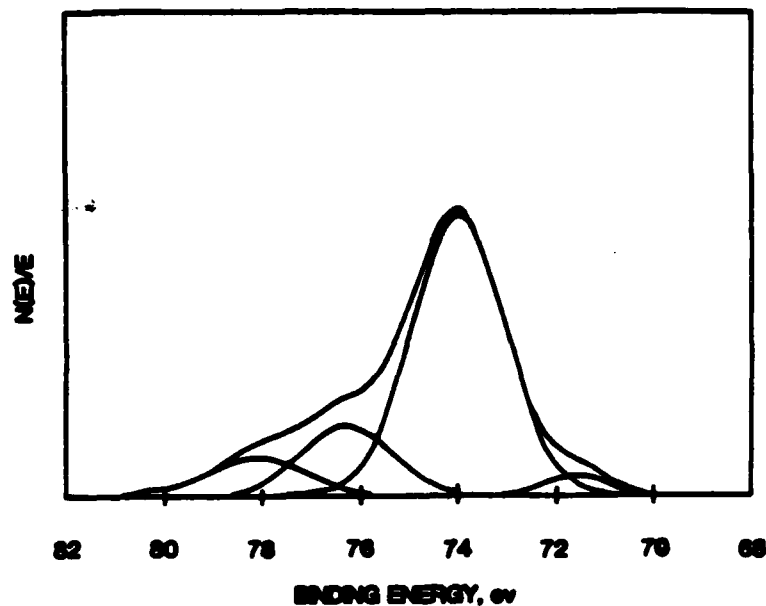


Figure 16. Deconvolution of Al(2p) XPS spectra of aluminum mirrors after adsorption of  $\gamma$ -APS for 15 minutes at pH 10.4.

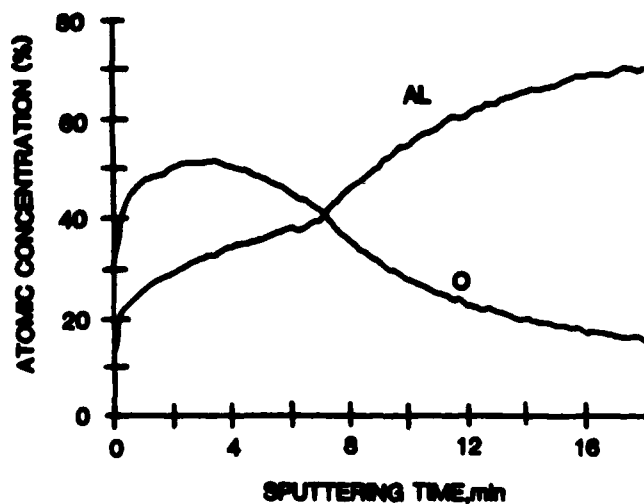


Figure 17. Aluminum and oxygen concentrations as a function of sputtering time for aluminum mirrors after adsorption of  $\gamma$ -APS for 15 minutes at pH 10.4.

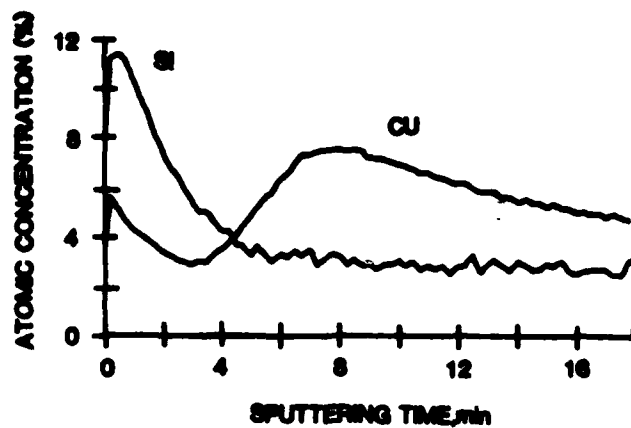


Figure 18. Silicon and copper concentrations as a function of sputtering time for aluminum mirrors after adsorption of  $\gamma$ -APS for 15 minutes at pH 10.4.

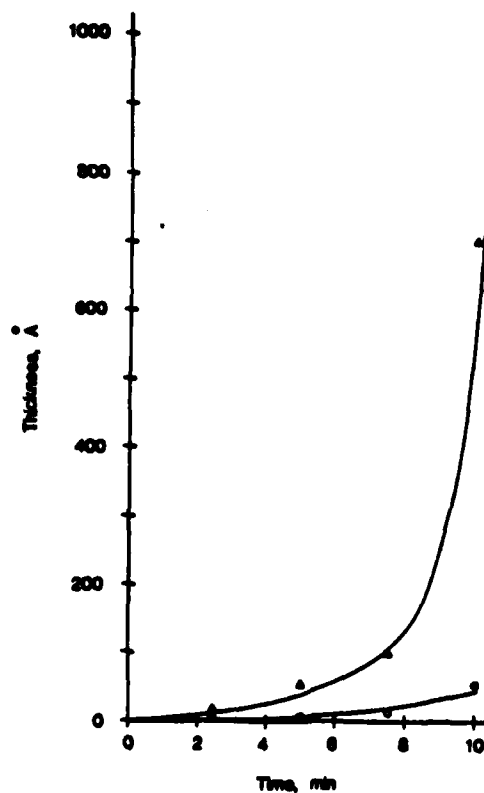


Figure 19. Hydration of air-formed oxide on aluminum mirrors during immersion in distilled, deionized water at 60°C:  $\Delta$ -no silane primer;  $\circ$ - $\gamma$ -APS primer applied at pH 7.0.

## VI. Publications and Presentations

The following is a summary of publications and papers presented at technical meetings during the preceding year based on work supported by this contract:

### A. Publications

"Structure and Properties of Silane Primers for Adhesive Bonding of Metals," *Polymer Preprints* 24, 204 (1983).

"Chemical Reactions of Coupling Agents on the Oxidized Surfaces of Metals," *Proc. 38th Ann. Tech. Conf., SPI Rein. Plastics/Composites Inst., Sec. 4C*, 1983.

"Structure and Properties of Silane Primers for Adhesive Bonding of Metals," in *Proc. Symp. Polymer Composites: Interfaces*, H. Ishida and N. G. Kumar, eds., Plenum Press, New York, in press, 1983.

"Hydrothermal Stability of Titanium/Epoxy Adhesive Joints," in *Proc. Intl. Symp. Adhesive Joints: Formation, Characteristics, and Testing*, K. L. Mittal, ed., Plenum Press, New York, in press, 1983.

"The Structure of Films Formed by  $\gamma$ -Aminopropyltriethoxysilane Adsorbed Onto Copper," *J. Colloid Interface Sci.* 91, 485 (1983).

### B. Papers presented at technical meetings

"Structure and Properties of Silane Primers for Adhesive Bonding of Metals," American Chemical Society, Seattle, WA, March 20-25, 1983 (invited).

"Characterization of Organic Films on Metal Surfaces Using Infrared and Raman Spectroscopy," American Vacuum Society (Minnesota Chapter), Minneapolis, MN, May 25, 1983 (invited).

"Structure and Properties of Silane Primers for Adhesive Bonding of Iron, Titanium, and Aluminum," presented at Adhesion Principles and Practice for Coating and Polymer Scientists, a short course sponsored by Kent State University, Kent, OH, June 6-10, 1983 (invited).

"Chemical Reactions of Coupling Agents on the Oxidized Surfaces of Metals," Society of the Plastics Industry, Houston, TX, February 7-11, 1983.

"Hydrothermal Stability of Titanium/Epoxy Adhesive Joints," American Chemical Society, Kansas City, MO, September 12-17, 1982.

"Adsorption of  $\gamma$ -Aminopropyltriethoxysilane Onto Copper," American Chemical Society, Kansas City, MO, September 12-17, 1982.

"Infrared Spectroscopy of Coatings on Metals," presented at Spectroscopy of Polymers and Energy Related Materials, a short course sponsored by Case Western Reserve University, Cleveland, OH, July 5-9, 1982.

"Surface Enhanced Raman Effect," presented at Spectroscopy of Polymers and Energy Related Materials, a short course sponsored by Case Western Reserve University, Cleveland, OH, July 5-9, 1982.

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