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AN INVESTIGATION OF THE CHEMISTRY OF SILANE COUPLING AGENTS FOR
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**AN INVESTIGATION OF THE CHEMISTRY OF
SILANE COUPLING AGENTS
FOR ADHESIVE BONDING OF ALUMINUM**

by

G.R. Peters and G.A. Luoma

Research and Development Branch
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AN INVESTIGATION OF THE CHEMISTRY OF SILANE COUPLING
AGENTS FOR ADHESIVE BONDING OF ALUMINUM.

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Gregory R. Peters and Greg A. Luoma

October 1989



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ABSTRACT

Adhesive bonding is gaining increasing attention as an alternative to more traditional methods such as welding and rivetting for in-field and permanent repair of military equipment. A major concern with adhesive bonding of metals such as aluminum is achieving reproducible high bond strengths when using epoxy adhesives. A number of commercially available silane, titanate and zirconate coupling agents have been proposed to chemically interact with both the aluminum surface and the adhesive, and thereby increase bond strength. This study was conducted to determine which of these coupling agents when used with DREP proprietary adhesives would provide the greatest improvements in bond strength, the best chemical form to apply the coupling agents, and the chemical basis for the improvements in bond strength. Results indicate that a particular silane coupling agent (γ -GPS) provides the greatest improvements in bond strength when applied from an ethanolic solution. Surprisingly, the studies indicate that the unhydrolysed silane is more effective as a coupling agent for bonding aluminum with epoxy adhesives than the hydrolysed form. This latter observation suggests that there is no direct chemical bonding of the aluminum surface to the coupling agent.

1. INTRODUCTION

Adhesive bonding has received considerable attention recently as an alternative to traditional welding and rivetting techniques for joining metals and composites. It has numerous advantages over other methods since adhesive bonding is not as likely to create localized stress points as is rivetting. Also, its ability to fill gaps prevents corrosion associated with water collecting in gaps produced by welding or rivetting. Adhesive bonding is also useful for situations where factory fastening equipment is not available or is too cumbersome when attempting to repair previously assembled objects in-the-field.

For these reasons, DREP is investigating the effectiveness of adhesive bonding for applications such as Battle Damage Repair, permanent repair and primary bonding of components. For each of these applications, it is necessary to produce reproducible, strong, environmentally resistant bonds. Aluminum is of particular interest as a substrate in these studies since numerous repairable aircraft components are made of this metal.

Pure silanes have been reported to improve the strength and durability of aluminum joints bonded with epoxy when used as additives or primers¹. Also, numerous commercial primers containing silanes and other coupling agents have been reported to improve the strength of adhesive bonds when applied to the aluminum surface prior to bonding. The presence of chemical bonds between the aluminum surface and silane coupling agent has also been proposed².

The purpose of this paper is to investigate some specific silane, titanate and zirconate coupling agents to determine if they are effective as coupling agents for aluminum bonding, to determine the methods of application which yield the greatest effectiveness, and to study the chemical interactions at the interface between the coupling agent and the aluminum surface.

Because there are no easy methods for pretreating aluminum surfaces in the field prior to bonding (eg. acid etching or anodizing) an aim of this

project is to develop methods usable in the field whereby strong, reproducible adhesive bonds may be made with a minimum of surface pretreatment.

2. EXPERIMENTAL

Bond strengths were determined by the single lap shear method. In this method two 200mm x 25mm x 3mm strips of 7075-T6 aluminum alloy are bonded to create a 25mm overlap with 625mm² of bond area (see figure 1).

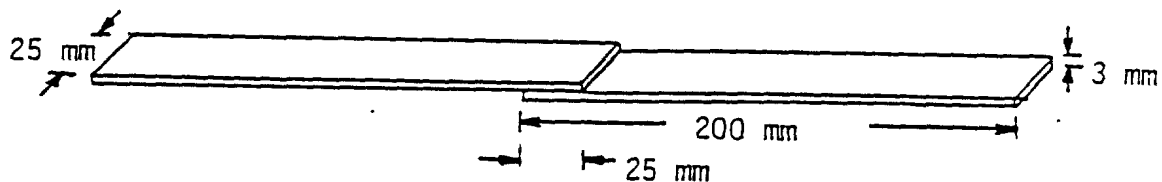


Figure 1: Single lap shear specimen used in this study.

The metal strips were pretreated prior to bonding by degreasing in Freon 113 for approximately 10 minutes, etching in 68°C chromic acid etch solution ($\text{Na}_2\text{Cr}_2\text{O}_7$ - 34g, and H_2SO_4 - 304g per litre in water), rinsing with deionized water and drying in anhydrous ethanol for 30 minutes before being air dried. Coupling agents (listed in Table 1) were applied by dissolving (or hydrolyzing) 0.5mL of the agent in 99.5mL of the solvent of choice resulting in a 0.5% (by volume) solution. The pretreated and air dried aluminum strips were then dipped in the coupling agent solution for 1 minute before being air dried.

A standard epoxy resin (LP2 - developed at DREP) was used for the adhesive bonding. This two part glue was mixed in a ratio of 3 parts resin to 1 part curing agent (by weight) and applied to each surface. Two pound weights were placed on each bond and the resin was allowed to cure overnight. The bonded bars were then placed in a 120°C oven for 3 hours to ensure complete curing. A premixed film adhesive was also used in some cases (LP2f, developed under contract to DREP) and was cured at 130°C for 3 hours. Once cured and cooled to room temperature, these bonded bars were then pulled apart by a Materials Testing System, and the maximum force endured immediately prior to bond failure was recorded.

Infrared studies of the silane coupling agent in solvent were performed using a Nicolet Model 6000 FTIR system fitted with a CIRCLE (Spectra Tech Inc.) accessory. The CIRCLE is a cell consisting of a cylindrical zinc selenide crystal into which the infrared beam enters at an angle, internally reflects through the length of the crystal and exits the crystal at the other end where it is focused on the detector. This crystal is located within an "open boat" shaped cell into which the solution may be placed. Due to absorption which takes place at the interface of the crystal and the solution each time the beam is internally reflected, a spectrum of the surrounding solution is obtained. By subtracting the spectrum of the pure solvent, a spectrum of the analyte as it exists in the solvent is produced. Although 0.5% solutions of the coupling agent were used for application to the aluminum it was necessary to use 5% solutions for infrared studies because the signal-to-noise ratio was not great enough to clearly discern the nature of the silane spectrum for lower concentrations.

Analysis of the coupling agents on the surface of the aluminum strips was also accomplished using the FTIR system configured for reflectance studies. Samples of the aluminum were polished to a "mirror finish" using an aluminum oxide suspension on a polishing wheel. The coupling agents were applied by placing a layer of a 1% silane in solvent solution on the surface and drying under an incandescent light overnight, leaving a thin film of the agent on the surface. An apparatus enabling the infrared beam to be

reflected at a 15° angle to the surface of the aluminum and then focused on the detector was used, allowing an absorption spectrum of the surface to be obtained. Samples of polymerized polysiloxane were analyzed by standard transmission techniques using sodium chloride crystals.

A Hewlett Packard 5988A GC-MS was used for mass spectrometric studies. The gas chromatograph oven was programmed to ramp from 100°C to 250°C at a rate of 15°C per minute. The silane peak (γ glycidoxypropyltrimethoxy-silane, γ -GPS) was positively identified by matching the mass spectrum of the peak with that of trimethoxy [3-(oxiranylmethoxy) propyl] silane in the instrument library.

3. RESULTS

3.1 Selection of Coupling Agent

To determine whether coupling agents improved bond strength over traditionally treated surfaces numerous silanes, titanates and one zirconate were applied to aluminum surfaces before bonding. Solutions of the coupling agents (0.5% by volume) were prepared in a 95% ethanol, 5% water (previously adjusted to pH=4 with acetic acid) solution. It is important to obtain a thin (sub micrometer) layer of agent on the metal surface since thicker layers may exhibit some lubrication effect which would be extremely detrimental to bond strength. Most agents were soluble in this solvent, however a significant amount of residue was visible in the neoalkoxy-tris(m-amino)phenyl titanate solution.

The results of the bond strength tests are summarized in Table 1, and are the averages of triplicate samples. Most primers lowered the effective shear strength of the bonded joints when used in combination with LP2 or LP2f epoxies, and only the neoalkoxy-tris(m-amino)phenyl titanate (Kenrich Petrochemicals, Inc.) and γ -GPS silane (Dow Corning Canada Inc.) maintained or improved the bond strength. Since the silane produced the greatest increase in bond strength, it was chosen for further study.

TABLE 1: Comparison of Shear Strengths For Aluminum Bonded With the DREP LP2 Adhesive and Pretreated with Various Silanes.

<u>COUPLING AGENT</u>	<u>SHEAR STRENGTH (MPa)*</u>
Control (no coupling agent)	27.1 0.5
<u>Silanes</u>	
N-[2-(Vinylbenzylamino) ethyl] 3-aminopropyl-trimethoxysilane	25.9
3-Glycidoxypropyltrimethoxy silane (γ -GPS)	27.6
<u>Titanates</u>	
neoalkoxy, tri(dioctylpyro- phosphato) titanate	25.9
neoalkoxy, tri(N-ethylamino- ethylamino) titanate	25.2
neoalkoxy, tri(m-amino)phenyl titanate	27.1
<u>Zirconates</u>	
neoalkoxy, tris(m-amino)phenyl zirconate	24.7

*1MPa = 145.1psi

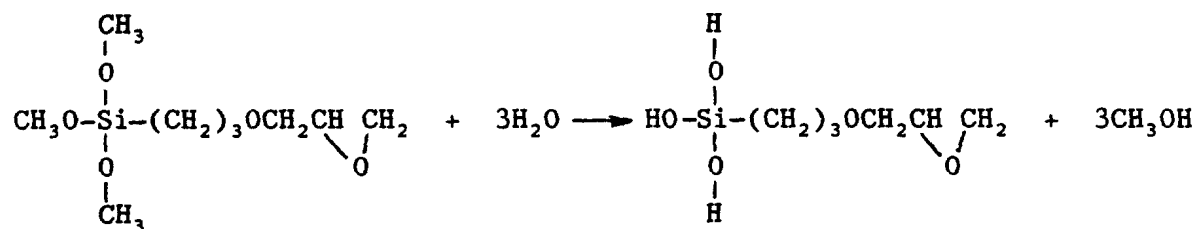
3.2 Selection of Solvent

To determine the most effective solvent from which to apply the γ -GPS silane primer, numerous studies were undertaken to determine the chemistry involved in the interaction of the silane and the metal surface. This included infrared and mass spectrometric analyses of the silane in various solvents, and infrared analysis of the silane on aluminum surfaces when applied as either the hydrolyzed silanol form (water solution) or the trimethoxy silane (other solvents).

The structure of γ -GPS is given in Figure 2. It has been reported³ that chemical bonding of the silane to aluminum occurs by hydrolysis of the

methoxy groups to form the silanol in an acidic aqueous environment followed by a condensation reaction between these silanol groups and the OH groups present on the surface of the aluminum to create a Si-O-Al linkage (Figure 2). While evidence for some interaction between the aluminum and the hydrolyzed silanol was found, no direct evidence of chemical bonding was seen and, in fact, superior adhesive bonds were achieved using the silane in the non-hydrolyzed methoxy form.

A)



B)

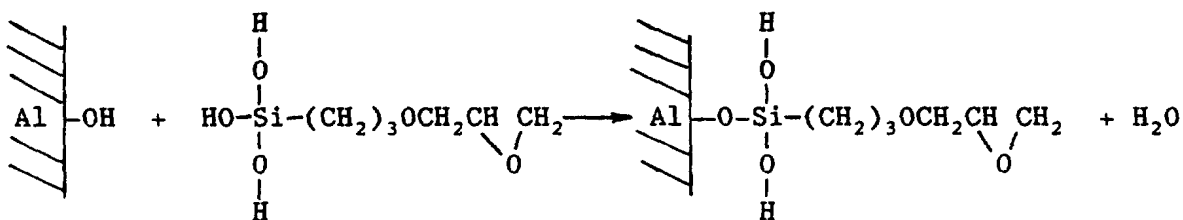


Figure 2: The reported chemical reactions of γ -GPS: (a) hydrolysis in an acidic aqueous solvent, and (b) condensation of the silanol with an aluminum surface.

Infrared analysis indicated that, when the silane was dissolved in a 95% ethanol, 5% water (pH=4) solution, it remained in the trimethoxy form. Figure 3 shows the IR spectrum of neat γ -GPS silane with the Si-OCH₃ bands at 1190cm⁻¹, 1075cm⁻¹, and 820cm⁻¹. Figure 4 shows the spectrum of 5% silane dissolved in the ethanol solution (ethanol spectrum subtracted out). These three peaks are clearly visible on this spectrum as well. A sample of this solution was also injected into the GC-MS where only one peak was found. This peak was positively identified as γ -GPS (see Figure 5).

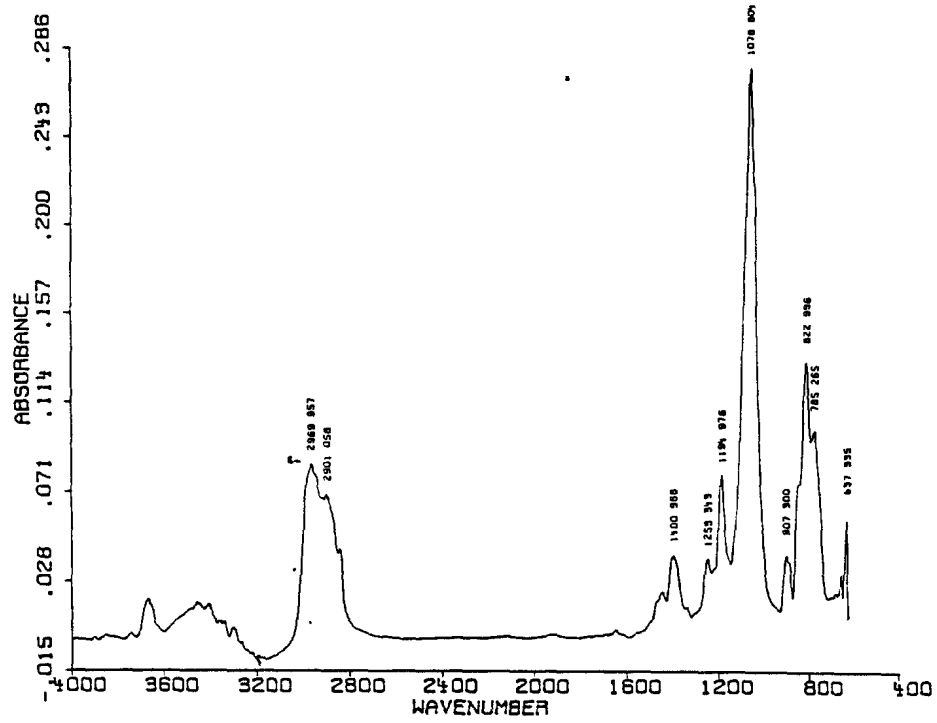


Figure 3: Infrared spectrum of pure γ -GPS.

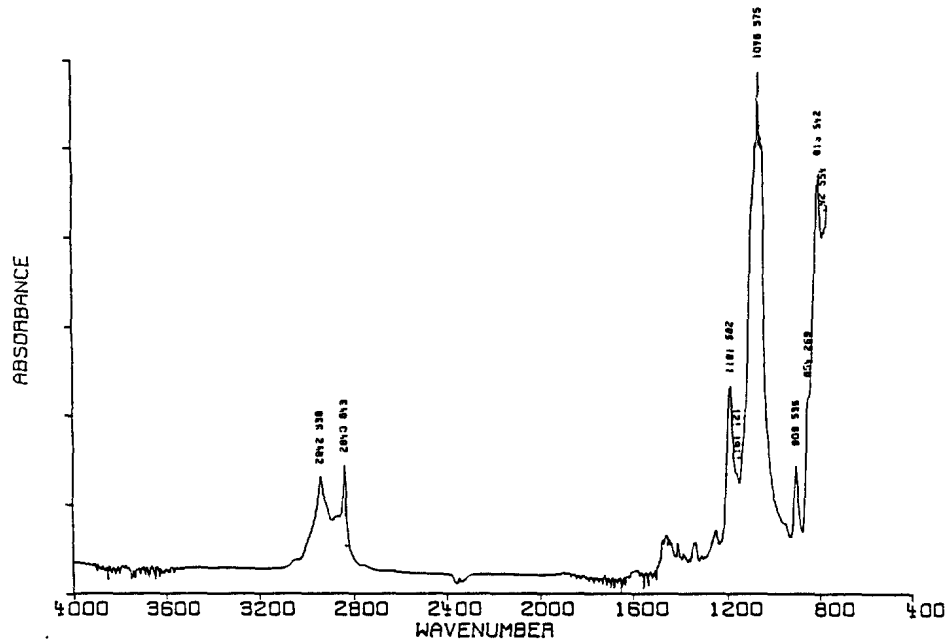


Figure 4: Infrared spectrum of 5% γ -GPS dissolved in 95% ethanol:5% water

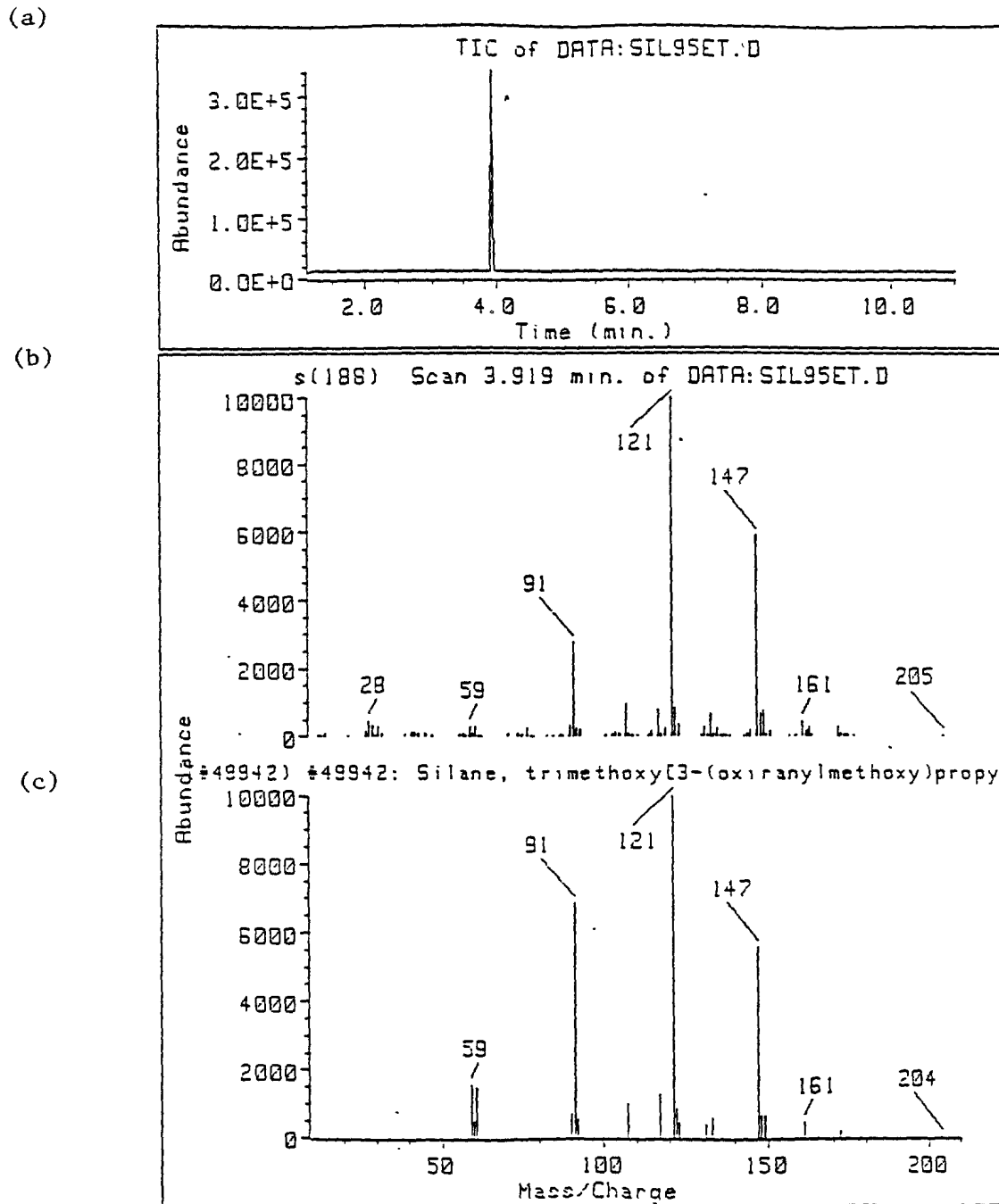


Figure 5: (a) Gas Chromatogram of γ -GPS in 95% ethanol:5% water.
(b) Mass spectrum of prominent peak from the TIC.
(c) Mass spectrum of γ -GPS from library.

When γ -GPS was dissolved in water at pH=4, the infrared spectrum (Figure 6) showed the disappearance of the Si-OCH₃ peaks at 1190cm⁻¹, 1075cm⁻¹, and 820cm⁻¹, as well as the appearance of Si-OH peaks at 1015cm⁻¹ and 910cm⁻¹. This indicates hydrolysis of the silane to the silanol (Figure 2). It was found that all concentrations of water would initiate hydrolysis and the greater the ratio of water to ethanol in the mixture, the faster the rate of hydrolysis. In pure water, hydrolysis takes place within 5 to 10 minutes, but when the solution contained 75% water and 25% ethanol complete hydrolysis required a few hours, allowing the reaction to be followed by infrared and gas chromatographic studies.

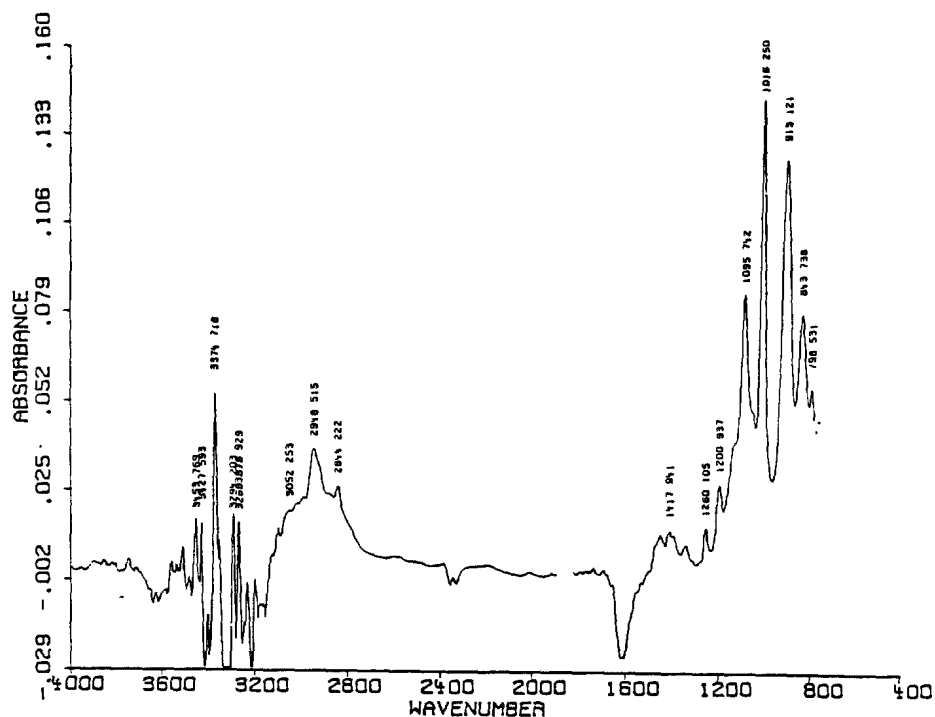


Figure 6: 5% γ -GPS hydrolyzed in water (adjusted to pH=4 with acetic acid).

Figure 7 shows four superimposed IR spectra of the silane in 75:25 water:ethanol solution taken at 1 minute, 10 minutes, 30 minutes, and 4 hours. These spectra clearly show the progressive disappearance of the methoxy peaks and the appearance of the silanol peaks. It is believed that the peak at 1095cm⁻¹ is an aliphatic silane peak which is present in all

four spectra but is overshadowed by the much larger peak at 1066cm^{-1} in the methoxy form. Although the silanol form does not elute from the gas chromatograph, the gradual disappearance of the silane peak can easily be followed.

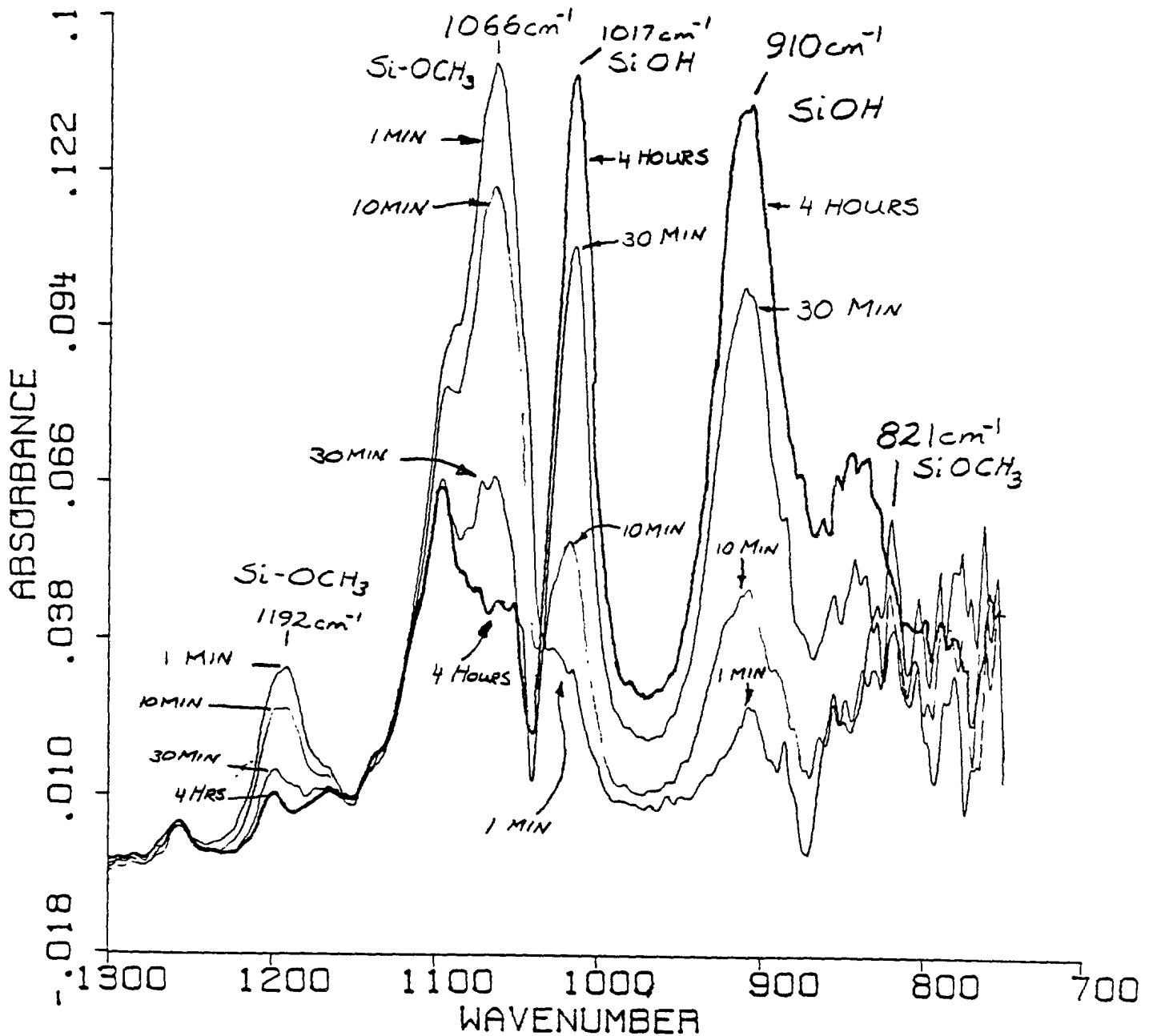


Figure 7: Superimposed IR spectra of 5% γ -GPS in 50% ethanol:50% water (pH=4) showing progression of hydrolysis at 1 minute, 10 minutes, 30 minutes and 4 hours.

Infrared reflectance studies of the silanes deposited on aluminum surfaces were carried out for both the non-hydrolyzed form (from 95% ethanol), and the hydrolyzed silanol (from water). The spectra obtained are given in Figures 8 and 9. The spectrum of the silane deposited from ethanol is practically identical to that of pure silane indicating that no significant change in the form of the coupling agent occurs when it is in contact with the aluminum (Figure 8a). When this film was rinsed off with ethanol, the resulting spectrum indicated that all detectable silane had been removed (Figure 8b). The spectrum of the coupling agent deposited from water shows significant changes from the aqueous silanol, and the film on the aluminum mirror was slightly rubbery indicating some polymerization had taken place (Figure 9a). There is a very prominent OH stretch peak visible which would indicate that polymerization is incomplete. To determine if the aluminum surface affected the rate of polymerization or the form of the polymer, a film of the silane was formed on a layer of polytetrafluoroethylene (PTFE, a non-reactive surface) instead of the aluminum. The film was then removed from the PTFE and a spectrum was obtained (Figure 9b). This spectrum is significantly different from the sample analyzed on the aluminum, and the Si-O-Si peaks at 1100cm^{-1} and 1030cm^{-1} , combined with the disappearance of the OH stretch at 3400cm^{-1} , indicate almost complete polymerization. Therefore, it appears that some interaction between the aluminum and the silane affects the polymerization of the silane on the aluminum surface.

Epoxy adhesive bonds were then made with aluminum strips which had been dipped in solutions of the silane in various solvents. The results in Table 2 indicate that when the surface was pretreated with the hydrolyzed silanol in water there was no increase in the shear strength. However, a significant improvement in shear strength was apparent for the aluminum strips which were pretreated with the silane in 95% ethanol, 5% water (pH=4). This difference may have been due to the fact that the solvents have significantly different surface tensions and the water tended to "bead up" while evaporating, concentrating the silanol to localized non-uniform patches. To test this hypothesis, adhesive bonds were made with the strips pretreated with solutions of 50% ethanol, 50% water (pH=4) solutions which had been allowed to hydrolyze for different lengths of time. Due to the

kinetics of the hydrolysis in this mixture, a four day old solution was determined by gas chromatography to be fully hydrolyzed, whereas a new solution was still in the methoxy form. This allowed the comparison of silane vs. silanol while keeping the physical properties of the solvent constant. These results are summarized in Table 3. The adhesive bonds made with the hydrolyzed silanol had a slightly lower shear strength than those made with no silane pretreatment, but those made with the silane in the trimethoxy form showed a significant increase in shear strength. This indicates that the effectiveness of the coupling agent is related to its chemical form when applied to the aluminum strips.

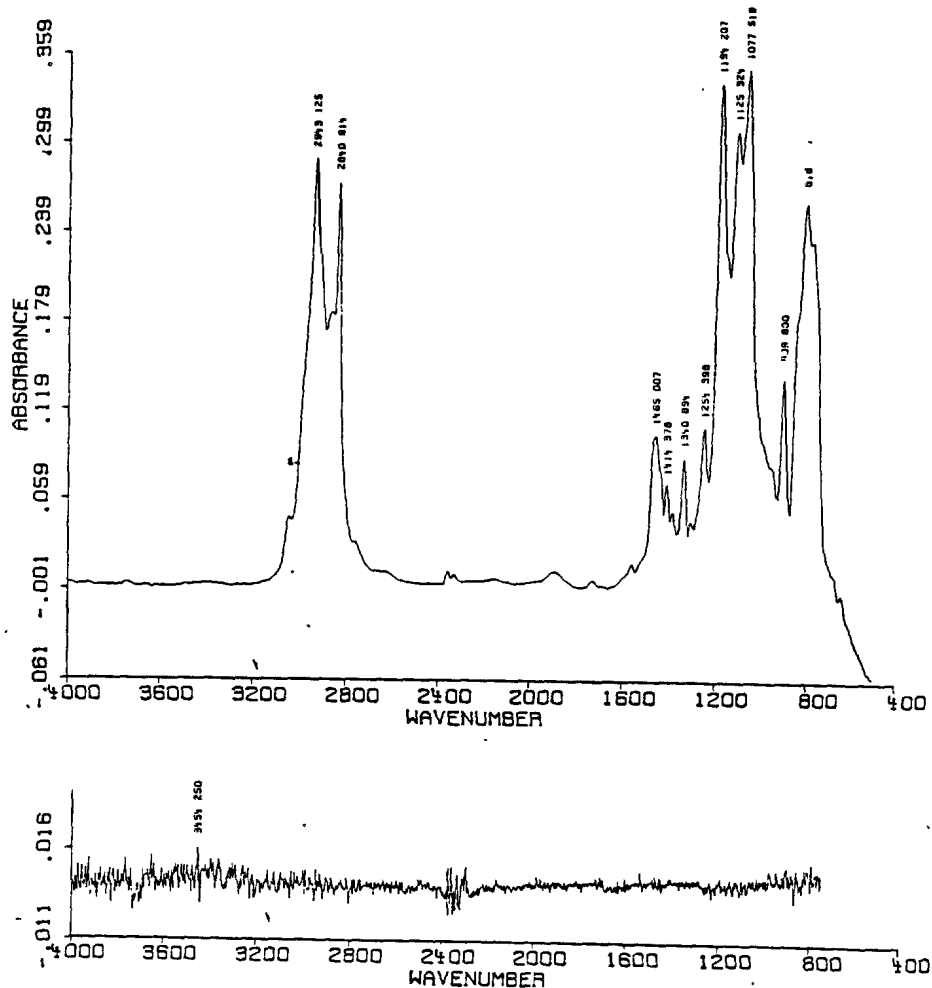
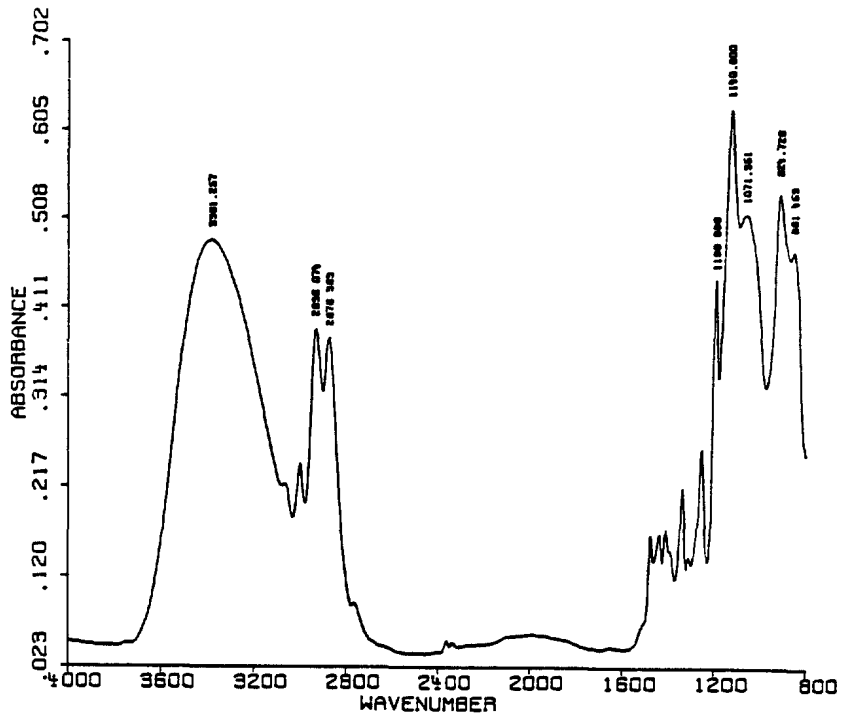


Figure 8: (a) Reflectance infrared spectrum of γ -GPS deposited on an aluminum mirror from 95% ethanol:5% water solution. (b) Reflectance infrared spectrum of aluminum mirror after removal of γ -GPS with ethanol.

(a)



(b)

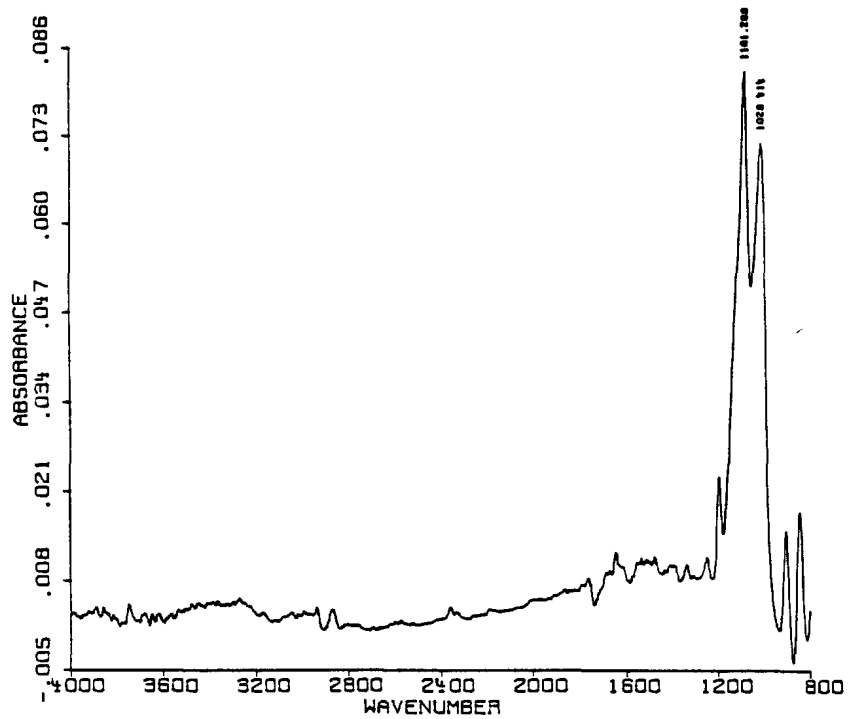


Figure 9: (a) Reflectance infrared spectrum of γ -GPS deposited on aluminum surface from water (pH=4).
(b) Infrared spectrum of polymerized γ -GPS deposited on PTFE surface from water (pH=4).

TABLE 2: Comparison of Shear Strengths of Adhesive (LP2) Bonds Made With γ -GPS in Acidic Water and 95% Ethanol Solution.

<u>SOLVENT</u>	<u>SHEAR STRENGTH (MPa)</u>
Control (no silane pretreatment)	25.0 \pm 0.5
Water (adjusted to pH=4 with acetic acid)	24.8
95% ethanol: 5% water	26.9

TABLE 3: Comparison of Shear Strengths of Adhesive (LP2f) Bonds Made With Silane Pretreatment in Both Silane and Silanol Forms Applied From a 50% Water:50% Ethanol Solution.

<u>SOLUTION AGE</u>	<u>SHEAR STRENGTH (MPa)</u>
Control (no pretreatment with γ -GPS)	19.6 \pm 0.5
4 days (hydrolyzed silanol)	18.1
0 days (non-hydrolyzed trimethoxy silane)	23.0

3.3 Stability of Coupling Agent in Solvent

It appears that once γ -GPS has hydrolyzed, polymerization in the solution will take place. While the rate of polymerization is reported to increase with pH, even at pH=4 there is evidence of polymerization after two weeks. A thin film of oily polymer could be detected by scraping the inside surface of the jar containing a solution of the hydrolyzed form of the silane. This is detrimental to long term storage of the adhesion promoter since, as functional groups become used in polymerization, the polymer will precipitate from solution onto the inside surface of the container. Also, the polysiloxane is much more sterically hindered than the monomer, making it more difficult to interact effectively with the metal surface. It was found, however, that the γ -GPS in 95% ethanol solution remained unchanged even after two months. This would indicate that solutions of γ -GPS made up

in 95% ethanol, 5% water are much more stable over long periods of time than those in aqueous solutions and would not require fresh preparation every time the coupling agent is to be used.

4. DISCUSSION

The choice of γ -GPS as a coupling agent for epoxy bonding appears reasonable since the functional group on the aliphatic chain is an oxiranyl (or epoxide) group which could react with the epoxy resin.

There are numerous possible reasons why the silane performs better when applied from the ethanol/water solution than from the pure aqueous solution. It is accepted that the presence of water between the epoxy and the metal is detrimental to the adhesive bond strength. It appears counterproductive to take elaborate steps (ethanol rinsing etc.) to dry the aluminum surface prior to bonding and then apply the silane from an aqueous solution. In addition, water (especially acidic water) will tend to cause "pitting" on the surface of the aluminum, leaving a non uniform surface which may hamper the adhesive efficiency.

Ethanol offers numerous advantages in this regard. Using ethanol as a solvent may help to remove extra water from the interface rather than adding more. There will always be some water molecules hydrogen bonded to the OH groups on the aluminum surface. No rinsing will remove these and, in fact, only high temperatures will succeed in creating a completely water free surface. However, if hydrolysis of the silane does occur prior to bonding with the aluminum, it is possible that this reaction, carried out on the aluminum surface rather than in solution, may scavenge these water molecules and create a much dryer surface at room temperature. The increase in adhesive bond strength when the silane is applied in the methoxy form is clearly evident from the shear strength tests.

While reflectance infrared analysis of the non-hydrolyzed silane on the aluminum surface does not indicate any chemical reaction with the aluminum

surface, it must be remembered that any bond formation will only occur at the interface, and it is possible that the spectrum is simply swamped by the bulk of the silane which is not in contact with the aluminum surface. It could be that the lack of any significant new bands in the spectrum is simply a result of insufficient sensitivity, and the "blank" spectrum obtained after rinsing the silane off with ethanol may have a residual monolayer of reacted silane on the aluminum surface which is invisible to the infrared beam.

The spectrum of the silanol on the aluminum surface is presumed to be due to polymerization of the silane itself rather than an interaction with the aluminum surface. Clearly, however, the surface does appear to affect the rate (or mode) of polymerization. This is indicated by the differences in the infrared spectra of polymerized silane from the aluminum surface versus that from the sample lifted from the PTFE, and may be due to some hydrogen bonding between the hydroxyl groups on the aluminum surface and the silanol OH groups. This would not be unusual since many metallic surfaces interact catalytically with organic molecules.

The adhesive bond shear strengths appear to indicate the superior performance of the methoxy form found in the ethanol solution. The problem mentioned earlier regarding the surface tension of the aqueous solvents and the uneven distribution of silane due to "beading" of the solvent on the aluminum surface is yet another reason why ethanol appears to be the superior solvent. Observations made during the evaporation of the solvents from the aluminum strips indicate that more even wetting of the surface occurs when the coupling agent is deposited from ethanol.

Finally, solutions of γ -GPS in ethanol appear to be stable for much longer periods of time than those in aqueous solvents, enabling the production of these solutions in the lab for use in the field. This eliminates the need for mixing up fresh solutions each time the coupling agent is required in the field, and would result in considerable savings in time and effort on the part of those responsible for repair work requiring adhesive bonding.

5. CONCLUSIONS

It is clear that the titanates, zirconates, and most of the silanes tested do not significantly improve adhesive bonding of aluminum with epoxy resins when used in combination with the DREP LP2 or LP2f epoxies, and many are detrimental to shear strength of the bond. Whether this is due to the coupling agent-aluminum surface interaction or a coupling agent-epoxy interaction is not clear.

It is evident, however, that γ -glycidoxypropyltrimethoxysilane improves the shear strength of adhesive bonds made with LP2 or LP2f epoxy resins. It does not appear to be necessary to have the silane in the hydrolyzed form for it to perform most effectively, and numerous factors indicate that the trimethoxy silane dissolved in 95% ethanol:5% water is actually a more useful formulation than the silanol in acidic water. The bond strength tests indicate that the silane applied from the ethanol solution increases bond strengths between aluminum surfaces. Because the trimethoxy form does not appear to be subject to the self condensation reactions which eventually occur in the silanol solutions, ethanol solutions of this silane not only produce stronger bonds but can be stored for extended periods of time without decomposition taking place. Therefore, if γ -GPS is to be used as a coupling agent for adhesive bonds, it is recommended that solutions be made from a mixture of 95% ethanol and 5% water which has been previously adjusted to a pH of 4 with acetic acid.

REFERENCES

1. Brevis, D.M., *Durability of Structural Adhesives*, Applied Science Publishers (1983), pp 215-254.
2. Boerio, F.J., and Gosselin, C.A., *Polymer Characterization - Spectroscopic, Chromatographic, and Physical Instrumental Methods*, American Chemical Society (1983), pp 541-558.
3. "A Guide to Dow Corning Silane Coupling Agents", Dow Corning Corporation, p. 6.

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AUTHORS: G.A. Luoma and G. R. Peters

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ABSTRACT

Adhesive bonding is gaining increasing attention as an alternative to more traditional methods such as welding and rivetting for in-field and permanent repair of military equipment. A major concern with adhesive bonding of metals such as aluminum is achieving reproducible high bond strengths when using epoxy adhesives. A number of commercially available silane, titanate and zirconate coupling agents have been proposed to chemically interact with both the aluminum surface and the adhesive, and thereby increase bond strength. This study was conducted to determine which of these coupling agents when used with DREP proprietary adhesives would provide the greatest improvements in bond strength, the best chemical form to apply the coupling agents, and the chemical basis for the improvements in bond strength. Results indicate that a particular silane coupling agent (γ -GPS) provides the greatest improvements in bond strength when applied from an ethanolic solution. Surprisingly, the studies indicate that the unhydrolysed silane is more effective as a coupling agent for bonding aluminum with epoxy adhesives than the hydrolysed form. This latter observation suggests that there is no direct chemical bonding of the aluminum surface to the coupling agent.

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