ELUCIDATION OF THE STRUCTURE OF SILANE COUPLING
AGENT FILMS FORMED ON METAL SURFACE

by

SIEW-HOON LEE

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENT
FOR THE DEGREES OF

BACHELOR OF SCIENCE

AND

MASTER OF SCIENCE

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

FEBRUARY, 1979

Signature of Author

Department of Chemical Engineering

January 19, 1979

Certified by

C.S.P. Sung, Thesis Supervisor

Accepted by

G.C. Williams, Chairman

Departmental Committee on Graduate Students

ARCHIVES

MAY 23 1979

LIBRARIES
ABSTRACT

ELUCIDATION OF THE STRUCTURE OF SILANE COUPLING
AGENT FILMS FORMED ON METAL SURFACE

by

SIEW-HOON LEE

Submitted to the Department of Chemical Engineering on January 19, 1979
in partial fulfillment of the requirements for the degrees of the Bachelor
of Science and the Master of Science.

Instead of using metal coupons, single crystal of metal oxide, namely
aluminium oxide or sapphire, were used as a model surface for metal. Films
of γ-aminopropyltriethoxy silane were deposited on the sapphire plates from
both aqueous and cyclohexane solutions and were then investigated using
Fourier transform infrared and ESCA techniques. FT-IR studies showed
that the films were polysiloxane networks. Some of the silane were deposit-
ed as internal zwitterions which were characterized by the \( \text{N}^+\text{H}_3 \text{IR} \) band in
the region of \( 1580 \text{ cm}^{-1} \) and the second nitrogen ESCA peak at around 403.5 ev.
Films of vinyltriethoxy silane were also studied using only FT-IR technique.
These were also found to be polymeric in nature.

The thickness of the γ-aminopropyltriethoxy silane films were deli-
berately changed so as to study the structure of the silane film as a func-
tion of the film thickness. Both the results of FT-IR and ESCA studies
strongly indicates that the silane network formed is more tightly cross-link-
ed at near the surface of the metal oxide than when it is in the region far
away from the surface. A gradient in the relative extent of cross-linking
was found for films deposited from both non-polar(cyclohexane) and polar
(water) solvents. The only difference between using the two types of solven-
ts is that the films deposited from cyclohexane appears to be relatively
more hydrolysed and polymerized than those deposited from water.

Removal of the outermost portion of the γ-aminopropyltriethoxy film
by washing with water followed by acetone, leaves a layer which is present in
trace amounts only and is tightly bound to the aluminium oxide surface. ESCA
studies of the surface reveals the presence of protonated amino groups. It
was thus suggested that the coupling agent may be bonded to the aluminium
oxide through a bond that is ionic in character.

From these findings, a suggestion has been put forward that accounts
for the role of trialkoxy silanes as adhesion promoters.

Thesis Supervisor: C.S.P.Sung
Title: Assistant Professor of Polymeric
       Department of Material Science and Engineering.
TABLE OF CONTENTS

TITTLE PAGE .................................................. 1
ABSTRACT ......................................................... 2
TABLE OF CONTENTS ........................................... 3
LIST OF FIGURES ................................................ 5
LIST OF TABLES .................................................. 7
ACKNOWLEDGEMENTS .......................................... 8
I. INTRODUCTION ............................................... 9

II. LITERATURE REVIEW ....................................... 11
   1. Thermodynamics of Joint Stability ..................... 11
   2. Properties of Silane Coupling Agents ................... 13
   3. Adsorbed Silane Coupling Agent films .................. 14

III. REVIEW OF THE EXPERIMENTAL TECHNIQUES ............... 22
    1. Model for the Metal Oxide Surface ..................... 22
    2. Fourier Transform Infrared (FT-IR) Spectroscopy ...... 24
    3. Electron Spectroscopy for Chemical Analysis (ESCA) ... 25

IV. EXPERIMENTAL ............................................... 29
    1. Sample Preparation ..................................... 29
    2. Infrared Analysis ....................................... 30
    3. ESCA Analysis of A-1100 Silane Film Adsorbed on .... 34
       Sapphire Plates .................................. 34

V. RESULTS ...................................................... 35
    1. IR Spectrum of Monomeric \(\gamma\)-aminopropyltriethoxy .... 35
       silane (A-1100) ................................... 35
    2. IR Transmission and Internal Reflection Spectra of ... 35
       A-1100 Films Applied From Aqueous Solutions to .... 35
       Sapphire Plates .................................. 35
<table>
<thead>
<tr>
<th>TABLE OF CONTENTS (Cont'd)</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3. IR Transmission Spectroscopic Studies of A-1100 Applied from Cyclohexane Solutions to Sapphire Plates</td>
<td>47</td>
</tr>
<tr>
<td>4. Internal Reflection Studies of A-1100 Films Applied from Aqueous Solutions to Sapphire Plates with KRS-5 as Reflection Plate</td>
<td>49</td>
</tr>
<tr>
<td>5. IR Spectra of Monomeric Vinyltriethoxy (A-151) silane and Polysiloxane Films Formed on Sapphire Plates</td>
<td>52</td>
</tr>
<tr>
<td>6. ESCA Studies of A-1100 Films Formed on Sapphire Plates</td>
<td>53</td>
</tr>
<tr>
<td>VI. DISCUSSION</td>
<td>66</td>
</tr>
<tr>
<td>VII. CONCLUSIONS AND RECOMMENDATIONS</td>
<td>71</td>
</tr>
<tr>
<td>VIII. REFERENCES</td>
<td>72</td>
</tr>
<tr>
<td>Figure No.</td>
<td>Description</td>
</tr>
<tr>
<td>-----------</td>
<td>---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>1.</td>
<td>Silane coupling agent in the form of 6-membered chelate rings</td>
</tr>
<tr>
<td>2.</td>
<td>Low molecular weight internal zwitterions</td>
</tr>
<tr>
<td>3.</td>
<td>Representation of the ionic bond suggested by Boerio and Greivenkamp to be present at the silane/metal interface</td>
</tr>
<tr>
<td>4.</td>
<td>Transmission IR Spectrum of Clean Sapphire Plate</td>
</tr>
<tr>
<td>5.</td>
<td>Energetics of Electron Binding Measurements in Solid</td>
</tr>
<tr>
<td>6.</td>
<td>Photoionization Process in ESCA</td>
</tr>
<tr>
<td>7.</td>
<td>Schematic Representation of the Experimental Set-ups for FT-IR Studies</td>
</tr>
<tr>
<td>8.</td>
<td>IR Spectra of Clean Sapphire Plates Put in Contact with KRS-5 which acts as the reflection plate</td>
</tr>
<tr>
<td>9.</td>
<td>IR transmission spectrum of monomeric γ-aminopropyltriethoxy silane as obtained between two NaCl plates</td>
</tr>
<tr>
<td>10.</td>
<td>IR transmission difference spectra of A-1100 films when applied from aqueous solution onto sapphire plate. The thickness of the film is 4μ for (a) 1.4μ for (b), 0.089μ for (c) and 450R for (d)</td>
</tr>
<tr>
<td>11.</td>
<td>IR internal reflection difference spectra of silane films obtained with an experimental setup shown in fig. 7(c) with the sapphire as a reflection plate. (a) is for A-1100 and (b) is for A-151</td>
</tr>
<tr>
<td>12.</td>
<td>Depth of penetration of IR beam as function of wavenumber with KRS-5 and Sapphire as reflection plates.</td>
</tr>
<tr>
<td>13.</td>
<td>IR transmission difference spectra of A-1100 films applied from C₆H₆ solution onto sapphire plates. The thickness of the film is 0.74μ for (a) and 0.4μ for (b)</td>
</tr>
<tr>
<td>14(1).</td>
<td>IR internal reflection difference spectra of A-1100 (a) and A-151 (b) films obtained with an experimental setup shown in fig. 7 (e) where KRS-5 is the reflection plate</td>
</tr>
<tr>
<td>Figure No.</td>
<td>Description</td>
</tr>
<tr>
<td>-----------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>14 (ii).</td>
<td>Reflection Spectra of A-1100 films formed on sapphire plates, using the set-up shown in fig. 7(d). (a) corresponds to the 450Å film and (b) the .92µ film.</td>
</tr>
<tr>
<td>15.</td>
<td>IR transmission spectrum of monomeric vinyltriethoxy silane as obtained between two NaCl plates.</td>
</tr>
<tr>
<td>16.</td>
<td>ESCA Spectra of sapphire plate (clean)</td>
</tr>
<tr>
<td>17.</td>
<td>ESCA Spectra of the .92µ A-1100 film</td>
</tr>
<tr>
<td>18.</td>
<td>Wide ESCA scans of the 450Å A-1100 film.</td>
</tr>
<tr>
<td>19.</td>
<td>ESCA Spectra of the 450Å A-1100 film.</td>
</tr>
<tr>
<td>20.</td>
<td>ESCA Spectra of the sapphire plate that was coated with A-1100 and then carefully washed with water and acetone</td>
</tr>
<tr>
<td>21.</td>
<td>Relative degree of cross-linking, expressed as the ratio of ANH₂/ACH₂ as a function of film thickness when A-1100 was adsorbed onto sapphire from aqueous solution.</td>
</tr>
</tbody>
</table>
## LIST OF TABLE

<table>
<thead>
<tr>
<th>Table No.</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Values of $W_A$ (work of adhesion in inert medium) and $W_{AI}$ (work of adhesion in the presence of wetting liquids)</td>
<td>12</td>
</tr>
<tr>
<td>2.</td>
<td>Frequencies of $\gamma$-aminopropyltriethoxy silane(A-1100) monomer and polysiloxane films</td>
<td>37</td>
</tr>
<tr>
<td>3.</td>
<td>Extent of cross-linking in A-1100 polysiloxane film as a function of film thickness.</td>
<td>42</td>
</tr>
<tr>
<td>4.</td>
<td>Depth of penetration of IR beam as a function of wavenumber</td>
<td>45</td>
</tr>
<tr>
<td>5.</td>
<td>IR absorption bands and tentative assignments of A-151 monomer and polysiloxane film</td>
<td>54</td>
</tr>
<tr>
<td>6.</td>
<td>ESCA peak positions and their assignments</td>
<td>64</td>
</tr>
<tr>
<td>7.</td>
<td>ESCA peak intensity ratios of A-1100 Films</td>
<td>65</td>
</tr>
</tbody>
</table>
ACKNOWLEDGEMENTS

I am deeply grateful to Prof. C.S.P. Sung, not only for her encouragement and patient guidance of this work but also the many personal kindness. I also wish to convey my gratitude to Prof. F. McGarry and Prof. Nakho Sung (Tufts University) for their assistance in one way or another. To Prof. L.B. Evans (Chemical Engineering Department), my undergraduate advisor, I wish to express my appreciation to him for the encouragement and support he gave me during those years.

Many other friends from the Polymer Division of the Material Science and Engineering Department have been very helpful and it has been enjoyable working together with them. I especially wish to thank Can B. Hu and Jeanne Courter for being most generous with the time they spent in discussing with me many questions that arose during the course of this work.

Thanks goes to Mr. S. Berger of the Silicones Division of Union Carbide for the silane samples, and all those in charge of the FT-IR and ESCA instruments. I am especially grateful to Dorienna Doyle for being so kind in typing the thesis and also to Christine Green for using her typewriter.

During my stay in the U.S, I have learned a great deal from the friendships that have developed. From them, I have learned much that I could not have done so by myself. My thanks to them is beyond words can expressed. Last but most of all, my heartfelt thanks goes to all those like my parents without whose love and hardwork, my education would not have been possible.

Financial support provided by M.I.T. and M.I.T. UROP office.
I. Introduction

Epoxy-resin based structural adhesives are extensively used for joining metals, plastics, carbon - and glass - reinforced composites in many diverse applications. However, in many of the applications of these structural adhesives, a serious problem frequently encountered is the adverse effects that water may have upon the strength of the bonded components. This is especially so when adhesive joints are also subjected to conditions of relatively high stress and temperature (1). Unfortunately, the fundamental mechanisms leading to this loss of strength are still not completely determined even though it is well-known that the material design and control of the adhesive/adherend interfaces are very important for achieving the strength and, especially, the durability of the adhesive bonds to various environmental attacks. The nature of this adhesive bond interphase depends largely on the surface condition of the adherend prior to bonding and the surface phenomena that occurs when the adherend and adhesive come together in the bonding operation.

Recently, it has been demonstrated that modification of the substrate surfaces prior to bonding by silane coupling agents may considerably increase the environmental resistance of joints consisting of aluminium alloys and mild-steel substrates bonded with a simple epoxide adhesives (2). Marked improvements in adhesion and wet strength in reinforced plastics can also be achieved by coating the reinforcing fibers or particles with an adsorbed film of silane coupling agent (3,4).

Although a large volume of literature on studies of the interface between polymer and mineral surfaces are available, there has been, as yet, no generally accepted theory of the function of adhesion-promoting silane coupling agents. The most commonly, but not universally, accepted mechanism
by which the wet-strength of adhesive joints is increased is the formation of strong covalent interfacial bonds. However, at present there is still a lack of an unequivocal proof of covalent bond formation between coupling agent and the metal surface. Therefore, the purpose of this project is to attempt to elucidate the structure of the silane coupling agent adsorbed onto metal surfaces. This information will be an important contribution towards a better understanding of the function of coupling agents in adhesion promotion.

The work here included the use of two recently developed techniques, namely Fourier Transform Infrared Spectroscopy (FT-IR) and Electron Spectroscopy for Chemical Applications (ESCA) to determine the structure of the films formed by silane coupling agent adsorbed onto metal surfaces.
II. Literature Review

1. Thermodynamics of Joint Stability (2)

The thermodynamic work of adhesion, $W_A$, required to separate unit area of two phases forming an interface may be related to the surface free energies by the Dupre equation. In the absence of chemisorption and inter-diffusion, the reversible work of adhesion in an inert medium may be expressed by:

$$W_A = Y_x + Y_y - Y_{xy} \quad \text{(1)}$$

where $Y_x$ and $Y_y$ are the surface free energies of the two phases and $Y_{xy}$ is the interfacial free energy. In the presence of a wetting liquid, the work of adhesion, $W_{AL}$, is:

$$W_{AL} = Y_{xL} + Y_{yL} - Y_{xy} \quad \text{(2)}$$

Kaelble et al (5) has shown that $W_A$ may also be given by:

$$W_A = 2 \left[ (Y_x^D Y_y^D)^{1/2} + (Y_x^P Y_y^P)^{1/2} \right] \quad \text{(3)}$$

and Kinloch et al (2) that:

$$W_{AL} = 2 \left[ Y_L - (Y_x^D Y_L^D)^{1/2} - (Y_x^P Y_L^P)^{1/2} - (Y_y^D Y_L^D)^{1/2} - (Y_y^P Y_L^P)^{1/2} \right.$$

$$\left. - (Y_y^P Y_L^D)^{1/2} + (Y_x^D Y_y^D)^{1/2} + (Y_x^P Y_y^P)^{1/2} \right] \quad \text{(4)}$$

where $Y^D$ and $Y^P$ are the dispersion and polar force components to the total surface free energy.

For a typical organic-metal oxide interface, $W_A$ usually has a large positive value indicating thermodynamic stability of the interface. However, in the presence of a wetting liquid like water, the thermodynamic work of adhesion, $W_{AL}$, may have a negative value indicating that the interface is unstable and will dissociate.
The values of the parameters on the right-hand side of the above equations can be determined experimentally and hence $W_A$ and $W_{AL}$ can be easily calculated using equations (3) and (4). Gledhill and Kinloch (2) have calculated values of $W_A$ and $W_{AL}$ which are shown in Table 1.

<table>
<thead>
<tr>
<th>Interface</th>
<th>Work of Adhesion</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Inert Medium</td>
<td>$m$ J/m$^2$</td>
<td>$mJ/m^2$</td>
</tr>
<tr>
<td>Epoxy-ferric oxide</td>
<td>291</td>
<td>-255</td>
<td></td>
</tr>
<tr>
<td>Epoxy-silica</td>
<td>178</td>
<td>-57</td>
<td></td>
</tr>
<tr>
<td>Epoxy-aluminum oxide</td>
<td>232</td>
<td>-137</td>
<td></td>
</tr>
</tbody>
</table>

As can be seen from Table 1, when the environment is dry, $W_A$ has a positive value indicating that the surface is thermodynamically stable. However, when a layer of moisture is adsorbed onto the interface, $W_{AL}$ becomes negative. The change in the work of adhesion from a positive to negative value provides the driving force for the displacement of the adhesive from the metal oxide surface by water.

Thus, the thermodynamics of joint stability suggests that in order for the joint to be durable in a humid environment, water must be prevented from reaching the interface or there must be present primary interfacial forces that are stronger than the force that causes the adhesive to be displaced from the metal oxide surface.
2. **Properties of Silane Coupling Agents**

The most common type of silane coupling agents used has the general structure \(X_3\text{Si(CH}_2\text{)}_n\text{Y}\), where \(n=0\) to 3, \(X\) is a hydrolyzable group on silicon, and \(Y\) is an organofunctional group selected for compatibility with a given adhesive. In many applications, neutral organofunctional silane coupling agents—where \(Y\) can be vinyl, methacryloxy, chloro, etc.—are applied from aqueous solutions which are slightly acidic (pH about 4). Under such conditions, the hydrolyzable groups react to generate intermediate silanols with the acid acting as a hydrolysis catalyst:

\[
X_3\text{Si(CH}_2\text{)}_n\text{Y} + 3\text{H}_2\text{O} \rightarrow (\text{HO})_3\text{Si(CH}_2\text{)}_n\text{Y} + 3\text{HX}
\]

if \(X\) is an ethoxy group, then

\[
R\text{Si(OCH}_2\text{CH}_3)_3 + 3\text{H}_2\text{O} \xrightarrow{\text{hydrolysis}} \text{RSi(OH)}_3 + 3\text{C}_2\text{H}_5\text{OH}
\]

The above reaction is fast and the intermediate silanols generated can then condense slowly to form siloxane structures:

\[
\begin{align*}
\text{RSi(OH)}_3 & \xrightarrow{\text{condensation}} \text{RSi-O-Si-R} \\
\text{R} & \text{R} & \text{R} \\
\text{OH} & \text{OH} \\
\text{O-Si-O-Si-O-Si-O-etc. (slow)} & \text{polysiloxane network}
\end{align*}
\]

When applied from aqueous solutions, the coupling agents are largely monomers or dimers with smaller proportions of oligomers (4). For example, a fresh aqueous solution of vinyl trimethoxysilane contains 82% monomer,
15% dimer and 3% trimer.

Unlike the neutral organofunctional silane coupling agents, amino-functional silane coupling agents show unique solution properties when the nitrogen is on the 3-carbon atom, for example, \( \text{aminopropyltriethoxy silane} \). They are autocatalytic and thus hydrolyze almost immediately in water. If polar solvent is used, the solution formed has unlimited stability due to the formation of 6-membered chelate rings which are extraordinarily stable:

![Silane coupling agent in the form of 6-membered chelate rings](Ref. 4)

The aqueous solutions, therefore, do not contain free silanol (\( \text{SiOH} \)) groups and instead, are relatively low molecular weight siloxanes with stabilized silanoate ions. The chelate ring structure is, however, lost when all the solvent has vaporized and forms again when solvent is added to it.

3. **Adsorbed Silane Coupling Agent Films**

Extensive effort has been directed to studying the nature of the adsorbed silane coupling agent films deposited on metal, glass, silica and other mineral surfaces. As a result, innumerable papers debating the resulting percentage improvement to the wet and dry strengths and how these compounds function have been published over the recent years. Many hypotheses attempting to explain the function of silane coupling agents have been
suggested, among which the principal one is the "coupling or chemical bond" theory. This theory suggests that an effective coupling agent is one that is able to bond chemically to the metal or glass surface through covalent oxane bonds and to the adhesive by reaction of the organofunctional group with the resin. Adhesion of the resin to the glass is, therefore, strengthened through the formation of a chemical bridge between the two phases. Although this theory has been useful in guiding the search for improved adhesion promoters as well as having been supported by the majority of the existing evidence, it is not able to explain completely all the observed facts. For example, it cannot explain why certain silanes are ineffective promoters even when they have organofunctional groups which are reactive. Furthermore, even though silane coupling agents may form metal siloxane bonds to metal surfaces, such bonds are easily susceptible to hydrolysis. This is inconsistent with the coupling theory which suggests that the ability of silane to improve adhesive bond wet-strength is partly attributed to the formation of strong covalent bonds with the adherend.

Another problem with the coupling theory is that the adsorbed film is suggested to be composed of a monolayer of silane monomer when actually it is usually adsorbed as the siloxane polymer. In practice, silane coupling agents are applied from solutions containing water and acid or base—a medium which is favorable for trialkoxysilane compounds to undergo hydrolysis and polymerization to form polysiloxane. It is therefore difficult, if not impossible, to deposit a film consisting of only a monolayer of the monomers.

A review of previous experimental works (8,9,10,14) suggests that silane coupling agents are deposited on the substrate as multilayers with a variable orientation that depends on the condition of deposition. Schrader
et al (8) investigated the nature of the adsorbed silane film by carrying out experiments in which γ-aminopropyltriethoxysilane (A-1100) was deposited from aqueous solution onto Pyrex and E-glass surfaces. As the A-1100 was extracted from the surface, the variation of the silane remaining on the surface was monitored by labelling the silane coupling agent with C-14 (gamma carbon). As a result, it was found that three distinct types of A-1100 were adsorbed on the surface. The first fraction, which constituted the majority (about 270 monolayers) of the adsorbed silane, was composed of hydrolyzed A-1100 attached by bonds no stronger than hydrogen bonds. The second fraction (about 10 monolayers) consisted of silane molecules attached to each other through single siloxane bonds and was removed by boiling the sample for three to four hours in water. The remaining A-1100 (about one monolayer), which made up the third fraction, was not removed by extraction with boiling water. It was thus concluded that this layer may be directly attached to the glass surface through multiple siloxane bonds. Though this explanation is plausible, one cannot rule out the possibility that this final fraction is so tenaciously bound because it is highly cross-linked within itself.

Evidence of chemical bonding at the interface is found in a study done recently by Getting and Kinloch (7). Two surface specific techniques, x-ray photoelectron spectroscopy (XPS) and static secondary ion mass spectroscopy (SSIMS) were used to investigate the interfaces between various types of silane coupling agents: γ-glycidoxypropyltriethoxysilane, (A), a styrene functional amine hydrochloride silane, (B), and γ-aminopropyltriethoxysilane, (C) and abraded mild-steel surfaces. Of the three silanes studied, only A was found to improve the adhesive joint durability in wet environment. When the
metal surface was coated with silane, FeSiO\(^{+}\) radicals were detected by SSIMS. However, when silanes B and C were used, no such radicals were detected. Furthermore, in the XPS results for all the silanes, shifts were observed in the binding energy of iron 2\(P_{3/2}\) photoelectron peak. However, the shift from 706.5 ev (assigned to pure iron) to the higher binding energy position for A was 4.8 ev, which is relatively larger than that for B (1.6 ev) and C (3.1 ev). The shifts for B and C were probably due to formation of various types of iron oxides. The shift for A, on the other hand, was too large to be due to iron oxide formation. Instead, it was speculated to be due to a more complex bonding, possibly between silicon, iron, and oxide. From this information, together with the SSIMS results, the conclusion thus drawn was that a chemical bond, probably –Fe-O-Si\(=\), formed between the metal oxide and polysiloxane coating accounted for the improved joint durability.

Ghent and Hsu (15) have also demonstrated direct chemical bonding between model silane compounds and finely divided silica particles which represent glass. The model silane compound studied was vinyltrimethylethoxy-silane which has only one hydrolyzable group. Using near infrared spectroscopy, it was found that the intensity of the absorption peak at 1.38\(\mu\)m, attributed to the surface silanol groups of silica, was reduced considerably after it was treated with silane in the presence of n-propylamine as a hydrolysis catalyst. This may be due to the addition of silane by condensation or exchange reactions with the surface silanols which were present according to a variety of experimental determinations. When the silica treated with vinylsilane was dispersed in poly(ethylene-co-propylene) and a free radical intermolecular cross-linking reaction was carried out, the vinyl groups partially disappeared, presumably as a result of radical combinations with the
polymer molecules. It was thus deduced that covalent bonding may have taken place between the silane and silica as well as between the silane and polymer.

Bascom\(^{(12,14)}\) has reported several investigations using contact angle measurements, internal reflection infrared (ATR) spectroscopy, ellipsometry, and scanning electron microscopy to elucidate the structure of vinyl, \(Y\)-aminopropyl, \(Y\)-chloropropyl and \(p\)-chlorophenylethyl trialkoxysilane deposited on glass and metal surfaces from polar and non-polar solvents. The infrared ATR study provided direct evidence that the silane films are polysiloxane coatings, part of which could be easily removed by rinsing them with organic solvents (e.g. acetone) or water. In all cases, there remained a coating which was composed of more firmly held polysiloxane networks. Contact angle determinations on this residual coating indicated that it might be an open polymeric structure since it was easily penetrated and swollen by water and organic liquids. Ellipsometric measurements have shown that films applied from non-polar solvents to be relatively thick (greater than 1000 Å) while those applied from polar solvents were in general thinner (less than 100 Å). Furthermore, the structure of the films was found to be approximately similar for different kinds of substrates, such as steel, glass, and internal reflection plates (germanium and KRS-5).

Since the silane films formed on adherend surfaces are essentially polysiloxane networks, which can be easily penetrated by liquids, it is very likely that when contacted with a liquid adhesive, the liquid will also penetrate the polysiloxane film \((11)\). Hence, when the adhesive is cured, an interphase region consisting of essentially interpenetrating networks of polysiloxane and epoxy-resin is formed and its thickness would be at least as
thick as the polysiloxane films (100-1000 Å).

Also, it has been speculated that the effect of the functional group of the silane coupling agent on the resin structure may be more extensive than just within the film itself, thereby influencing the resin structure near the interface (13). From electron and optical microscopy, it is known that the resin structure consists of micelles of high density polymer separated by narrow boundary regions of lower molecular weight materials. At the interface, this low density region can provide pathways for easy entry of water into the interfacial region. But, if the silane coating was present, entanglement of this low density resin into the loose siloxane structure would increase its density and thus act as a barrier to water penetration. The siloxane films cannot by itself act as a waterproof layer because it is not dense enough to block the diffusion of water molecules. Alternatively, a dense polymer may also be formed at the interface if the silane film were to initiate polymerization of the resin.

At the present time, relatively little is still known about the structure of silane films at the molecular level when they are adsorbed on metal surfaces. Very recently, Boerio and Greivenkamp (17) have studied the adsorption of silanes (γ-aminopropyltriethoxy, A1100, and γ-methacryloxypropyltrimethoxy, A-174, silanes) on iron and copper coupons using reflection-absorption infrared spectroscopy. The A-1100 films formed on the iron coupons were found to be thick and on drying, the outermost portion became highly hydrolyzed polysiloxane networks which were weakly bound and easily desorbed by water. This fraction has a characteristic band at 1575 cm⁻¹ which was assigned to the NH₂ deformation mode and a structure where the amino group is coordinated to the silicon atom to form a cyclic complex. However, after washing with water, new IR bands are observed near 1600 cm⁻¹ and 1510 cm⁻¹ which Boerio assigned to NH₃⁺ deformation modes and the film was estimated to be 25 Å thick. It was suggested that these results may be an indication that A-1100
was adsorbed onto iron as low molecular weight (mainly dimers) internal cyclic zwitterions:

\[
\begin{array}{c}
\text{CH}_2 \quad \text{CH}_2 \\
\text{CH}_2 \quad \text{Si-O-Si} \\
\text{N}^+ \text{H}_3 \quad \text{O} \\
\text{O} \\
\text{CH}_2 \quad \text{CH}_3
\end{array}
\]

Fig. 2. Low molecular weight (mainly dimers) internal zwitterions

When the film was about 17 Å thick (corresponds to 2 molecular layers), their results indicate that A-1100 may be adsorbed as a dimerized siloxane attached to the substrate through salt formation with the ionized surface metal oxide. A shoulder was observed at near 2970 cm\(^{-1}\) (which was assigned to \(-\text{OCH}_2\text{CH}_3\)) indicating that the adsorbed silane was not completely hydrolyzed. The structure of the silane at interface, as proposed by Boerio and Greivenkamp, appears as shown in the figure below:

\[
\begin{array}{c}
\text{Fe-O}^- \quad \text{(surface)} \\
\text{H}_3^+ \quad \text{N} \\
\text{H}_3\quad \text{Si-O-Si} \\
\text{O} \\
\text{O} \\
\text{CH}_2 \quad \text{CH}_3 \\
\text{CH}_2 \quad \text{CH}_3
\end{array}
\]

Figure 3.

\text{Y-methacryloxypropyltriethoxysilane or A-174 film was also found to be several molecular thick. Most of the material was loosely bound and}

-20-
hence easily desorbed by cyclohexane to leave a thin film of one to two monolayers thick. Observation of a shoulder on the low frequency side of the C=O band at 1720 cm\(^{-1}\) was proposed to be due to the interaction between A-174 and the copper coupon through the C=O groups.

So far, two types of chemical bonding between silane and metal substrates have thus been proposed. The first one, suggested by Gettings and Kinloch (7), was a metallosiloxane bond of the type -Fe-O-Si=c, while the second one, suggested by Boerio and Greivenkamp, was an ionic band as illustrated in Figure 3. From the reports of their investigations, it is difficult to decide which of the two types of bonding is the correct one, or may be both of them are present at the interface. While the technique (reflection absorption IR) used by Boerio and Greivenkamp is very difficult to use when one wants to study the interaction of various coupling agents and metals (17), SSIMS technique, used by Gettings and Kinloch, is also subjected to various kinds of experimental problems. Therefore, an attempt was made in this project to develop a better and simpler technique involving IR spectroscopy to elucidate the structure of silane.
III. Review of the Experimental Techniques

1. Model for the Metal Oxide Surface

 Prior to adhesive bonding, it is a common practice to clean the metal surfaces by a series of steps that usually begin with solvent degreasing followed by sand blasting or chemical etching. These steps are supposed to remove oil, scale, and at least some of the oxide so as to leave a coherent oxide layer and also to roughen the surface. In general, a coating of oxide is found on most metal surfaces, even after careful cleaning. The thickness, morphology and chemical composition of the oxide that finally develops on the etched metal are probably determined by the water rinse. The processes involved are essentially still unknown, though it is well known that large differences in the properties of the metal oxide can be brought about by subtle factors (11).

 When silane coupling agents are applied to metal surfaces, it is safe to assume that it interacts mostly with the oxide rather than the metal itself. Hence, in this project, instead of using aluminum metal coupons, single crystalline aluminum oxide were used as a model for metal oxide surface. Using single crystal aluminum oxide for elucidating the structure of silane films adsorbed on it offers two major advantages. Firstly, it can transmit IR radiation down to about 1500 cm$^{-1}$ wavenumber as shown in Figure 4. This makes it possible for using IR technique to study the interaction between silanes and aluminum oxide in the region where aluminum oxide transmits most of the IR radiation. The second important advantage is that when the silane films is very thin and cannot be detected using transmission IR spectroscopy, aluminum oxide (sapphire) plate can be used as an internal reflection crystal since its refractive index (=1.78) is greater
**Figure 4. Transmission IR spectrum of clean sapphire plate**
than that of the silane film (approximately 1.5). By using internal reflection IR spectroscopy, very thin films can be studied because the IR absorption intensity can be magnified many times by multiple reflections.

2. Fourier Transform Infrared (FT-IR) Spectroscopy (Ref. 20, 21, 22)

Fourier transform infrared (FT-IR) spectroscopy has been used successfully to study the structure and chemical composition of thin surface films (20). The important advantages that FT-IR spectrometer has over conventional dispersive spectrometers are.

(1) Multiplexing of spectral information—Fellgett's advantage

(2) Enhanced optical through put—Jacquinot's advantage

(3) Frequency accuracy—Connes advantage

(4) Computerization and spectral manipulation

In contrast to conventional dispersive spectrometers, which use a monochromator and slit system to divide the IR radiation into frequency elements, FT-IR system uses the Michaelson interferometer, which contains no slits and, hence, the amount of infrared energy falling on the detector is greatly enhanced. The multiplexing advantage arises from the fact that data from all spectral frequencies are measured simultaneously in one scan. Multiple scanning, therefore, can be done within a short period of time to increase the signal to noise ratio, enabling small changes in the sample to be detected. The frequency accuracy of each individual spectrum is achieved by incorporating a small monitoring laser into the FT-IR system.

More importantly, for the purpose of this project, is that the FT-IR spectrometer is interfaced to a mini-computer. This resulted in the development of signal averaging techniques and sophisticated software, which enables
the storage of digitized data and mathematical manipulation of the spectra. In this project, the spectral subtraction routine is used to obtain the spectra of silane directly by subtracting away all the undesired absorption spectra, thereby allowing the structural changes of silane coupling agents on metal surface to be followed.

3. **Electron Spectroscopy for Chemical Analysis (ESCA)**

Over the past decade, ESCA or XPS (x-ray photoelectron spectroscopy) has been widely used for probing the structure and chemical composition (23,24,25). The fundamental physical process involved in ESCA is the photo-ionization process shown schematically in Figure 6. When a specimen is bombarded with x-rays, an atom A interacts with a photon to produce a discrete energy electron (photoelectron) and an excited ion. In ESCA experiments, it is the ejected photoelectrons which are measured. In general, most of the ejected photoelectrons come from the core orbitals of an atom.

During photoionization (Figure 5), part of the incident x-ray energy, $h\nu$, is used in overcoming the binding energy of the ith shell, $E_{b,i}$, while the rest of it appears as the kinetic energy of the escaping electron. The kinetic energy, $E_{kin}$, of the photoelectron analyzed in ESCA is related to the binding energy by the expression:

$$E_{kin} = h\nu - (E_{b,i} + \phi_{sp} + E_r)$$  \hspace{1cm} (ref. 25)

where: $E_{b,i}$ is the binding energy, corresponding to orbital i, referred to the Fermi Level, $E_{kin}$ is the kinetic energy in the analyzer, $\phi_{sp}$ is the spectrometer work function, $E_r$ is the recoil energy (normally neglected).

The advantages of using ESCA for studying chemical changes at the inter-
FIGURE 5. Energetics of Electron Binding Measurements in Solid Photoelectrons are initially emitted from the sample with kinetic energy, $E'_{\text{kin}}$, but due to the potential gradient between the sample and the monochromator, the kinetic energy ultimately measured is $E_{\text{kin}}$. As the primary electrons travel through the sample to the vacuum environment, they recoil with energy, $E_r$, which is usually very small in magnitude and is neglected in ESCA. (25)
Figure 6. **Photonization Process** (26)

[Diagram showing energy levels and transitions involving K, L, and M levels, Fermi level, and MgKα₁,₂ X-ray.]

**KIN ETIC ENERGY**

**BINDING ENERGY**

- **FREE PHOTOELECTRON**
- **FERMI LEVEL**
- **MgKα₁,₂ X-RAY**

**NUCLEUS**
faces are as follows (24):

1. All elements with the exception of hydrogen should theoretically produce electron lines that are characteristic of the elements only. In ESCA, elements adjacent to each other in the periodic chart produce photoelectron lines which are well separated from one another so that no ambiguity exists in the identification of adjacent elements.

2. ESCA has sensitivity between 0.1% and 1% \((10^{-8} - 10^{-9} \text{ g})\) of a monolayer, depending on the element.

3. It is a non-destructive technique compared to other surface techniques like secondary ion mass spectrometry (SIMS). This is due to the fact that low electron beam intensity is used.

4. Chemical shifts are observed. The binding energy of the core electrons is very sensitive to the electronic environment around the atom. Changes in the electronic environment will appear in the ESCA spectra as chemical shifts which can be correlated with the oxidation state or atomic charge, as well as the functional groups in organic molecules. In this way, the nature of the chemical bonding at the interface may be established.

5. Relative concentrations of elements can be quantitatively determined.

6. Depth profiling can be accomplished by combining ESCA with argon ion bombardment. By using ESCA alone, it is possible to obtain information on the elemental composition of the top 50 - 100Å of a surface.

Though ESCA offers many advantages, the data obtained from ESCA experiments are by themselves insufficient to provide unambiguous information on the structure, bonding and surface morphology. Hence, in this project, ESCA is employed to help interpret the data obtained from FT-IR studies, and vice-versa.
IV. Experimental

1. Sample Preparation

Single crystal aluminium oxide or sapphire windows were purchased from Tyco. These are rectangular windows of two sizes, 2 inch x 1 inch, and 2 inch x 1/2 inch. The bigger windows (2 inch x 1 inch) were bought in the form as they were grown industrially, whose surfaces have a slight ripple finish and are ultra-smooth, but not optically flat. The smaller windows have both sides polished to one microinch. All these windows are about .016 inch thick. The optically polished sapphire reflection plate (52mm x 20mm x 1mm) was purchased from Harrick Scientific, while the KRS-5 (thallium bromide iodide salt mixture) internal reflection plate - 52mm x 20mm x 2mm with the 20mm edges beveled to 45° - was from Wilkes Scientific. Prior to application of silane coupling agent, the sapphire windows and reflection plate were cleaned by soaking them in distilled water, rubbed against kimwipe or linen, and followed by an acetone rinse. They were then dried overnight at about 100-150°C.

The silane coupling agents studied in this project are γ-aminopropyltriethoxysilane \( \left[ \text{H}_2\text{N CH}_2\text{CH}_2\text{CH}_2 \text{Si-(OCH}_2\text{CH}_3)_3 \right] \) designated as A-1100 and vinyltriethoxysilane \( \left[ \text{H}_2\text{C}=\text{CH} \text{Si-(OCH}_2\text{CH}_3)_3 \right] \) designated as A-151. Both were used as obtained from Union Carbide without further purification. The solvents used for applying A-1100 were distilled water and cyclohexane. Unlike A-1100 which is autocatalytic as mentioned earlier, vinyltriethoxysilane has to be prepared in 5% acetic acid solution (pH ~ 4) where the acid can act as a catalyst for hydrolysis of A-151. Freshly prepared silane solutions of concentrations varying from 0.5 to 5.0% by weight were applied to the newly cleaned sapphire windows by dipping them in the solution overnight. They were then removed from the solutions and the solvent was allowed to evaporate. To obtain thicker films, a few samples were prepared by putting a few drops of the silane solution on the
substrate, and then allowing the solvent to evaporate away.

2. **Infrared Analysis**

The infrared instrument used for this study was a Fourier transform infrared spectrometer (Digilab FTS-14). The IR absorption spectra were obtained using both transmission and internal reflection techniques. When the silane films were thick, transmission was used as shown in Figure 7a. However, when the films were very thin, the IR absorption intensity using the set up shown in Figure 7a, was not strong enough to be detected. In order to increase the absorption intensity, many rectangular plates coated with silane coupling agents on both sides had to be stacked together as shown in Figure 7b. Alternatively, the absorption intensity can be increased by using internal reflection technique. The internal reflection spectra were obtained by using a trapezoidal sapphire plate as an internal reflection plate at an incident angle of 60° with the Wilkes model # attachment which was placed in the sample compartment of the Fourier Transform IR Spectrometer. Figure 7c shows the diagram of this set-up.

Since sapphire starts to absorb IR radiation from 5.5µ onwards, an alternative procedure had to be used in order to obtain the IR spectra of silane coupling agents in the region above 5.5µ wavelength. It was found that when a clean sapphire plate was pressed against a KRS-5 internal reflection plate, the reflection spectrum obtained after subtracting away the KRS-5 spectrum is as shown in fig.8a. From this spectra, it is clear that Al₂O₃ only starts to absorb at about 800 cm⁻¹. However, by putting a piece of rubber sheet between the sample holder and sapphire plate and applying maximum pressure, contact between the sapphire and KRS-5 plate can be improved because the rubbers are flexible and can therefore be more easily pressed than the sapphire which is extremely hard. Thus, from the reflection spectrum obtained and illustrated in Figure 8b, it can be seen that Al₂O₃
Figure 7 (continue on next page)
FIGURE 7. Schematic representation of the experimental set-ups: (a) transmission IR technique using only one sapphire window, (b) transmission technique using several sapphire windows, (c) internal reflection technique with sapphire as a reflection plate, (d) internal reflection with KRS-5 as a reflection plate (number of internal reflections shown in the figure is smaller than the true number) and placed in contact with sapphire windows on both sides and, (e) same as (d) except that KRS-5 reflection plate is placed in contact with the sapphire (formerly used as reflection plate in (c).) on one side only.
Figure 8. IR reflection spectra of clean sapphire plates placed in contact with KRS-5 (acting as reflection plate) as shown in fig. 7(d). However, (a) was obtained when the rubber sheets were not used while (b) and (c) were for two separate experiments done when rubber sheets were used.
started to absorb at below 1000 cm\(^{-1}\) wavenumber. When two pieces of sapphire windows, coated with silane coupling agent, were pressed against KRS-5 reflection plate, as shown in Figure 7d, it was possible to expand its internal reflection spectrum to below the 1600 cm\(^{-1}\) wavenumber. Scanning was repeated at least 100 times before all the internal reflection spectra were recorded. The difference spectra were obtained directly by digital subtraction and the resolution of the spectrometer used was 4.0 cm\(^{-1}\).

3. **ESCA Analysis of A-1100 Silane Film Adsorbed on Sapphire Plates**

ESCA spectra were taken with a PHI 11055 electron spectrometer, using Mg/K\(\alpha\) (x-ray = 1253.6 ev) radiation as the exciting photons. The pressure within the spectrometer while doing the scans varied from 10\(^{-8}\) to 10\(^{-9}\) torr. Only A-1100 films of three thicknesses were studied here. For each of these samples, a broad, low resolution was obtained first. Then high resolution spectra of the peaks of interest were taken by decreasing the size of the analyzer window.
V. Results

1. IR Spectrum of Monomeric γ-Aminopropyltriethoxysilane (A-1100) (27)

Figure 9 shows the transmission spectra of A-1100 monomer obtained by putting a few drops of the solution between two sodium chloride windows. A summary of the major peaks and their band assignments are listed in Table 2.

In order to calculate the thickness of the silane film, Lambert-Beers Law was assumed to be applicable here:

\[ A_i = a_i c_i d \]

where: \( A_i \) is the absorbance or optical density due to component \( i \),  
\( c_i \) is the concentration of \( i \),  
\( d \) is the average thickness of the film,  
\( a_i \) is the absorptivity or extinction coefficient of component \( i \).

Since the extinction coefficient of CH\(_2\) (at 2935 cm\(^{-1}\)) is known to be 75\( \mu \) mole\(^{-1}\) cm\(^{-1}\) and the concentration of CH\(_2\) in silane coupling agent (monomeric form) is 4.3 molelitre\(^{-1}\), the average thickness, \( d \), of silane film can be calculated. The thickness of the monomer liquid film was calculated to be 1.1\( \mu \).

Two distinct peaks at 3390 cm\(^{-1}\) and 3300 cm\(^{-1}\) characteristic of the N-H stretching mode of free amino group are observed in the monomer spectrum. Other peaks of interest are the CH\(_3\) peak at 2985 cm\(^{-1}\), the CH\(_2\) peak at 2940 cm\(^{-1}\), and the NH\(_2\) peak at 1620 cm\(^{-1}\). The stretching mode Si-O-C of the Si-O-CH\(_2\)CH\(_3\) functional group appear as a very intense doublet at 1087 cm\(^{-1}\) and 1110 cm\(^{-1}\) (27).

2. IR Transmission and Internal Reflection Spectra of A-1100 Films Applied From Aqueous Solutions to Sapphire Plates
Figure 9. IR transmission spectrum of γ-aminopropyltriethoxy silane monomer as obtained between two NaCl plates.
<table>
<thead>
<tr>
<th>MONOMER</th>
<th>1800 Å film</th>
<th>450 Å film</th>
<th>TENTATIVE ASSIGNMENTS</th>
<th>GROUP</th>
</tr>
</thead>
<tbody>
<tr>
<td>3390</td>
<td></td>
<td></td>
<td>free N-H stretching</td>
<td>-NH₂</td>
</tr>
<tr>
<td>3300</td>
<td>3000 (broad)</td>
<td></td>
<td>hydrogen bonded N-H stretching</td>
<td>-NH₂</td>
</tr>
<tr>
<td>2985</td>
<td>2960 (shoulder)</td>
<td></td>
<td>( \nu ) (_{\text{as CH₃}} )</td>
<td>-CH₃</td>
</tr>
<tr>
<td>2940</td>
<td>2920</td>
<td>2930</td>
<td>( \nu ) (_{\text{as CH₂}} )</td>
<td>-CH₂</td>
</tr>
<tr>
<td>2880</td>
<td>2850</td>
<td>2880</td>
<td>( \nu ) (<em>{\text{s CH₂}} ), ( \nu ) (</em>{\text{s CH₂}} )</td>
<td>-CH₃, -CH₂</td>
</tr>
<tr>
<td>1620</td>
<td></td>
<td></td>
<td>N-H bending</td>
<td>-NH₂</td>
</tr>
<tr>
<td></td>
<td>1570</td>
<td>1565</td>
<td>N-H bending</td>
<td>-N⁺H₃</td>
</tr>
<tr>
<td>1490</td>
<td>1490</td>
<td>1485</td>
<td>CH₂ scissor</td>
<td>-CH₂⁻</td>
</tr>
<tr>
<td>1400</td>
<td>1390</td>
<td>1385</td>
<td>( \nu ) (_{\text{s CH₃}} )</td>
<td>-CH₃</td>
</tr>
<tr>
<td>1178</td>
<td>1180 (strong)</td>
<td>1180 (weak)</td>
<td>Si-O stretching</td>
<td>Si-OCH₂CH₃</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Si-O stretching</td>
<td>Si-OH</td>
</tr>
<tr>
<td></td>
<td>1110 (very intense)</td>
<td>1120</td>
<td>Si-O stretching</td>
<td>Si-OCH₂CH₃</td>
</tr>
<tr>
<td></td>
<td>1087 (very intense)</td>
<td>1082</td>
<td>1075</td>
<td>Si-O stretching</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Si-O stretching</td>
<td>Si-O-Si</td>
</tr>
</tbody>
</table>

-37-
In order to see the effect of film thickness on the structure of the adsorbed films, a series of silane films of various thicknesses were prepared, a few of which were thicker than one normally finds in industrial practice. Figure 10a and 10b illustrate the IR spectra of the silane films prepared by putting a few drops of the aqueous silane solution on sapphire plates and then drying at 35-50°C under vacuum (which only served to speed up the drying process). The spectra were obtained by using the set-up illustrated in Figure 7a. From the intensity of the CH$_2$ peak at near 2930 cm$^{-1}$, the films were calculated to be 4.0μ and 1.4μ thick.

A comparison of the IR spectrum of the 4.0μ film and monomer spectrum provides direct evidence that these films consisted of polysiloxane molecules. Distinct bands at 3390 cm$^{-1}$ and 3300 cm$^{-1}$ are observed, not only in the spectrum of the monomer, but also in the silane film, indicating the presence of free NH$_2$ group. However, the CH$_3$ peak at near 2970 cm$^{-1}$, which shows up as an intense peak in the monomer spectrum, has decreased considerably here. The CH$_2$ peak at 2930 cm$^{-1}$ has also decreased in relation to that of NH$_2$, but not at such a fast rate as the CH$_3$ peak. Such changes can only be due to the occurrence of hydrolysis and polymerization, as postulated below:

```
\[ \text{CH}_2\text{CH}_3 \quad \text{OH} \]
\[ \text{H}_2\text{N} - \text{CH}_2\text{CH}_2\text{CH}_2 - \text{Si} - \text{OCH}_2\text{CH}_3 \quad \text{hydrolysis} \quad \text{H}_2\text{N} - \text{CH}_2\text{CH}_2\text{CH}_2 - \text{Si-OH} \]
\[ \text{OH} \]
\[ \text{polymerization} \]
\[ \text{NH}_2 \quad \text{NH}_2 \quad \text{NH}_2 \]
\[ (\text{CH}_2)_3 \quad (\text{CH}_2)_3 \quad (\text{CH}_2)_3 \]
\[ \text{Si} - 0 - \text{Si} - 0 - \text{Si} \]
\[ 0 \quad 0 \quad 0 \quad \text{polysiloxane network} \]
```
Figure 10. IR transmission difference spectra of A-1100 film when applied from aqueous solution onto sapphire plates. The thickness of the film is 4μ for (a), 1.4μ for (b), 0.039μ for (c) and 450Å for (d).
Fig. 11. IR internal reflection difference spectra of silane films obtained with an experimental set-up shown in fig. 7(c) with the sapphire as reflection plate. (a) is for A-1100 and (b) is for A-151.
Since only half the contribution of the CH₂ group is from the triethoxy part of the monomer, while the other half is from the propyl group, the intensity of the 2930 cm⁻¹ band is therefore predicted to decrease when hydrolysis and polymerization occur, but not as rapidly as the CH₃ band (2970 cm⁻¹). The concentration of the amino group should not be affected and therefore the NH₂ band at near 1600 cm⁻¹ can be used as an internal standard. The ratio of its intensity to that of CH₂ at near 2930 cm⁻¹ was used to monitor the extent of cross-linking. Instead of the CH₃ band at 2970 cm⁻¹, the CH₂ band (~2930 cm⁻¹) was chosen because of the difficulty in finding the optical density of the former. The intensity ratio of A₁₆₁₀/A₂₉₃₀ was found to be 0.07 and 0.33 for the monomeric silane and the 4.0μ silane film respectively. When the thickness of the monomer was 1.9μ, its intensity ratio was found to be 0.07 also. The change in intensity ratio together with the presence of the 2970 cm⁻¹ shoulder (due to Si−OCH₂CH₃) suggests that only partial hydrolysis and polymerization had occurred.

When the silane film decreased to 1.4μ thick, the NH peaks at 3390 and 3300 cm⁻¹ are no longer well defined as they were in the two spectra discussed earlier. Instead, a broad band is observed at about 3000 cm⁻¹ which is assigned to H-bonded NH₂ group. On the high frequency side of this band is a small shoulder which may be due to H-bonded hydroxyl group (from Si−OH) which normally appears at about 3400 cm⁻¹. In this case the OH peak is probably overlapped with the NH₂ peak. Similar kind of observation was also reported by Bascom (14). Again, the CH₃ band (2980 cm⁻¹) has decreased but this time more drastically than before and is no longer resolvable from the CH₂ band (2930 cm⁻¹) which has also decreased. This observation, together with the broadening of the band at near 2930 cm⁻¹, clearly indicates that hydrolysis-polymerization reactions have taken place. Furthermore, the amide II peak is now shifted from 1610 cm⁻¹ in the monomer to
<table>
<thead>
<tr>
<th>SILANE FILM THICKNESS (μ)</th>
<th>RELATIVE EXTENT OF CROSS-LINKING</th>
</tr>
</thead>
<tbody>
<tr>
<td>MONOMER</td>
<td></td>
</tr>
<tr>
<td>1.1</td>
<td>$A_{1610}/A_{2940} = .07$</td>
</tr>
<tr>
<td>FROM AQUEOUS SOLUTION</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>$A_{1600}/A_{2930} = .33$</td>
</tr>
<tr>
<td>1.4</td>
<td>$A_{1580}/A_{2930} = 1.14$</td>
</tr>
<tr>
<td>.089</td>
<td>$A_{1580}/A_{2940} = 1.66$</td>
</tr>
<tr>
<td>.045</td>
<td>$A_{1565}/A_{2930} = 1.7$</td>
</tr>
<tr>
<td>FROM C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt; SOLUTION</td>
<td></td>
</tr>
<tr>
<td>0.74</td>
<td>$A_{1590}/A_{2940} = 1.11$</td>
</tr>
<tr>
<td>0.4</td>
<td>$A_{1600}/A_{2940} = 1.89$</td>
</tr>
</tbody>
</table>
the 1580 cm\(^{-1}\) position. The intensity ratio of \(A_{1580}/A_{2930}\) is calculated to be 1.14, that is greater than the thicker silane film.

Figure 10c shows the spectrum of silane film that was adsorbed on sapphire windows by dipping them in the aqueous solution of A-1100. A total of three sapphire plates coated with A-1100 were used and the spectrum was obtained by subtracting away the spectrum of the clean aluminium oxide. From the absorbance of the CH\(_2\) band (2940 cm\(^{-1}\)), the thickness of the film was calculated to be 0.089\(\mu\) (895Å). Like the 1.4\(\mu\) film, the amide II peak has also shifted to the 1580 cm\(^{-1}\) position and a broad band is observed at 3000 cm\(^{-1}\) due to N-H stretching mode. Here, no shoulder is observed on the higher frequency side of 3000 cm\(^{-1}\), but its broad width (\(\sim3000-3500\) cm\(^{-1}\)) is probably due to overlapping with O-H stretching band which is less intense than the 1.4\(\mu\) film. The intensity ratio of \(A_{1580}/A_{2940}\) is found to have increased to 1.66. The results so far thus suggest that the relative extent of cross-linking increases near the aluminium oxide surface.

Next, silane coupling agent was applied to a set of five optically polished sapphire windows by immersing them in a 0.5\% aqueous solution of A-1100 and drying them at room temperature. The transmission spectrum is obtained by stacking the five specimens together instead of three as in the previous case (Figure 7b). The resultant difference spectra after subtracting away the absorption due to sapphire is shown in Figure 10d. The average thickness of the silane film is found to be approximately 450Å. The general shape of this spectrum is very similar to that of the 0.089\(\mu\) film except for a few differences, like the amide II peak has shifted slightly to 1565 cm\(^{-1}\) and the relative intensities of the peaks have also changed. The intensity ratio of \(A_{1565}/A_{2930}\) is found to be about 1.7 which is larger than the 0.089\(\mu\) film. However, the value of the intensity as cal-
culated for this film is subjected to a considerable degree of error because of the difficulty in determining the baseline.

A very thin silane film was adsorbed on the sapphire internal reflection plate by dipping it in aqueous solution of A-1100 and then allowing the solvent to evaporate. The incoming IR beam at incident angle of 60° (Fig.7(c) ) was internally reflected twenty-eight times on one side. Since the silane films were formed on both sides of the plate, the absorbance for each reflection can be calculated by dividing the total absorbance by 56. Figure 11a shows the difference spectrum obtained in this experiment. The average thickness of the film is calculated to be about 150Å thick. For this calculation to be true, the depth of penetration of the IR beam has to be greater than the thickness of the silane film. The depth of IR penetration (dp) can be calculated according to the following equation proposed by Harrick (30):

\[
dp = \frac{\lambda}{2\pi n_1 (\sin^2 \theta - n_2^2)^{1/2}} \quad \text{..........................}(5)
\]

where:  
\(n_1\) is the refractive index of sapphire,  
\(n_2\) is the refractive index of silane film,  
\(n_{21}\) is the ratio \(\frac{n_2}{n_1}\),  
\(\lambda\) is the wavelength of the IR radiation, and  
\(\theta\) is the angle of incidence of the IR beam on the reflection plate.

The values of \(dp\) with the corresponding wavenumber are listed in Table 4 and Figure 12 shows a plot of \(dp\) as a function of wavenumber. At wavenumber 2933 cm\(^{-1}\), \(dp\) is calculated to be 0.934μ which is much greater than the thickness of the silane film.
Table 4

Depth of Penetration of IR Beam as a Function of Wavenumber

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>KRS-5 as reflection plate ((\mu))</th>
<th>Sapphire as reflection plate ((\mu))</th>
</tr>
</thead>
<tbody>
<tr>
<td>4000</td>
<td>0.265</td>
<td>0.68</td>
</tr>
<tr>
<td>3650</td>
<td>0.29</td>
<td>0.32</td>
</tr>
<tr>
<td>3300</td>
<td>0.32</td>
<td>0.83</td>
</tr>
<tr>
<td>3050</td>
<td>0.35</td>
<td>0.90</td>
</tr>
<tr>
<td>2500</td>
<td>0.42</td>
<td>1.09</td>
</tr>
<tr>
<td>2000</td>
<td>0.53</td>
<td>1.40</td>
</tr>
<tr>
<td>1600</td>
<td>0.66</td>
<td>1.71</td>
</tr>
<tr>
<td>1400</td>
<td>0.76</td>
<td>1.96</td>
</tr>
<tr>
<td>1200</td>
<td>0.88</td>
<td>2.28</td>
</tr>
<tr>
<td>1100</td>
<td>1.05</td>
<td>2.71</td>
</tr>
<tr>
<td>1000</td>
<td>1.06</td>
<td>2.74</td>
</tr>
<tr>
<td>800</td>
<td>1.32</td>
<td>3.42</td>
</tr>
<tr>
<td>699.8</td>
<td>1.51</td>
<td>3.91</td>
</tr>
<tr>
<td>599.9</td>
<td>1.77</td>
<td>4.57</td>
</tr>
</tbody>
</table>
FIGURE 12. Depth of Penetration of IR beam as function of Wavenumber with KRS-5 and Al2O3 and Sapphire as Internal Reflection Plates.
Unfortunately, using internal reflection technique also caused the absorption intensity of the sapphire below 2000 cm\(^{-1}\) to be increased so tremendously that even after digital subtraction of the sapphire spectrum from that of silane coated sapphire, the resultant difference spectrum obtained was not useful at below 2000 cm\(^{-1}\) as can be seen in Figure 1. Hence, it is impossible to calculate the ratio of \(\frac{A_{\text{NH}_2}}{A_{\text{CH}_2}}\) for this silane film. A broad band is still observed at 3000 cm\(^{-1}\) (assigned to NH\(_2\)) and is as wide as for the film 0.089\(\mu\) or 450\(\AA\) films. This might be an indication of the silanol (-SiOH) groups being present in relatively small concentration in this polysiloxane film.

3. **IR Transmission Spectroscopic Studies of A-1100 Film Applied from Cyclohexane Solutions to Sapphire Plates**

Several investigators including Bascom (14) and Plueddemann (4) have reported that silane coupling agent films deposited from non-polar solvents are thicker than that from polar solvents (eg. water). Hence this experiment was carried out to see how the structure of films varied as the film thickness changed when cyclohexane (non-polar) was used as a solvent instead of water (polar). Figure 13a shows the spectrum of a silane film whose thickness was calculated (from the 2940 cm\(^{-1}\) band) to be 0.74\(\mu\). The intensity ratio of \(\frac{A_{1600}}{A_{2940}}\) is found to be 1.11. When the film thickness was reduced to 0.4\(\mu\), the intensity ratio of \(\frac{A_{1600}}{A_{2940}}\) is also increased to be 1.89, indicating that the cross-link density was greater near the aluminium oxide surface. Both the IR spectra are very similar to one another as can be seen in Figure 13, with a broad band at 3000 cm\(^{-1}\) assigned to NH stretching, 2940 band assigned to CH\(_2\) stretching and a band at near 1600 cm\(^{-1}\) assigned to NH\(_2\) bending. A shoulder on the higher frequency side of the 3000 cm\(^{-1}\) band assigned to OH was, however, observed for 0.74\(\mu\) film only.
Figure 13. IR transmission spectra of A-1100 films applied from C$_6$H$_6$ solution onto sapphire plates. The thickness of the film is .74μ for (a) and 0.4μ for (b).
4. Internal Reflection Studies of A-1100 Films Applied from Aqueous Solutions to Sapphire Plates with KRS-5 as a Reflection Plate

Fig. 14(1)a shows the difference reflection spectrum obtained from the internal reflection IR experiment of the trapezoidal sapphire plate (coated with the 150Å A-1100 film) placed in contact with the KRS-5 reflection plate with the spectra of KRS-5 and sapphire subtracted away digitally. Using KRS-5 with the IR beam at the incidence angle of 60°, the depth of penetration of the IR beam can be calculated using equation 5 and the refractive index, n₁, of KRS-5 as 2.37. The results of this calculation is shown in Table 4. From Fig. 14(1)a it can be seen that above 1500 cm⁻¹, the IR intensity is rather small (because of the shorter penetration depth of the IR beam) and is therefore not suitable for quantitative study. The amount of IR intensity obtained is also highly dependent on the contact efficiency between the reflection plate and the sample. When a sheet of rubber was placed between the sapphire and sample holder, better contact was achieved as demonstrated by the higher IR intensity of the internal reflection spectra [Fig. 14(ii)] at above 1500 cm⁻¹ wavenumber. The thickness of the silane film in Fig. 14(ii) has been found earlier to be approximately 450Å, while the other silane film [Fig. 14(ii)b] is about 0.92μ.

Two peaks at 1039 cm⁻¹ and 1130 are tentatively assigned to Si-O-Si and Si-OH respectively and are clearly observed for the spectra of all the silane films in Fig. 14(ii), but not in the monomer spectrum of A-1100. Since Si-O-Si can only be formed as a result of hydrolysis and polymerization, the presence of these peaks thus strongly indicates a polysiloxane network being formed. The band at about 1080 cm⁻¹ is however assigned to Si-OCH₂CH₃ and appears very intensely in the monomer spectrum, and not as intensely in all the three silane films. (In the spectra of the .92μ and 450Å film,

-49-
Figure 14 (1), IR internal reflection difference spectra of A-1100 (a) and A-151 (b) films obtained with an experimental set-up shown in fig. 7(e) where KRS-5 is used as the reflection plate.
Fig 14(ii). Reflection spectra of A-1100 films formed on sapphire plates, obtained using the set-up shown in Fig. 7(e). The absorption due to KRS-5 and sapphire has already been subtracted away. (a) corresponds to the 450μ and (b) the .92μ film.
the peak at about 1570 cm\(^{-1}\) can be clearly seen, but not in the 0.089\(\mu\)
film which has relatively poor contact with the KRS-5 reflection plate).

5. IR Spectra of Monomeric Vinyltriethoxy (A-151) Silane and Polyvinyl-
siloxane Films Formed on Sapphire Plates (29)

The IR spectrum of vinyltriethoxysilane (A-151) monomer was obtained
by putting a few drops between two sodium chloride plates. This spectrum
is shown in Figure 15 and its major peaks and their assignments are listed
in Table 5. An intense peak due to C-H stretching of \(-\text{CH}_2\) group appears
at 2980 cm\(^{-1}\) while the doublet at 2930 cm\(^{-1}\) and 2890 cm\(^{-1}\) are tentatively
assigned to the \(-\text{OCH}_2\text{CH}_3\) group. A small shoulder at 2960 cm\(^{-1}\) is pro-
ably due to the \(\text{CH}_3\) group. Another peak of interest here is at 3065 cm\(^{-1}\) and
is due to the asymmetric stretching of the unsaturated methylene group.
Therefore, if hydrolysis occurred, the intensity of the \(\text{CH}_2\) peak at 2930
\(^{-1}\) would decrease relative to that of the vinyl peak at 3065 cm\(^{-1}\) which
should not be affected. Hence, using the vinyl peak (3065 cm\(^{-1}\)), the in-
tensity ratio of \(A_{3065}/A_{2930}\) can be used to monitor the relative extent of
cross-linking. The value of this intensity ratio for the monomer is 0.19.

The IR spectrum A-151 film adsorbed on the sapphire which was then
used as a reflection plate (as shown in Figure 7c), is illustrated in fig.11
(b). The thickness of the film was calculated to be about 1600\(\AA\). A broad
band at 3425 cm\(^{-1}\), which is absent in monomer spectrum, is found here and
is due to the O-H stretching of silanol group. Hence, hydrolysis and pro-
bably polymerization must have taken place. The intensity ratio of \(A_{3065}/
A_{2930}\) has also increased to 0.5.

In order to record the spectrum of the silane film below 2000 cm\(^{-1}\),
KRS-5 plate was used as the internal reflection plate with the silane film
placed in contact with it as described before and shown schematically in
Figure 7e. This spectrum is shown in Fig.14(i)a and the IR peaks with their assignments are in Table 5.

In place of the two sharp peaks at 1105 cm^{-1} and 1085 (assigned to Si-OCH_{2}CH_{3}) observed in the monomer spectrum, a very broad peak at 1050 cm^{-1} with a shoulder at 1120 cm^{-1} are found in the spectrum of the silane film. These are evidently due to Si-O-Si and SiOH groups respectively. Thus, the presence of the Si-O-Si bands together with the increase in the ratio of A_{3065}/A_{2930} provide direct evidence that adsorbed silane film consists of polyvinylsiloxane network.

6. ESCA Studies of A-1100 Films Formed on Sapphire Plates

A wide scan over the first 1000 ev of binding energies was obtained so as to check on the main features of the spectrum and the impurity levels. Then high resolution spectra of the peaks were taken and these are illustrated in Figure 16. The aluminium 2s and 2p photoelectron lines appear at 123.5 ev and 78.3 ev respectively, while the O1s peak is observed at 535.4 ev. In addition to this, a low intensity peak, due to carbon impurity, showed up at 288.9 ev. The aluminium and oxygen peaks observed are clearly those of aluminium oxide (31).

A wide ESCA scan was taken of a sapphire plate coated with A-1100 applied by putting a few drops of 5.0% aqueous solution on it and then allowing the solvent to evaporate. The average thickness of this film was determined from IR experiment to be 0.92μ thick. The wide ESCA scan revealed several major peaks which are listed in Table 6. Two of these peaks, namely nitrogen and silicon peaks, were not observed before in the ESCA spectra of the clean sapphire plate, thereby suggesting that they must be due to the silane coating. A comparison of this ESCA spectra with that of clean
<table>
<thead>
<tr>
<th>MONOMER</th>
<th>A-151 FILM</th>
<th>ASSIGNMENTS</th>
<th>GROUP</th>
</tr>
</thead>
<tbody>
<tr>
<td>3010</td>
<td>3065</td>
<td>$\nu_{as} CH_2$</td>
<td>$=CH_2$</td>
</tr>
<tr>
<td>3025</td>
<td>3025</td>
<td>$\nu_{s} CH_2$</td>
<td>$=CH_2$</td>
</tr>
<tr>
<td>2980</td>
<td>2980</td>
<td>$\nu_{s} CH_2$</td>
<td>$=CH_2 &amp; -CH_3$ overlap</td>
</tr>
<tr>
<td>2935</td>
<td>2930</td>
<td>$\nu_{as} CH_2$</td>
<td>$-CH_2-$</td>
</tr>
<tr>
<td>2890</td>
<td>2890</td>
<td>$\nu_{s} CH_3, \nu_{as} CH_2$</td>
<td>$-CH_2=CH_2$</td>
</tr>
<tr>
<td>1602</td>
<td>1605</td>
<td>$\nu C=C$</td>
<td>$-CH_2=CH_2$</td>
</tr>
<tr>
<td>1485</td>
<td>-</td>
<td>CH bending</td>
<td>$-OCH_2CH_3$</td>
</tr>
<tr>
<td>1443</td>
<td>-</td>
<td>$\delta CH$ bending</td>
<td>$=CH_2$</td>
</tr>
<tr>
<td>1408</td>
<td>1410</td>
<td>$\delta CH$(in-plane)</td>
<td>$=CH_2$</td>
</tr>
<tr>
<td>1175</td>
<td>-</td>
<td>Si-O stretching</td>
<td>Si-OCH$_2$CH$_3$</td>
</tr>
<tr>
<td>-</td>
<td>1120</td>
<td>Si-O stretching</td>
<td>SiOH</td>
</tr>
<tr>
<td>1105</td>
<td>-</td>
<td>Si-O stretching</td>
<td>Si-OCH$_2$CH$_3$</td>
</tr>
<tr>
<td>1085</td>
<td>-</td>
<td>Si-O stretching</td>
<td>Si-OCH$_2$CH$_3$</td>
</tr>
<tr>
<td>-</td>
<td>1050(broad)</td>
<td>Si-O stretching</td>
<td>Si-O-Si</td>
</tr>
<tr>
<td>1012</td>
<td>1008</td>
<td>$\delta CH$ (out of plane)</td>
<td>$-CH=CH_2$</td>
</tr>
<tr>
<td>963</td>
<td>964</td>
<td>$\delta CH$ (out of plane)</td>
<td>$=CH_2$</td>
</tr>
</tbody>
</table>
Figure 15. IR transmission spectrum of monomeric vinyltriethoxy silane as obtained between two NaCl plates.
sapphire plate shows that the oxygen peak has shifted by about 0.8 ev to the 534.6 ev position. This can be easily explained by the fact that the major contribution to this oxygen came from the silane coating which has oxygen species that have electronic environment different from that of sapphire (aluminium oxide). The contribution from the sapphire is probably very small since only a very weak intensity aluminium peak is observed at 78.3 ev. Even though the average thickness of the silane coating is much larger than the mean free path of the aluminium photoelectrons through the polymeric film, aluminium is still detected indicating that in some places, the film is at least as thin as the escape depth of aluminium electrons through a carbon film. This thickness has been approximated as 20Å by Hercules et al (32).

A careful observation of the high resolution nitrogen ESCA peak in Figure17 shows the presence of a shoulder on the higher binding energy side of the nitrogen peak. The appearance of this extra ESCA peak at 403.8 ev, which is 1.5 ev higher than the major nitrogen peak, indicates the presence of more than one type of nitrogen species present in the silane coating. The higher binding energy specie may be tentatively assigned to positively charged nitrogen specie, such as $^{+}\text{NH}_3$. (33)

Next, a wide scan of the sapphire plate coated with a 450Å silane film (studied earlier using FT-IR) was taken and illustrated in Figure 18, while the major peaks with their tentative assignments are listed in Table 6. A comparison of this ESCA spectrum with that of the thicker silane film shows the oxygen and carbon peak position to be approximately the same. The nitrogen high resolution peak (Figure 19), which appears at 401.2 ev, however, no longer has a distinct shoulder. But careful observation shows that the
peak is not symmetrical and is slightly tilted to the lower binding energy side. This may be due to the presence of a very small intensity ESCA peak (at 403.5 ev) which overlaps with a much more intense peak at 401.2 ev. Similar kind of observation was made for the thicker film except that the 403.5 ev peak was relatively more intense than this one.

Though no aluminium ESCA peak shows up in the spectra, a second scan of the same specimen at a different spot was taken and found to have aluminium ESCA peaks as shown in Figure 18. The rest of the peaks in this ESCA spectrum appear at the same positions as the spectrum obtained in the previous scan. Such an observation clearly shows the silane film to be of uneven thicknesses, as was also found for the other silane film.

Figure 20 shows the results of the ESCA experiments on a sapphire plate which was modified with γ-aminopropylsilane and then cleaned by first soaking the plate in distilled water overnight, then wiped with linen and followed by degreasing with acetone. The spectra show peaks due to nitrogen and silicon, thereby giving evidence that not all the silane coupling agent had been washed away. The nitrogen ESCA peak appears at 403.9 ev, which corresponds with the ESCA shoulder observed for the other two silane films discussed earlier. The carbon peak on the other hand, shows up at the same position as for the clean sapphire plate. Clearly, this suggests that most of the contribution to this carbon peak must be from the impurity present in sapphire with comparatively little contribution from the silane, which is probably only present in trace amounts.

In order to get more quantitative information, the ESCA intensity ratio of Si/C and Si/N were calculated by comparing the total area under each peak. On hydrolysis of silane, the concentration of N and Si should remain un-
changed while concentration of carbon should decrease due to the reaction of \(-\text{OCH}_2\text{CH}_3\) with water. Hence, using the silicon peak as an internal standard, the ratio Si/C can be used to monitor the extent of hydrolysis and polymerization while the ratio Si/N should remain constant. A summary of the values of the ESCA peak intensity ratios are listed in Table 7. The results show that as the thickness of the films increases, the ratio of Si/C was found to increase while the ratio Si/N remained constant as predicted. One assumption made in this calculation is that the contribution of the carbon impurity in the sapphire to the carbon ESCA peak of the 0.92\(\mu\) film is very small compared to the contribution from the silane coating and can therefore be neglected. Also the results used in the above calculation for the 450\(\AA\) film are those obtained from the first scans.
FIG. 16. ESCA SPECTRA OF SAPPHIRE PLATE (CLEAN)

**OXYGEN (1x)**
- pass energy = 50 ev
- sensitivity = 30K

**CARBON (1x)**
- pass energy = 50
- sens. = 10K

**ALUMINIUM (1x)**
- pass energy = 25 ev
- sens. = 1K

- Binding Energy (eV) -
FIGURE 17. ESCA SPECTRA OF THE 0.92μ A-1100 FILM
(Intensity ratios were calculated using areas under the unreduced ESCA peaks).

**OXYGEN (7/16 x)**
pass energy = 50ev
sensitivity = 10K (sens.)

**CARBON (5/8 x)**
pass energy = 25ev
sens. = 3K

**NITROGEN (7/16 x)**
pass energy = 25ev
sens. = 300

**SILICON (7/16x)**
pass energy = 25ev
sens. = 300

**ALUMINIUM (7/16 x)**
pass energy = 25ev
sens. = 100

---

INTENSITY (ARBITRARY UNITS)

BINDING ENERGY (EV)
FIGURE 18. WIDE ESCA SCANS OF THE 450Å A-1100 FILMS
FIGURE 19. ESCA SPECTRA OF 450Å A-1100 film (applied from aqueous solution.) (All intensity ratios were taken using the areas under peaks which were not reduced.)
**OXYGEN** \((5/8 \times)\)
- pass energy = 50 ev
- sensitivity = 10K

**CARBON** \((5/8 \times)\)
- pass energy = 50 ev
- sens. = 300

**NITROGEN** \((1x)\)
- pass energy = 50 ev
- sens. = 1K

**ALUMINIUM** \((7/16 \times)\)
- pass energy = 50 ev
- sens. = 1K

**SILICON** \((1x)\)
- pass energy = 50 ev
- sens. = 1K

---

**FIGURE 20.** ESCA SPECTRA OF SAPPHIRE PLATE THAT WAS COATED A-1100 AND THEN CAREFULLY WASHED WITH WATER AND ACETONE.
<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>CLEAN SAPPHIRE PLATE</th>
<th>92Å A-1100 FILM</th>
<th>450Å A-1100 FILM</th>
<th>SAPPHIRE PLATE COATED WITH SILANE AND CAREFULLY CLEANED</th>
</tr>
</thead>
<tbody>
<tr>
<td>OXYGEN 1s</td>
<td>535.4</td>
<td>534.6</td>
<td>534.3</td>
<td>535.4</td>
</tr>
<tr>
<td>NITROGEN 1s</td>
<td>-</td>
<td>401.5</td>
<td>401.5</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>403.8</td>
<td>403.5</td>
<td>403.9</td>
</tr>
<tr>
<td>CARBON 1s</td>
<td>288.9</td>
<td>287.5</td>
<td>286.9</td>
<td>288.8</td>
</tr>
<tr>
<td>SILICON 1s</td>
<td>-</td>
<td>105.0</td>
<td>104.5</td>
<td>105.9</td>
</tr>
<tr>
<td>ALUMINIUM 1s</td>
<td>78.3</td>
<td>77.8</td>
<td>78.0</td>
<td>78.3</td>
</tr>
</tbody>
</table>
Table 7

ESCA PEAK INTENSITY RATIOS OF A-1100 FILMS

<table>
<thead>
<tr>
<th>INTENSITY RATIO</th>
<th>0.92μ FILM</th>
<th>450 Å FILM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon/Nitrogen</td>
<td>0.726</td>
<td>0.734</td>
</tr>
<tr>
<td>Silicon/Carbon</td>
<td>1.636</td>
<td>2.72</td>
</tr>
<tr>
<td>Silicon/Oxygen</td>
<td>1.004</td>
<td>1.42</td>
</tr>
</tbody>
</table>
VI. Discussion

The results of the FT-IR studies have demonstrated that the adsorbed silane films, both A-1100 and A-151, to be polysiloxane network. Evidence for this is found in the differences between the spectra of all the adsorbed films and the monomer spectra, especially in the region between 1000 cm⁻¹ and 1100 cm⁻¹, where broad bands, due to the Si-O-C and Si-O-Si stretching vibration modes, are observed for all the films. In the spectra of A-1100 films new peaks are observed at 1130 cm⁻¹ and 1030 cm⁻¹ attributed to the Si-OH and Si-O-Si stretching vibration modes respectively. For A-151, a very broad band not observed in the monomer spectrum appears in the film spectra and is probably due to the Si-O-Si stretching mode. Furthermore, in all of the film spectra and regardless of whether they were applied from polar or non-polar solvents, the intensity of the C-H stretching peak at near 2940 cm⁻¹ or at 1395 cm⁻¹ is found to decrease relative to that of the vinyl or amino groups, hence giving more evidence of hydrolysis and polymerization in the adsorbed films.

From the summary (listed in Table 3) of the calculations of the intensity ratio of the NH peak at near 1600 cm⁻¹ to the CH₂ stretching band at 2940 cm⁻¹ for A-1100 films applied from aqueous solution, it was found that the intensity ratio increases as the film thickness increases, suggesting a gradient in the relative extent of cross-linking. However, when the film thickness decreases from .089µ to 450Å, the intensity does not change as fast as before and this is clearly illustrated in figure 21, where the gradient of the curve changes drastically at .089µ. Unfortunately, not many data points were available for films thinner than this thickness.

Though the increase in the intensity ratio can also be caused by the
Figure 21. Relative degree of cross-linking, expressed as the ratio of $A_{\text{NH}_2}/A_{\text{CH}_2}$ as a function of film thickness when A-1100 was adsorbed on sapphire plate from aqueous solution.
increase in the extent of hydrolysis alone and without polymerization occurring after hydrolysis reaction, this possibility is ruled out because the O-H stretching band, which appears as a shoulder in the 1.4μ film, becomes no longer distinct as the thickness of film decreases. Furthermore, the N-H stretching band at about 3300 cm\(^{-1}\), which is broadened because of hydrogen bonding and the overlapping O-H stretching band, becomes narrower as the silane film becomes thinner, suggesting a decrease in the concentration of the hydroxyl groups.

A similar kind of behavior is observed for the A-1100 films applied from cyclohexane solutions as can be seen from the results in Table 3. However, the intensity ratio, \(\frac{A_{1590}}{A_{2940}}\), is greater for a given film thickness when compared to that of a film applied from aqueous solution. This difference suggests that silane films adsorbed from non-polar solvents have a higher relative extent of cross-linking.

In order to monitor the relative extent of hydrolysis-polymerization in the A-151 film adsorbed onto sapphire plate, the intensity ratio of \(\frac{A_{3065}}{A_{2930}}\) is calculated and found to be 0.5 which is much larger than the value obtained for the monomer (0.19). A fairly intense and broad band at about 3450 cm\(^{-1}\) due to O-H stretching vibration mode clearly indicates that the silane film is extensively hydrolyzed. More evidence of hydrolysis and polymerization is found by comparing the intensity of the 1410 cm\(^{-1}\) peak (assigned to C=C) and that of 1395 cm\(^{-1}\) peak (assigned to CH) in Figure 14(i)a with those of the monomer spectra (Figure 15). In Figure 14(i) a, the intensity of the 1395 cm\(^{-1}\) peak relative to that of 1410 is smaller in the A-151 film than in the monomer.

The results obtained from ESCA studies provide more evidence of hydroly-
sis and polymerization of the A-1100 films applied from aqueous solutions. For example, the ESCA peak intensity ratio of Si/C increases as the film becomes thinner. This evidence, together with that from FT-IR studies, strongly supports the idea of a gradient in the extent of cross-linking in the silane film. Presumably, as the distance from the surface of the metal oxide decreases, the cross-linking density in the silane film becomes greater.

In the spectra of the A-1100 films, a large shift is observed for the NH₂ deformation vibration. The peak shifts from the 1610 cm⁻¹ position in the monomer to the 1565-1600 cm⁻¹ positions, as can be seen in fig.10 and table 2. Similar kind of behavior has been observed by Boerio (17) when silane (A-1100) was adsorbed onto iron coupons. According to his investigation, the 1575 cm⁻¹ peak was not only absent in the monomer spectra, but also the spectra of the polymer obtained by hydrolysis and condensation of A-1100. This thus indicates that there might be differences in the structure between films formed on metal oxide and the polymer itself. Furthermore, ESCA experiments have shown that two species of nitrogen atoms are present in the silane films while only one specie (the higher binding energy one) was observed for the plate which was coated with A-1100 and then washed. The higher binding energy or second ESCA peak of the films at around 403.5 eV is of lower intensity than the other peak which appears at about 401.5 eV. From comparing the ESCA spectra for the two films, it is found that the 403.8 ESCA line for the .92μ film is more intense. This can be due to the fact that part of the area studied by ESCA is of about 20 Å thick or less as confirmed by the presence of the Al ESCA line while no Al ESCA line was observed for the 450Å film (refer to the spectra obtained for the first scan only), suggesting that the region studied has thick-
ness greater than at least 200\(^\circ\). Nordberg et al (33) have studied many nitrogen compounds and reported that the nitrogen 1s ESCA peak for organic amines appeared in the region of 398.0 eV and protonation of the amines resulted in a shift of about 2.4 eV to the higher binding energy side. As a result, the second nitrogen specie observed for silane films is probably due to the presence of ammonium nitrogen, \(\text{NH}_3^+\). Similarly, the shift in the IR band from 1610 cm\(^{-1}\) in the monomer to the 1580 cm\(^{-1}\) region for the silane film may be caused by the formation of ammonium ions (26). It is therefore possible that some of the silane is deposited on sapphire plate as internal zwitterions which Plueddemann had suggested to be present in silane solutions (4,18).

The presence of nitrogen and silicon peaks in the ESCA spectra of the sapphire plate which was first coated with silane and then cleaned with water and acetone as shown in fig. 20, indicates that there is present a layer of silane which is very strongly attached to the sapphire plate. The amount present on the plate is too little to be detected using FT-IR reflection technique. The results here suggest very strongly that there probably exists a monolayer of silane which is very tightly bound to the sapphire surface, perhaps through some kind of chemical bonding. Alumina has being known to have acidic sites which are reactive and it is probable that sapphire may have such sites too. Though no direct evidence of the type of chemical bonding is available, both ESCA and FT-IR studies give evidence that suggests a kind of ionic bond being formed between the reactive sites on the sapphire surface and the ammonium group of the silane.
VII. Conclusions and Recommendations

Using both infrared spectroscopic and ESCA techniques, the silane coupling agents have been demonstrated to be deposited on aluminium oxide surface as a kind of polysiloxane network. There was evidence that some of the silane was deposited as internal zwitterions which were characterized by NH$_3^+$ absorption band at near 1580 cm$^{-1}$ and the ESCA peak at near 403.8eV.

γ-aminopropyltriethoxysilane films were found to have a gradient in the cross-link density such that the polysiloxane network is more tightly cross-linked near the aluminium oxide surface. This was found to be true not only in the silane films applied from aqueous solution, but also those applied from cyclohexane. It seems that the only difference that arose from using the two solvents was that the films applied cyclohexane were relatively more hydrolyzed and polymerized than those from water. Furthermore, flatness of the sapphire plates used did not seem to affect the structure of the films at all.

Although no direct evidence of chemical bonding was obtained, the results from FT-IR and ESCA studies strongly suggest the presence of chemical bonding at the silane/aluminium oxide interface. A residual amount of silane, less than thick, was left on a sapphire plate even after careful cleaning with water and acetone, suggesting that silane is probably bonded to aluminium oxide through a hydrolytically stable bond. This bond is believed to be ionic in character and is formed between aluminium oxide and the functional group of A-1100. Hence, one can view the interface as consisting of a silane network, which is chemically bonded to aluminium oxide and is more tightly cross-linked at near the surface of the sapphire plate and gradually becomes more loosely bound as one moves to the outer
region of the film. Such a structure, also suggested by Bascom (14), will allow the easy penetration of adhesive molecules into the silane film to form an interpenetrating network of resin and silane that is resistant to water penetration. From the thermodynamics of adhesive joint stability, it is definitely desirable to prevent water from reaching the interface. Application of silane to adherend probably serves this role and hence leads to an improvement in the strength of adhesive bonds in both wet and dry environment.

In order to arrive at a general theory of the role of silane coupling agents in promoting adhesion, it is necessary to do similar kinds of studies using various kinds of silane coupling agents and substrate surfaces. Furthermore, it has been suggested (13) that the functional group of the silane coatings influences the resin polymerization, and hence the resin structure which, as a result, becomes more water resistant. More investigation of this should be done in any future work.

Though a simple technique, using single crystal aluminium oxide as a model surface, together with ESCA and infrared spectroscopic techniques, has been successfully developed to elucidate the structure of silane adsorbed on aluminium oxide, there is still a need to find a way of obtaining direct evidence of chemical bonding at the interface.
VIII. References


