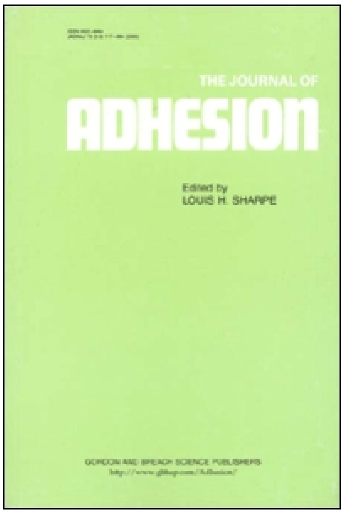

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ESCA Studies of Laminated Safety Glass and Correlations with Measured Adhesive Forces

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Electron Spectroscopy for Chemical Analyses (ESCA) has been used to examine surfaces of safety glass specimens. These specimens consisted of tin float glass laminated with plasticized polyvinyl butyral. ESCA was used to characterize the glass surface after the plasticized polyvinyl butyral had been peeled away. The results show clearly that the specimens fail cohesively and a layer of the plasticized polyvinyl butyral is left on the glass surface. The thickness of this layer was measured and was found to be directly proportional to the force of adhesion, measured as 90° peel strength.

I. INTRODUCTION

Laminated safety glass has been used by the automobile industry for approximately 40 years. A windshield made from laminated glass serves a dual purpose of protecting the driver from foreign objects and lessening, *via* its energy absorption characteristics, the potential severity of injury to the driver or passengers in the event of a collision. While a number of materials are potential laminate candidates, plasticized polyvinyl butyral has been used as the interlayer in safety glass because of its outstanding properties of tear strength, optical clarity and adhesive strength.

It is common practice to prepare plasticized polyvinyl butyral interlayers which provide the range of peel strengths that are necessary for a particular application. For example, the peel strength of laminates used for windshields is kept within a narrow range to provide the required absorption properties in case of an accident in which the driver or passenger impacts the windshield. On the other hand, higher peel strengths are required in architectural applications where the laminates are used as glazings in buildings.

In the present study, it is anticipated that Electron Spectroscopy for Chemical Analysis (ESCA) might be a useful tool for studying the layers of molecules that participate in the adhesion process. The purpose of this study then was to determine if there was some correlation between the peel strength for laminated glass specimens and the amount or type of material remaining on the glass surface after peeling away the laminate.

II. EXPERIMENTAL

Standard procedures of peel specimen preparation were used in which triplicate 0.76 mm thick samples of Saflex® covered with aluminium foil backing were laminated to 6 × 18 cm standard tin float glass plates. Two of the samples from each set were tested for peel strength while the other was retained for characterization *via* ESCA. A number of peel tests[1] could have been used. In this study, however, a 90° peel test was employed for both samples of each set.

In order to obtain specimens suitable for ESCA examination, the remaining sample from each set was scored with a cutting tool to obtain a specimen approximately 0.64 × 1.9 cm. The aluminium foil backing plus the Saflex® interlayer were then removed. The experimental technique for handling the samples was to hand peel the interlayer from the glass at room temperature (~23°C) so that the adhesive layer remaining on the glass could be examined. Since the active adhesive film is a separate entity which exists between the interlayer and the glass, we will refer to it as an "interphase".

Saflex®—Registered Trademark of the Monsanto Co., consisting of plasticized polyvinyl butyral.

Butvar®—Registered Trademark of the Monsanto Co., consisting of polyvinyl butyral.

The glass specimens containing the remaining interphase layer were placed on a suitable sample holder and immediately loaded into the ESCA spectrometer. Fresh surfaces of the bulk polymers of Butvar® and Saflex® were also examined as part of this study. The ESCA spectrometer employed in this work is an AEI-ES-100. The spectrometer has been extensively modified by adding a Heinke magnesium X-ray source, a 200 ℓ/sec. turbo-molecular pump, and a 100 ℓ/sec. ion pump for evacuation of the sample chamber, and a Varian 3 keV ion gun for use with argon ion sputtering.

III. RESULTS AND DISCUSSION

The peel specimens that were utilized in the present study are listed in Table I. For each of the specimens, the Saflex® formulation was varied slightly in order to control the peel strength.

Quantitative results were obtained from high resolution scans of the most intense photoelectron peak for each element. The area under each peak was then multiplied by relative sensitivity factors,[2] normalized and converted to percentages. These results are also listed in Table

TABLE I
Approximate atom per cent surface composition for glass surface/interphase layer from peel adhesion samples, bulk polymers, and glass substrate (only elements of interest are included)

Sample peel specimens	C	O_{533}	O_{531}	Si
1st set				
#1	48.9	30.8	3.4	12.5
#2	33.7	39.5	4.8	16.8
#3	62.8	26.2	0.74	7.7
#4	53.0	30.3	1.8	11.4
#5	38.5	36.8	4.5	14.2
#6	55.8	27.0	2.9	10.8
2nd set				
#7	42.5	33.8	6.1	13.5
#8	18.4	51.2	9.6	16.3
#9	45.1	33.2	5.3	12.8
#10	30.4	40.7	7.0	17.4
#11	44.9	32.9	5.9	13.2
#12	26.5	41.9	8.8	18.0
Control glass	8.5	55.7	8.7	20.1
Butvar®	81.7	19.3	—	—
Saflex®	78.2	21.7	—	—

I. Note that oxygen was detected in two different chemical states as evidenced by separate peaks at 531 eV and 533 eV. This will be discussed later in more detail.

Additional treatment of the data in Table I required establishing whether or not the carbon was proportional to interphase film thickness. One way to determine interphase film thickness is to obtain sputter depth profiles of the glass surfaces and use previously established sputter rate data to calibrate the depth scale. This technique of sputter depth profiling is described in a review by Wehner.[3] Another way to determine the film thickness is to correlate the intensity of the silicon 2p peak (from the glass substrate) as a function of the overlayer thickness. Since precise sputter rate data were unavailable for this system, the latter approach was used.

If it is assumed that the polymer interphase film remaining on the glass surface has uniform thickness, t, then t can be calculated using a method described by Carlson and McGuire.[4] The intensity of the Si 2p peak, I_{Si}, will be given by

$$I_{Si} = F\alpha Dk\lambda_{Si}\,(e^{-(\sqrt{2})t/\lambda_{Si}}) \tag{1}$$

where F is the X-ray flux, α is the cross-section for photoionization, D is the density of silicon in the glass, k is a spectrometer factor and λ_{Si} is the mean free path of the Si 2p photoelectron. The intensity of the Si 2p peak from a glass surface without the polymer interphase film present will be

$$I_{Si}{}^{*} = F\alpha Dk\lambda_{Si} \tag{2}$$

Solving between equations (1) and (2) gives

$$t = -\lambda_{Si} \approx \frac{\sqrt{2}}{2}\ \ln\,(I_{Si}/I_{Si}{}^{*}) \tag{3}$$

The average thickness of the polymer film can also be written in terms of the measured C 1s intensity I_C:

$$t = -\lambda_C(\sqrt{2})\ \ln\,(1 - I_{C/C*}) \tag{4}$$

where I_{C*} is the C 1s intensity from an infinitely thick polymer layer and λ_C is the mean free path of the C 1s photoelectron in the interphase film. Solving between these two expressions for t and assuming that $\lambda_{Si} \sim \lambda_C$[5] ($\lambda_C = 27$ Å, $\lambda_{Si} = 30$ Å).

$$I_{Si}/I_{Si*} = 1 - I_C/I_{C*} \tag{5}$$

It can be seen that a plot of I_{Si} *versus* I_C should be a linear plot with an intercept of I_{Si*}. This plot gave a value of 1050 counts/second for I_{Si*}. The mean free path of the Si 2p photoelectron can be estimated to be ~30 Å from the data of Seah and Dench.[5] From Equation 1 and the mean free path of the Si 2p photoelectron, the interphase film thicknesses were calculated and are listed in Table II.

TABLE II

Interphase adhesive layer thicknesses, corresponding peel strengths, and Saflex® O_{533} intensities for peel adhesion samples

Set # 1	Thickness, Å	Peel strength, N/CM	Intensity O_{533s}
1	19	50.1	10.25
2	12	26.6	9.21
3	29	70.0	13.80
4	22	54.3	11.90
5	14	25.4	8.65
6	23	56.3	11.10
Set # 2			
7	16	53.8	9.26
8	7	29.7	4.14
9	18	69.7	10.40
10	10	41.4	6.53
11	17	62.4	9.53
12	9	34.6	5.99

They also are plotted as a function of the logarithm of the peel strength (in Newtons/cm) in Figure 1. Two separate curves were obtained (Figure 1) due to the utilization of two different batches of glass with different washing and preparation procedures. However, the interphase layer thickness is seen to be directly proportional to peel strength for both sets of samples.

An ESCA scan of the control glass is shown in Figure 2. The sodium, potassium and calcium modifiers are detected in this scan. Tin is also observed. Sieger[6] has reported that tin is incorporated as SnO and SnO_2 in the surface of float glass.

Figure 3 shows a high resolution O 1s scan of the float glass sur-

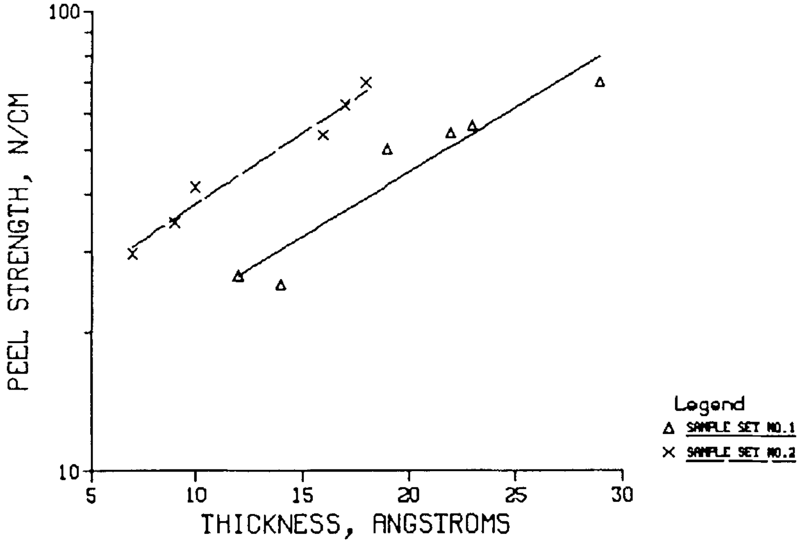


FIGURE 1 Peel Strength *vs.* Interphase Adhesive Layer Thickness.

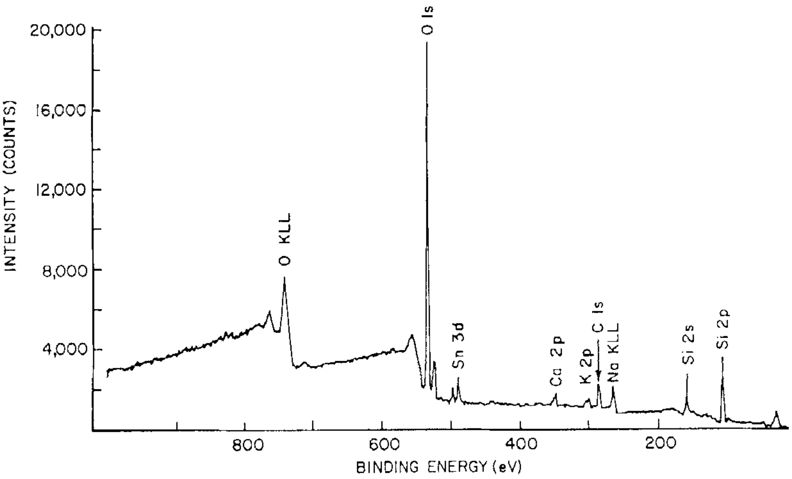


FIGURE 2 ESCA spectrum of Control Glass.

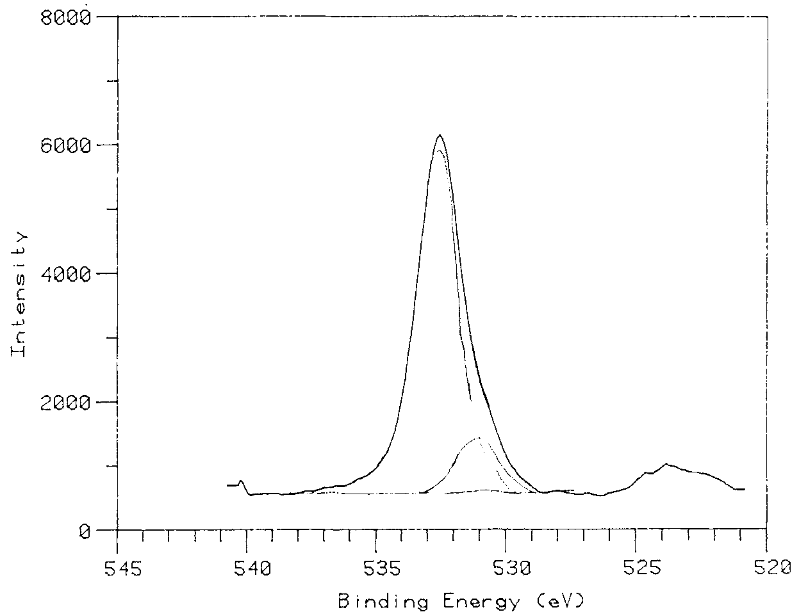


FIGURE 3 ESCA spectrum of O 1s of Control Glass.

face which was used in preparing the peel specimens. From the asymmetry in the peaks it can be determined that there are contributions from oxygen in two different chemical environments. This asymmetric peak was deconvoluted into two symmetric peaks, at 531 eV and 533 eV, using a DuPont 310 Curve Resolver. The O 1s peak at 531 eV is due to the bridging oxygens from $-Si-O-Na^+$.[7] There is also some contribution to the 531 eV peak from oxygen in SnO_2.

Figure 4 shows the O 1s scan of the polyvinyl butyral (Butvar®) from which Saflex® is made. The O 1s scan of Saflex® is shown in Figure 5. Both of these scans exhibit a symmetrical peak that occurs at a binding energy of about 533 eV. Since the most intense O 1s peak from the glass occurs at 533 eV this prevents unequivocal assignment of the Saflex® contribution to the peak at the 533 eV binding energy. An ESCA scan representative of the Saflex® interphase O 1s response is shown in Figure 6. Table I lists the quantitative values at these binding energies. Therefore, in order to be able to evaluate the response of the O_{533} 1s oxygens of Saflex® as a function of thickness,

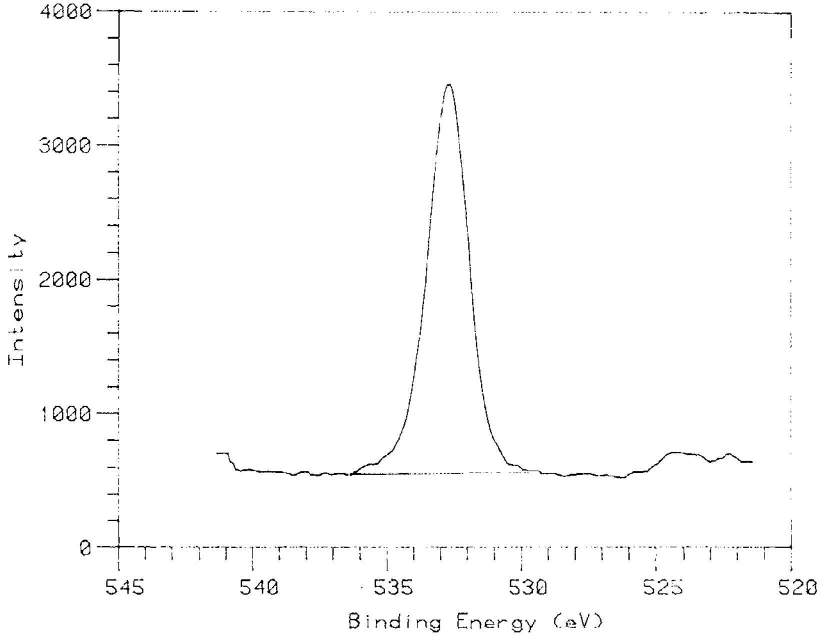


FIGURE 4 Polyvinyl Butyral (New Surface) O 1s ESCA spectrum

the response of the O_{533} 1s has to be resolved into its component contributions of Saflex® and glass.

For this purpose we consider the model shown in Figure 7. Again, using the method of Carlson and McGuire,[4] the intensity of O_{533} peak from the Saflex®, $I_{O_{533s}}$, will be

$$I_{O_{533_S}} = \lambda_{O_S} F\alpha(D_O)_S k(1 - e^{\sqrt{2}t/\lambda_{O_S}}) \tag{6}$$

where $(D_O)_S$ is the density of the oxygen in g/cm^3 for the Saflex®, λ_{O_S} is the mean free path of the O 1s photoelectron in the Saflex®, and the other variables have the same values as given previously. Similarly, for the glass, the intensity *f* the O_{533} peak, $I_{O_{533_G}}$, will be

$$I_{O_{533_S}} = \lambda_{O_G} F\alpha(D_O)_G k e^{-\sqrt{2}t/\lambda_{O_G}} \tag{7}$$

The ratio of intensities of O 1s photoelectrons emanating from Saflex® and glass will be:

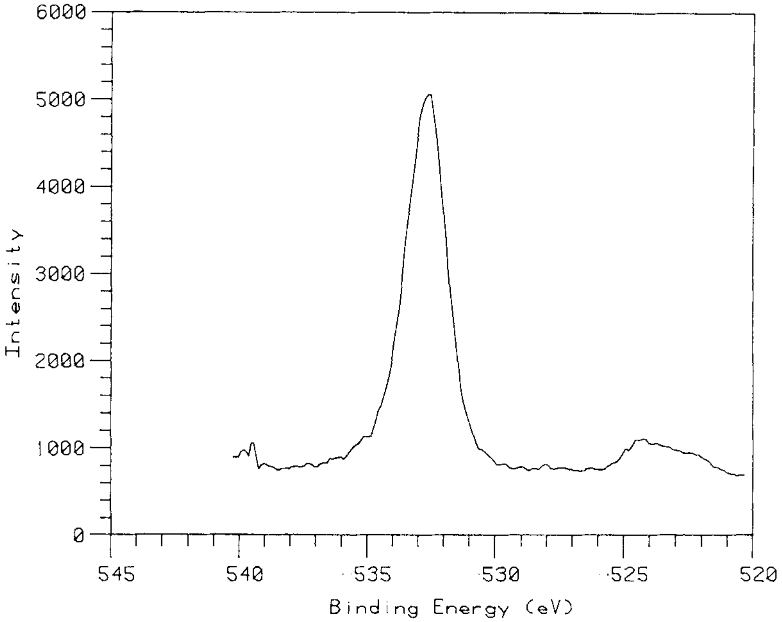


FIGURE 5 SAFLEX® O 1s ESCA spectrum.

$$R = \frac{I_{O_{533_G}}}{I_{O_{533_S}}} = \frac{(D_O)_G \lambda_{O_G} e^{-\sqrt{2}t/\lambda_{O_G}}}{(D_O)_S \lambda_{O_S}(1 - e^{-\sqrt{2}t/\lambda_{O_S}}} \qquad (8)$$

Substituting the calculated values for $(D_O)_S$ and $(D_O)_G$ and using the approximation that $\lambda_{O_S} \sim \lambda_{O_G}$ R becomes

$$R = \frac{4.44 e^{-\sqrt{2}t/\lambda_{O_G}}}{1 - e^{-\sqrt{2}t/\lambda_{O_S}}} \qquad (9)$$

But, $\lambda_{O_G} \sim \lambda_{O_S} \sim 23$Å[5] and t is the interphase adhesive layer thickness (given in Table II).

The following simultaneous equations were then used to solve for $I_{O_{533_G}}$ and $I_{O_{533_S}}$

$$I_{O_{533_G}} = I_{O_{533_S}} \times R \qquad (10)$$

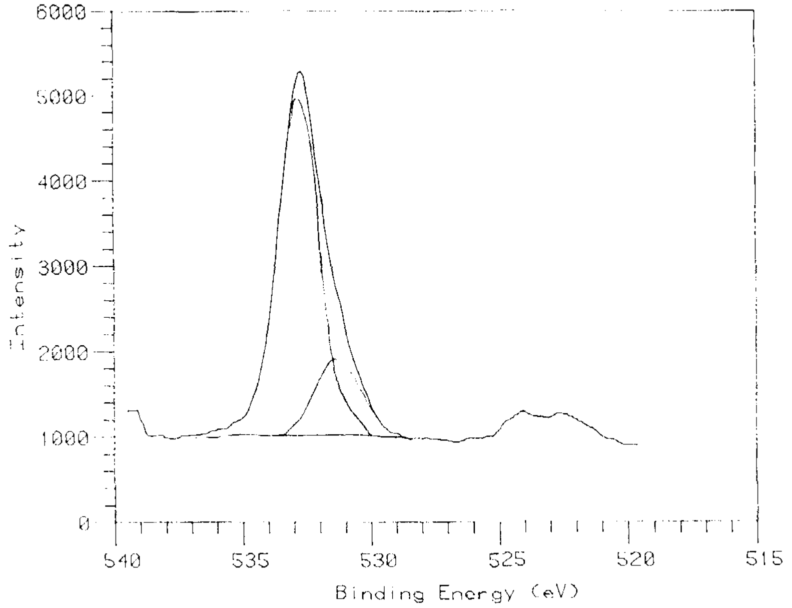


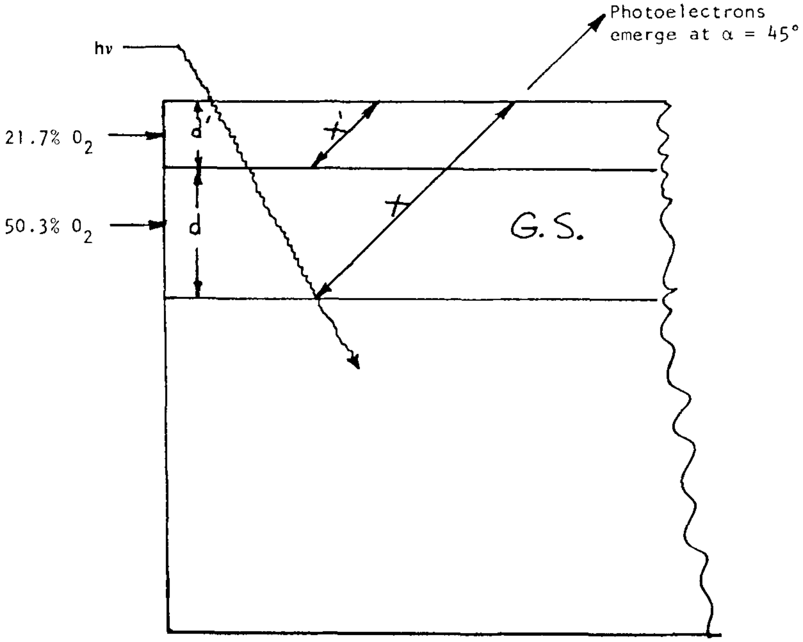
FIGURE 6 ESCA 1s Response of SAFLEX® Interphase Layer.

$$I_{O_{533_{ttl}}} = I_{O_{533_G}} + I_{O_{533_S}} \tag{11}$$

A solution of Equations 10 and 11 gave the individual oxygen intensities due to glass and Saflex®. A plot of interphase layer thickness as a function of intensity of O_{533_S} (Figure 8) provides essentially a single curve. This illustrates that the O_{533} 1s response of the Saflex® is a monotonically increasing function that is described strictly by the interphase adhesive layer thickness and could be used to measure film thickness.

IV. CONCLUSIONS

From the results of this study, it can be concluded that upon peeling the Saflex® away from laminated glass specimens, a layer of the polymer is left on the glass surface. This indicates that the laminated glass specimens fail cohesively at the glass/Saflex® interface. The amount



d' = film thickness

x' = distance of travel of O photoelectrons emerging from film

x = total distance of travel of O photoelectrons through film and substrate

d = bulk thickness

G.S. = Glass substrate

FIGURE 7 Model of SAFLEX® Interaction with Photon Flux.

of material left on the glass surface increases in direct proportion to the forces of adhesion in a given laminate, as measured by peel strength.

V. Acknowledgement

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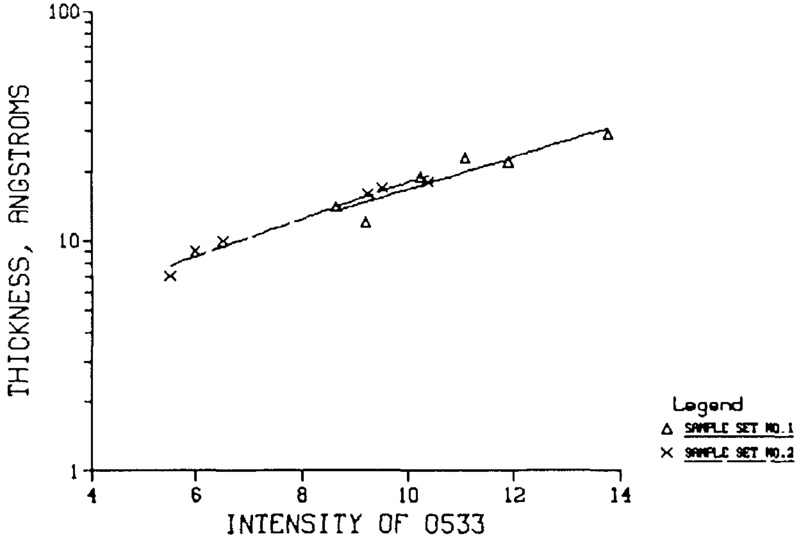

FIGURE 8 Interphase Adhesive Layer Thickness *vs.* Intensity of O_{533}.

ted in this program either directly by providing experimental help or indirectly through discussions and counsel. We would like specifically to recognize Mr. John Grover whose efforts and guidance constituted an invaluable portion of this program.

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