

Project MMS8

Report No 3

**Assessment of Characterisation
Techniques for Evaluating Surface
Treatments for Adhesive Bonding**

W R Broughton and M J Lodeiro

June 2003

Assessment of Characterisation Techniques for Evaluating Surface Treatments for Adhesive Bonding

W R Broughton and M J Lodeiro
NPL Materials Centre, National Physical Laboratory
Teddington, Middlesex
TW11 0LW, UK

ABSTRACT

This report presents the results of an experimental study carried out to assess techniques for evaluating surface treatments of metallic and polymeric composite materials for adhesive bonding. The techniques assessed include: contact and non-contact profilometry (surface roughness), contact angle (wettability), micro-hardness, gloss/reflectivity, colorimetry, ellipsometry and surface resistivity. Optically stimulated electron emission (OSEE) is also examined. The techniques are assessed in terms of: ability to differentiate between treatments and level of treatment, suitability for laboratory trials or on-line inspection, ease of use, equipment costs, material compatibility and measurement uncertainty. Trials were conducted on grit-blasted, chromic acid etched and anodised aluminium alloys, oil lubricated hot-dipped galvanised steel, and corona discharge treated glass fibre-reinforced polypropylene. The report also includes mechanical test data obtained at the National Physical Laboratory (NPL) and extracted from published literature.

The results from the study show that most of the techniques studied were useful in determining changes in surface properties for different levels of treatment. Contact angle and colorimetry techniques proved the most suitable for relating surface changes to the level of treatment and could potentially be used to improve or optimise adhesive strength and environmental durability.

© Crown copyright 2003
Reproduced by permission of the Controller of HMSO

ISSN 1473 - 2734

National Physical Laboratory
Teddington, Middlesex, UK, TW11 0LW

No extract from this report may be reproduced without the
prior written consent of the Managing Director, National
Physical Laboratory; the source must be acknowledged.

Approved on behalf of Managing Director, NPL, by Dr C Lea,
Head of NPL Materials Centre.

CONTENTS

1	INTRODUCTION	1
2	SURFACE PROFILOMETRY	1
2.1	GRIT-BLASTED AND CHROMIC ACID ETCHED SURFACES	2
2.2	ANODISED SURFACES	4
3	GLOSS/REFLECTIVITY, COLORIMETRY AND ELLIPSOMETRY	5
3.1	GLOSS/REFLECTIVITY	5
3.2	COLORIMETRY	7
3.3	ELLIPSOMETRY	10
4	CONTACT ANGLE TECHNIQUES.....	13
5	MICRO-HARDNESS	18
6	SURFACE RESISTIVITY.....	18
7	OPTICALLY STIMULATED ELECTRON EMISSION (OSEE).....	19
8	DISCUSSION AND CONCLUDING REMARKS	22
	ACKNOWLEDGEMENTS.....	24
	REFERENCES	24

1 INTRODUCTION

Surface preparation is recognised as the most critical step in the adhesive bonding process and considerable effort is frequently expended in optimising the surface treatment. Correct surface preparation is essential for good bond strength and ensuring the long-term structural integrity of bonded structures, particularly under hostile service conditions [1-5]. Unsatisfactory surface preparation will result in premature and unpredictable interfacial failure of bonded joints. The selection of surface treatments is usually based on adhesive manufacturers' recommendations, although technical, environmental and economic considerations (preparation costs and time), also play a role. An essential part of ensuring good adhesion and long-term durability is the ability to monitor and control changes in surface morphology and chemistry of the substrate materials during surface preparation and storage.

An experimental study was undertaken to evaluate the efficacy of various characterisation techniques for evaluating changes in surface properties of metallic materials and polymer composites resulting from changes in surface treatments and the level of treatment. The techniques assessed include: contact and non-contact profilometry (surface roughness), contact angle (wettability), micro-hardness, gloss/reflectivity, colorimetry, ellipsometry, surface resistivity and optically stimulated electron emission (OSEE) – see also [6-8]. The work forms part of the Measurements for Materials Systems (MMS) project “Interfacial Adhesion Strength” funded by the United Kingdom Department of Trade and Industry.

The techniques are assessed in terms of: ability to differentiate between treatments and level of treatment, suitability for laboratory trials or on-line inspection, ease of use, equipment costs, material compatibility and measurement uncertainty. Trials were conducted on grit-blasted, chromic acid etched and anodised aluminium alloys, oil lubricated hot-dipped galvanised steel, and corona discharge treated glass fibre-reinforced polypropylene. The report also includes mechanical test data obtained at the National Physical Laboratory (NPL) and extracted from published literature.

The report is divided into eight sections including the Introduction (Section 1). Section 2 covers contact and non-contact surface profilometry techniques. Gloss/reflectivity, colorimetry and ellipsometry are covered in Section 3. Section 4 examines contact angle measurement techniques. Micro-hardness, surface resistivity and OSEE are covered in Sections 5, 6 and 7, respectively. Discussion and concluding remarks are given in Section 8.

2. SURFACE PROFILOMETRY

This section examines the use of surface profilometry and surface roughness in the examination of metallic surfaces. The techniques evaluated were:

- (i) Contact (stylus) profilometry – Surtronic hand-held contact surface roughness meter (diamond stylus with a radius of 5 μm – see Figure 1).
- (ii) 3-D interferometric profilometry – Phase Shift MicroXAM white light interferometer (measurements courtesy of AG Electro-Optics Limited).
- (iii) Atomic force microscopy (AFM).

2.1 GRIT-BLASTED AND CHROMIC ACID ETCHED SURFACES

Contact and non-contact surface profilometry measurements were carried out on “as-received” (or untreated), grit-blasted (GB) and chromic acid etched (CAE) 5251 aluminium alloy. Surface roughness measurements were also conducted on six (6) sets of AA5754-O aluminium alloy samples with different surface treatments, which were supplied by Alcan (Banbury Laboratories).

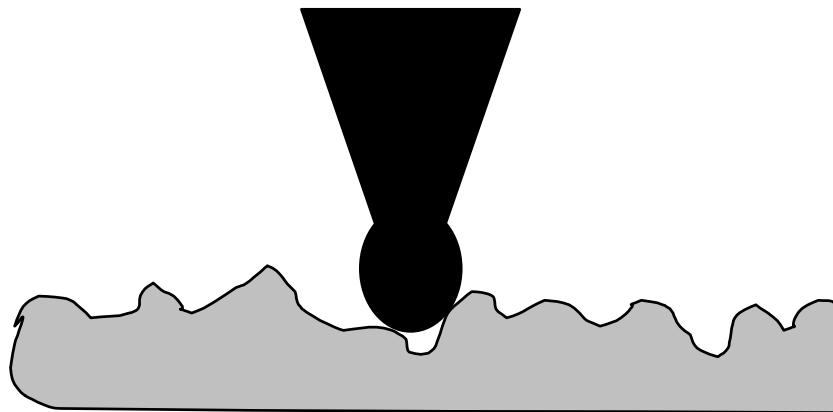


Figure 1: Contact (stylus) profilometry.

A series of trials, using both contact and optical interferometric profilometry techniques, were carried out on 5251 aluminium alloy. Specimens were grit-blasted using 80/120 grade white alumina at a pressure of 85 psi for 10, 30, 60 and 120 seconds. The nozzle outlet was kept at a constant separation distance (150 mm) and normal to the sample surface. The same two methods were also used to measure the surface roughness of specimens that had been subjected to CAE treatment. These specimens were immersed in CAE solution at 60°C for 10, 20, 30 and 60 minutes. On removal, specimens were sprayed with acetone, rinsed in cold water for 1 minute, rinsed in hot water for 2-3 minutes and finally air dried at 100°C in a circulating oven. The etching solution consisted of 37.5 grams of sodium dichromate dissolved in 500 ml of distilled water to which 75 ml of sulphuric acid was added. The solution was heated for 30 minutes at 60°C. Untreated material was also measured as a control.

Table 1: Surface Roughness Measurements on Grit-Blasted and CAE Aluminium

Treatment	Optical Profilometry		Contact Profilometry	
	R_a (μm)	R_q (μm)	R_a (μm)	R_q (μm)
Untreated	0.20	0.25	0.24	-
<u>Grit-Blasted (secs)</u>				
10	2.05	2.67	1.83	-
30	2.36	3.03	1.79	-
60	2.60	3.30	1.98	-
120	2.37	3.01	2.08	-
<u>CAE (mins)</u>				
10	0.26	0.35	0.19	-
20	0.31	0.42	0.31	-
30	0.26	0.35	0.30	-
60	0.28	0.40	0.38	-

The results presented in Table 1 show distinct differences in the values of R_a (average roughness deviation) and R_q (root mean square (RMS) roughness deviation) between untreated and grit-blasted surfaces, and between untreated and CAE surfaces. Differences between the levels of treatment are minimal.

$$R_a = \frac{1}{L} \int_0^L |y(x)| dx \quad (1)$$

$$R_q = \sqrt{\frac{1}{L} \int_0^L y^2(x) dx} \quad (2)$$

where L is the sampled length, x is the position along the sampled length and $y(x)$ are the roughness profile values.

The results for the two methods were in reasonable agreement, and hence either technique could be used to check for untreated regions, particularly where the technique results in large changes in surface roughness (i.e. grit-blasting). The optical interferometric system is particularly suitable for on-line inspection. Figure 2 shows a 3-D surface map of grit-blasted aluminium obtained using optical interferometric profilometry.

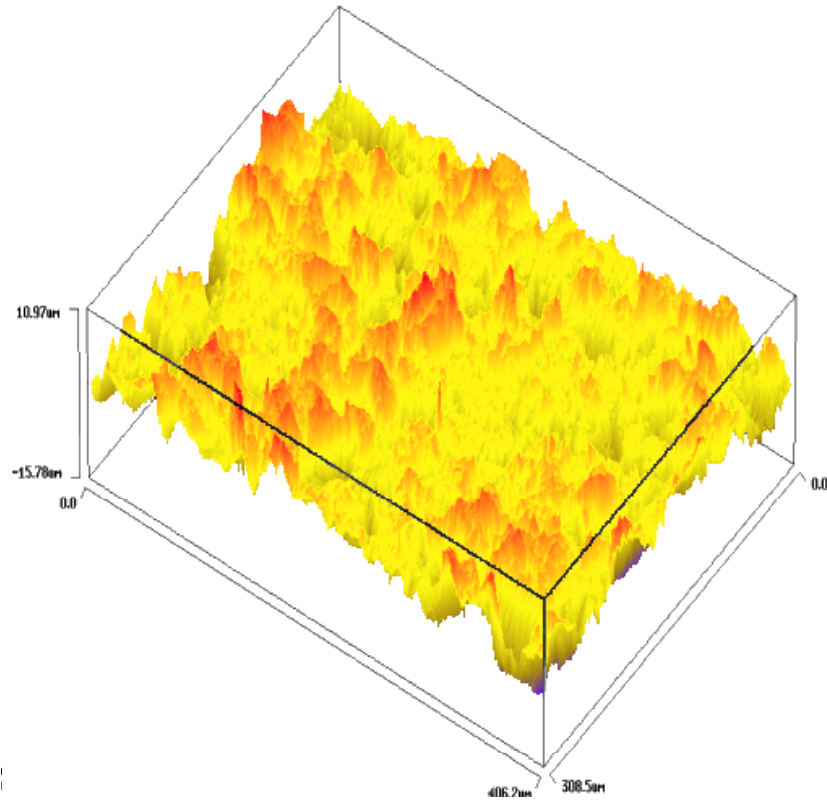


Figure 2: 3-D surface map of grit-blasted aluminium (courtesy of AG Electro-Optics).

AFM proved successful in differentiating between levels of CAE treatment. Measurements were carried out using a Thermo-microscopes M5 AFM operated in contact mode. The AFM probe was used to scan an area 100 µm square. The applied load on the probe was 50 nN. The surface roughness parameters for CAE specimens that had been treated for 10 minutes and 120 minutes are shown in Table 2. R_{p-v} denotes the average peak to valley distance.

Table 2: AFM Surface Roughness Measurements on CAE Aluminium

Treatment Time (mins)	R _a (nm)	R _q (nm)	R _{p-v} (nm)	Mean Height (nm)
10	73	105	1,258	595
120	266	333	2,682	1,306

AFM measurements were also carried out on anodised aluminium samples supplied by Alcan and compared with surface roughness measurements obtained using the Surtronic contact surface roughness meter. The results are presented in Table 3 (see also Figure 3).

2.2 ANODISED SURFACES

Six different anodised surface treatments (described below) were evaluated.

- (i) **Mill-finish** (a non-treated surface).
- (ii) **Light clean** (lightly degreased to remove oils – most of the surface structure and oxides still remaining).
- (iii) **Full clean** (an extensive electrolytic acid etch - equivalent of the optimised system without an anodised layer).
- (iv) **Full clean + 25 nm barrier film** ("optimised" system with a full etch and a 25 nm barrier anodised film).
- (v) **Light clean + 25 nm barrier film** (a variant of (iv) to give a lower level of etch).
- (vi) **Full clean + over-anodised** (a variant with a 25 nm barrier + 75 nm anodised film).

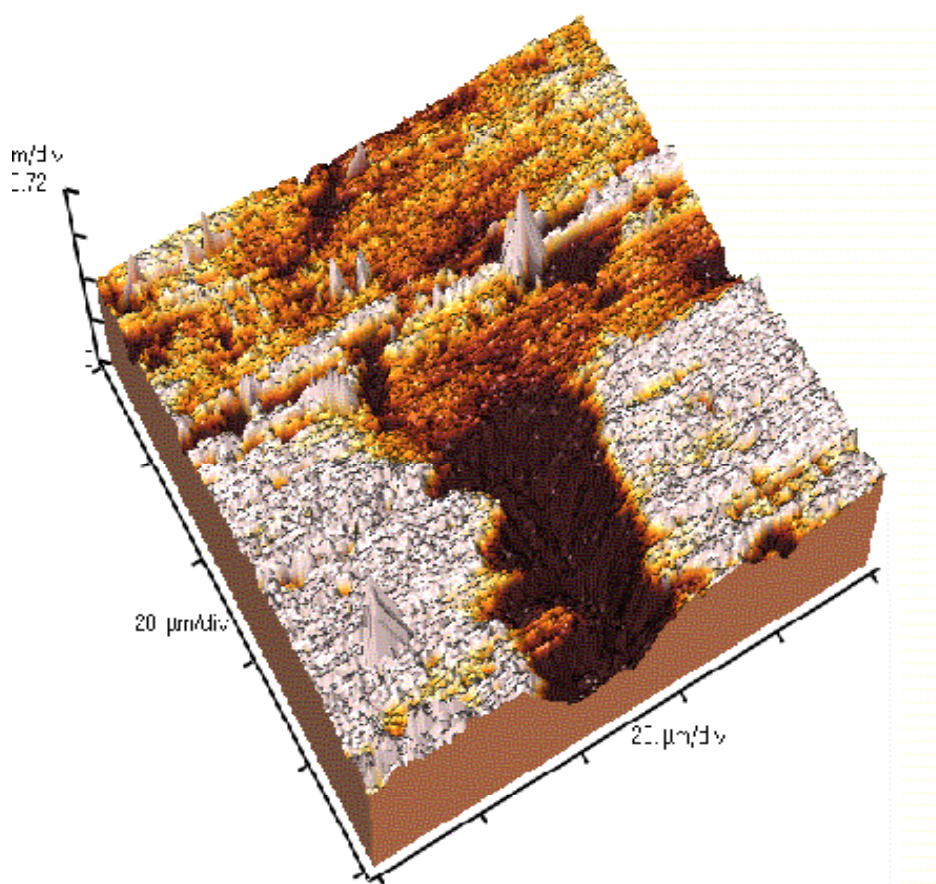


Figure 3: AFM surface map of “optimised” anodised aluminium surface.

Table 3: Surface Roughness Measurements on CAE Aluminium

Treatment	AFM		Contact Profilometry	
	R_a (μm)	R_q (μm)	R_a (nm)	R_q (nm)
Mill finish	89	133	250	-
Light clean	120	175	390	-
Full clean	124	177	210	-
Full clean + 25 nm barrier (optimised)	161	249	160	-
Light clean + 25 nm barrier	214	288	410	-
Full clean + 25 nm barrier + 75 nm anodised film	166	237	160	-

Although surface roughness parameters R_a and R_q tended to differ for the various anodised treatments (see Table 3), there was no way of ranking the treatments using either parameter. No clear trends in surface roughness were evident between light clean to full clean, or degree of cleaning for light and full clean surfaces for the two techniques. It was possible, however, to distinguish between milled, cleaned and anodised surfaces, but not within groups. The operating range for the different instruments used to measure surface roughness is shown below.

- (i) Surtonic hand-held contact surface roughness meter – 100 to 4,000 nm.
- (ii) Phase Shift MicroXam white light interferometer – 0.2 nm to 100 μm .
- (iii) Thermo-microscopes M5 AFM – 10 to 7,000 nm.

NB. Measurement reliability decreases as R_a approaches the lower limit (i.e. smooth surfaces).

3. GLOSS/REFLECTIVITY, COLORIMETRY AND ELLIPSOMETRY

This section examines techniques that measure changes in optical properties (e.g. reflectivity, spectral reflectance, phase shifts, etc.) of surfaces produced as a result of mechanical abrasion or chemical treatment. The following techniques were considered:

- (i) Gloss/reflectivity – Rhopoint Surface Instruments hand-held Novo-Gloss meter.
- (ii) Colorimetry – Datacolor Spectraflash 500 spectrophotometer.
- (iii) Single wavelength ellipsometry – measurements courtesy of BP (Sunbury).
- (iv) Variable angle spectroscopic ellipsometry (VASE) – measurements courtesy of Alcan (Banbury Laboratories).
- (v) Infrared VASE (or IR-VASE) – measurements courtesy of J A Woollam Co., Inc.

3.1 GLOSS/REFLECTIVITY

The Novo-Gloss meter was used to measure surface reflectivity of the grit-blasted, CAE and anodised aluminium surfaces described in Section 2 at two fixed angles (20° and 60°). This instrument projects a beam of white light (filtered to give a spectrum response similar to that of the human eye) onto the target surface at a specific angle and measures the amount of specular reflected light. Surface roughness causes incident light to be scattered at other angles, such that the scatter increases with roughness. The instrument provides quantitative data on the uniformity and quality of the surface treatment [9-10].

Table 4: Gloss Measurements for Grit-Blasted and CAE Aluminium

Treatment	Inspection Angle	
	20°	60°
Untreated	121 ± 6	> 200
<u>Grit-Blast (secs)</u>		
10	0.8 ± 0.1	2.9 ± 0.1
30	0.8 ± 0.1	3.1 ± 0.2
60	0.7 ± 0.1	3.0 ± 0.1
120	0.7 ± 0.1	2.9 ± 0.1
<u>CAE (mins)</u>		
10	35.7 ± 1.1	133 ± 3
20	30.6 ± 1.2	102 ± 1
30	15.6 ± 0.3	76 ± 1
60	9.3 ± 0.9	50 ± 2

The results from tests conducted on the grit-blasted 5251 aluminium alloy (see Table 4) show clear differences between treated and untreated surfaces, but no differences between the degree of treatment. However, clear differences in gloss value are evident between levels of CAE treatment, with the surface becoming less reflective as treatment time increases. Although there is a clear difference in specular reflectivity between the mill finish and the anodised surface treatments, it is difficult to subsequently differentiate between the various anodised treatments (see Table 5).

Table 5: Gloss Measurements for Anodised Aluminium

Treatment	Inspection Angle	
	20°	60°
Mill finish	91 ± 9	142 ± 8
Light clean	42 ± 3	115 ± 1
Full clean	46 ± 1	128 ± 1
Full clean + 25 nm barrier (optimised)	40 ± 1	108 ± 2
Light clean + 25 nm barrier	48 ± 1	125 ± 1
Full clean + 25 nm barrier + 75 nm anodised film	37 ± 1	118 ± 1

Other researchers [11] have shown that some differentiation between surface treatments was possible using laser reflectivity. Tables 6 and 7 present the results of measurements carried out by AEA Technology on CR1 mild steel and aluminium, respectively. The FPL (Forest Product Laboratory) treatment referred to in Table 7 is chromic-sulphuric acids etch treatment used for aluminium alloys.

Table 6: Average Laser Reflectivity for CR1 Mild Steel [11]

Treatment	Average Laser Reflection	Scatter
As received	41.6	18.4
Alumin grit-blast	11.7	11.0
Alumina grit-blast + SIP primer	8.7	8.5
Acid etch	7.6	6.8
Zinc phosphate conversion	17.8	8.2
Scotchbrite abrasion	43.7	15.1

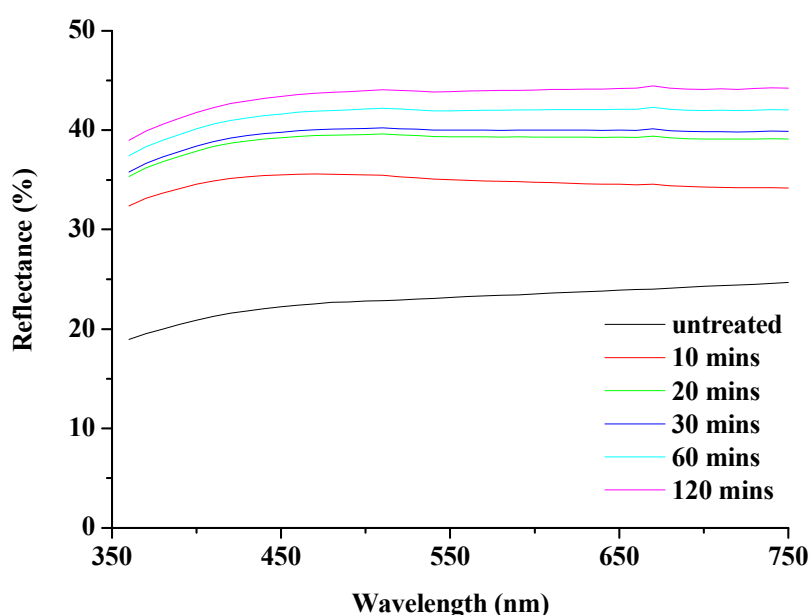
Table 7: Average Laser Reflectivity for Aluminium [11]

Treatment	Average Laser Reflection	Scatter
As received	65.2	23.8
Phosphoric acid anodised (PAA)	42.7	21.0
Chromic acid anodised (CAA)	12.5	4.3
Alkaline etch	58.9	25.1
Standard FPL etch	53.5	23.2
Cold FPL etch	71.3	20.5

Reflectivity/gloss measurement techniques are generally less effective in differentiating between different surface treatments for polymeric materials since the reflection from untreated surfaces is already low, particularly when compared with metallic surfaces.

3.2 COLORIMETRY

The spectral reflectance of CAE and anodised aluminium alloy materials were measured using a Datacolor Spectraflash 500 spectrophotometer. The spectrophotometer exposes a 10 mm diameter circular area on the surface to a light source with a daylight colour temperature and compares the percentage reflectance within the visible spectrum (360 – 750 nm wavelength) to that of reference white and black colour tiles.

**Figure 4: Reflectance spectra for untreated and CAE aluminium.**

The colorimetry results shown in Figure 4 clearly indicate differences in surface reflectance between levels of CAE treatment. The reflectance increases with increasing oxide film thickness. As the oxide layer grows, the colour of the surface changes (i.e. becomes whiter). Colorimetry is able to differentiate between untreated and treated surfaces, and between short and long treatment times. It is difficult, however, to differentiate between treatment times that are closely spaced. Also, consideration needs to be given to accurately measuring reflectance of the substrate prior to treatment. Variability in reflectance of surfaces may cause difficulties in data interpretation and quantification. Instrumented colorimetry systems are available for on-line inspection.

Colorimetry also proved successful in detecting differences in reflectivity between the various anodised treatments (see Figure 5). As with gloss measurements, there is a clear difference between the mill finish and the anodised surfaces. It is also possible to differentiate between light and clean surfaces, and between fully clean surfaces with and without a barrier layer. Cleaning increases reflectivity and the presence of the barrier layer reduces reflectivity. The spectrum for the over-anodised surface was also different to the other surface treatments where reflectivity decreased linearly with increasing wavelength.

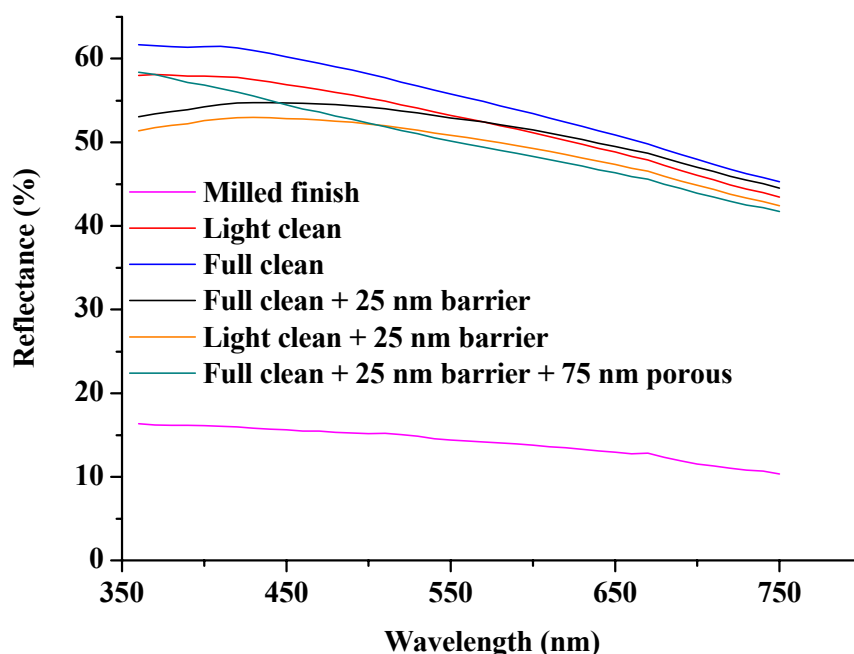


Figure 5: Reflectance spectra for anodised aluminium.

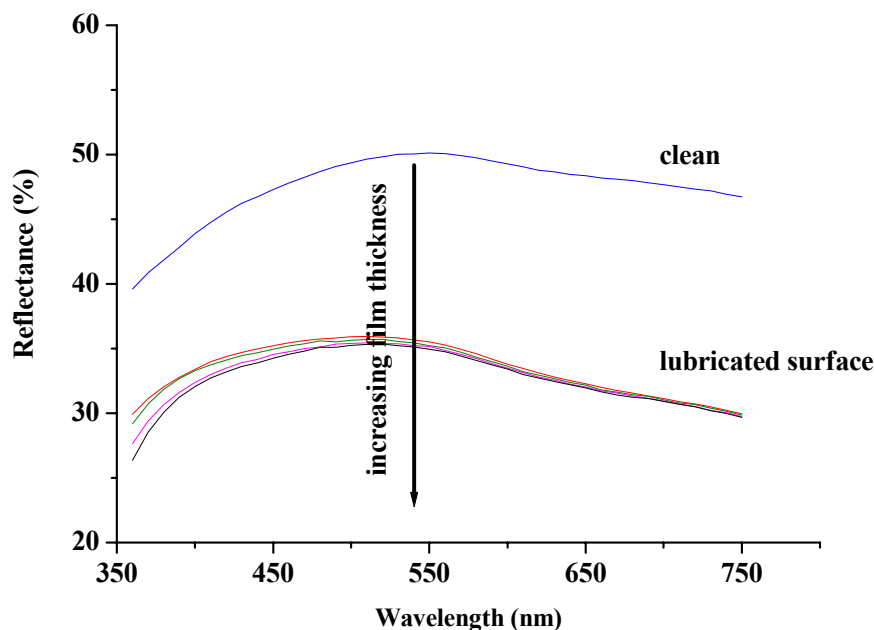


Figure 6: Reflectance spectra for increasing thickness of oil coating on galvanised steel.

Recent developments have seen the formulation of adhesives that are tolerant of oily surfaces, thus eliminating the need for expensive surface treatments and enabling assembly in factory environments or in the field. Many of these systems require the presence of lubricating oil, although in small amounts, on the adherend surface, such that attempts to ensure a clean surface can be counterproductive. A key issue in this case relates to controlling the thickness and uniformity of lubricants on areas to be bonded. In order to assess the practicality of using colorimetry for this purpose, measurements were carried out on double-sided, hot-dipped galvanised steel (Zintec) samples in which the amount of oil (i.e. thickness) on the surface was steadily increased. The galvanised steel samples, which were supplied by Corus, were coated in MP404 oil. An electronic pipette was used to apply a known quantity of oil on the galvanised steel surface, which was dispersed over the entire surface and allowed to settle for 24 hours to produce a uniform layer.

Colorimetry proved successful in detecting increments in oil film thickness (Figure 6) with differences in reflectance more marked at the shorter wavelengths. However, it is difficult to quantify small reductions in reflectance due to increasing oil film thickness. This difficulty was overcome by summing the total reflectance over the entire spectral range of 350 to 750 nm. The approach provides a convenient metric for quantifying the amount of oil on the adherend surface, and enables users to directly relate the film thickness to a measurable parameter (i.e. total visible reflectance). Figure 7 shows a comparison of total reflectance as a function of film thickness, although the reduction is evidently small.

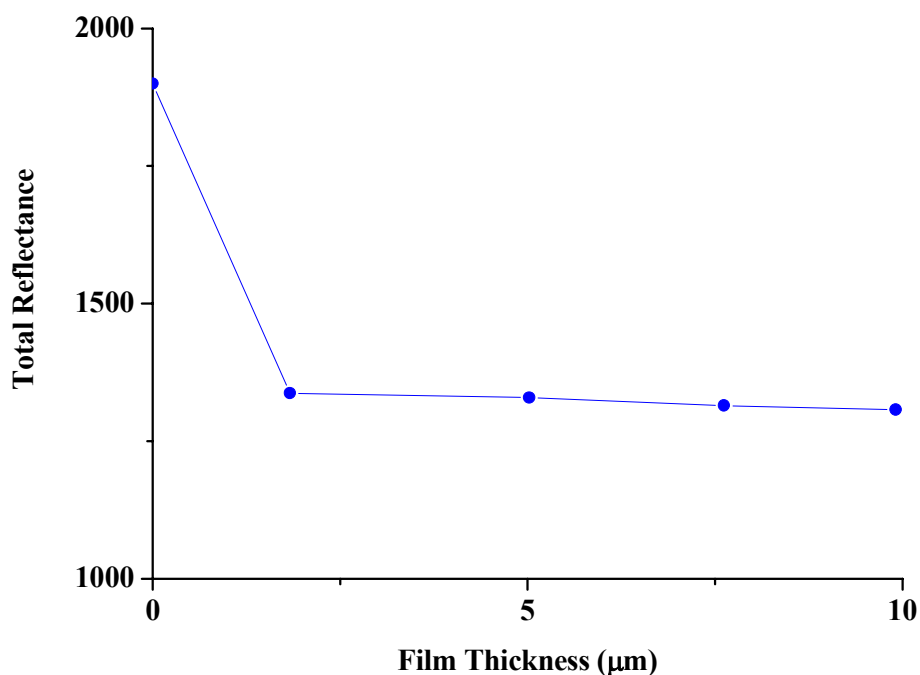


Figure 7: Total reflectance of oil coated galvanised steel with increasing film thickness.

It was found that the reflectance spectra obtained from clean galvanised steel prior to the addition of MP404 varied markedly from sample to sample (Figure 8), hence the need to inspect/map the entire surface to obtain background reflectance values prior to coating the surface. It is possible to subtract background reflectance data (i.e. data from the clean surface) from the reflectance data obtained for the coated material. The results clearly indicate that colorimetry can be used to quantify the amount of oil present on an adherend surface, provided due care is taken when carrying out the measurements.

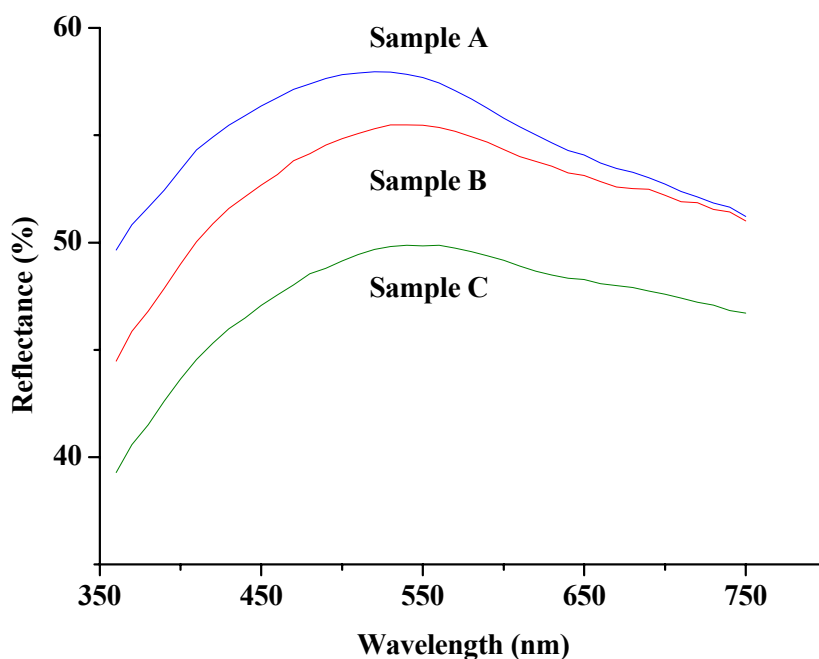


Figure 8: Variability in colorimetry reflectance for clean galvanised steel.

3.3 ELLIPSOMETRY

Ellipsometry uses polarized light to measure the thickness and refractive index of thin films [6-7, 12-13]. The technique consists of directing a polarised light beam onto surface at an oblique angle of incidence and measuring the phase change and intensity (amplitude) of the reflected light. Multiple reflections interfere, as illustrated in Figure 9, to provide information about the layer thickness t , optical constant $\mathbf{n}$ (index of refraction) and extinction coefficient $\mathbf{k}$ (a measure of absorption) for each layer interacting with the incident beam. The optical properties of isotropic materials can be represented by the complex index of refraction $\tilde{\mathbf{n}}$ ($\tilde{\mathbf{n}} = \mathbf{n} + i\mathbf{k}$). Ellipsometry can yield information about the thickness, morphology and chemical composition of layers that are thinner than the wavelength of the light source.

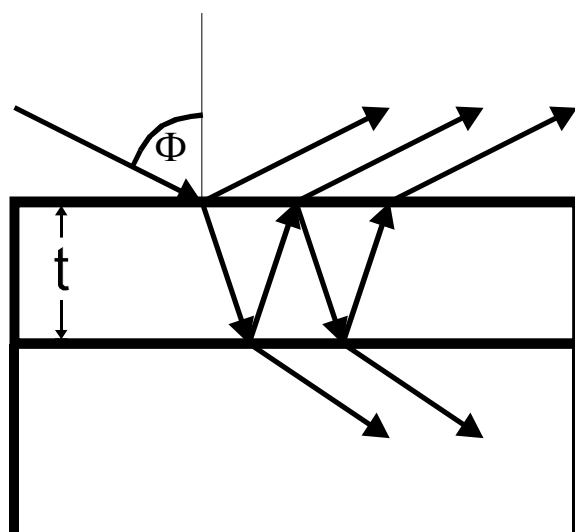


Figure 9: Schematic of multiple reflections (courtesy of J A Woollam, Co., Inc.).

The oxide layer thickness and optical properties (refractive index and absorbance) of the anodised aluminium samples (described previously) were measured using:

- (i) Single-wavelength ellipsometer;
- (ii) Variable angle spectroscopic ellipsometer (VASE); and
- (iii) Infrared VASE or IR-VASE.

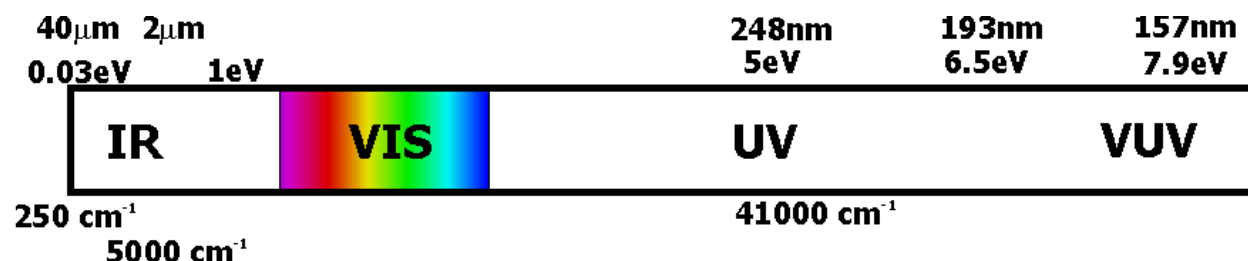


Figure 10: Spectral range for different ellipsometers (courtesy of J A Woollam, Co., Inc.).

Alcan (Banbury Laboratories) carried out VASE measurements on the anodised aluminium samples and were able to determine the structure of the multi-layered oxide system present on each material. Table 8 compares the VASE results with those obtained using single-wavelength (courtesy of BP, Sunbury) and IR-VASE (courtesy of J A Woollam, Co., Inc.). VASE measurements were taken over the spectral range 193 to 2,200 nm, whereas the IR-VASE measurements were taken over the spectral range 2 to 30 μm (see Figure 10). Both were recorded at multiple angles of incidence (70° - 75° by 5°). The beam diameter in each case was fixed at 6 mm. The fixed-angle single-wavelength instrument uses a He-Ne laser source with a wavelength of 632.8 nm and 45° polarisation.

Table 8: Ellipsometry Film Thickness Measurements for Anodised Aluminium

Treatment	Inspection Angle	
	Barrier Layer	Porous Layer
<u>VASE Measurements</u>		
Full clean + 25 nm barrier (optimised)	26	n/a
Light clean + 25 nm barrier	25	n/a
Full clean + 25 nm barrier + 75 nm anodised film	24	80
<u>IR-VASE Measurements</u>		
Full clean + 25 nm barrier (optimised)	14	n/a
Light clean + 25 nm barrier	7	n/a
Full clean + 25 nm barrier + 75 nm anodised film	7	124
<u>Single-Wavelength Fixed Angle Measurements</u>		
Full clean + 25 nm barrier (optimised)	7-8	n/a
Light clean + 25 nm barrier	2-7	n/a
Full clean + 25 nm barrier + 75 nm anodised film	-	52

n/a – not applicable

The molecular bond absorption bands for the different surface treatments were readily distinguishable in the IR ellipsometry data (Figure 11), therefore it was possible to fingerprint the surface chemistry (molecular bonds) present in the surface layers. Although the samples without a barrier layer have an oxide layer, it was impossible to determine the film thickness for these materials.

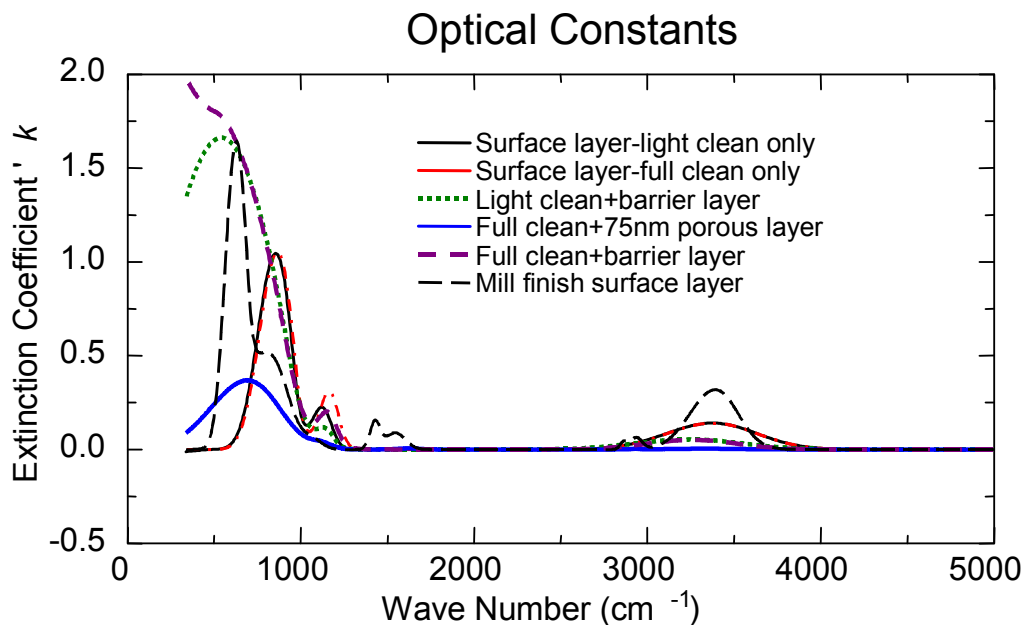


Figure 11: Molecular bond absorption IR-VASE data for anodised aluminium.
(courtesy of J A Woollam Co., Inc.)

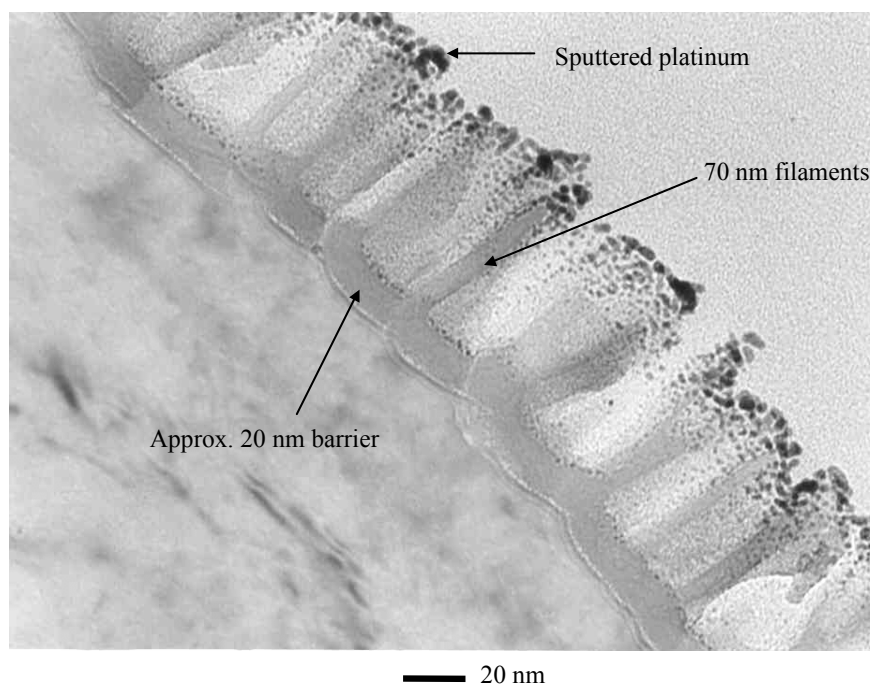


Figure 12: TEM image of the "over anodised" sample.
(courtesy of Alcan International Ltd)

Ellipsometry analysis requires a baseline set of known properties of the surface, which in the case of aluminium is an oxide layer. The technique will only measure properties of the additional oxide layer. Modelling the optical properties of multi-layered systems is a complex process, requiring a good knowledge of the optical properties of individual layers, and unless this information is available it is impossible to accurately determine the thickness of individual layers. Better knowledge of the optical properties of the oxide film may help explain differences in results. Transmission electron microscopy (TEM) was used by Alcan (Banbury Laboratories) to confirm the VASE results (see Figure 12).

IR-VASE and single-wavelength ellipsometry results, presented in Table 8, were determined from data obtained from all six anodised materials, with and without barrier and porous layers. It was assumed for modelling purposes that the surface layer had a refractive index close to Al_2O_3 ($n = 1.766$). The presence of a barrier layer or contamination (i.e. light clean) results in an increase in molecular bond absorption (Figure 11). Mill finish material showed the lowest absorption for any given wavelength. The single-wavelength technique was able to detect differences in oxide film thickness (Table 8) and the presence of contamination on the aluminium surface, although it was not possible to determine the refractive indices for the various oxide films. There was also evidence in all cases of differences in optical properties in the X- and Y-directions resulting from the milling process.

4. CONTACT ANGLE TECHNIQUES

This section examines the use of dynamic and sessile drop methods for measuring contact angle, and hence wettability, of anodised aluminium and corona discharge treated glass fibre-polypropylene. Good wettability of a surface is a pre-requisite for ensuring good adhesive bonding. Ideally, the contact angle should be minimized in order to enhance adhesive strength. The lower the contact angle, the greater the tendency for the liquid to wet the solid surface, until complete wetting occurs at an angle $\theta = 0$. Large contact angles are associated with poor wettability.

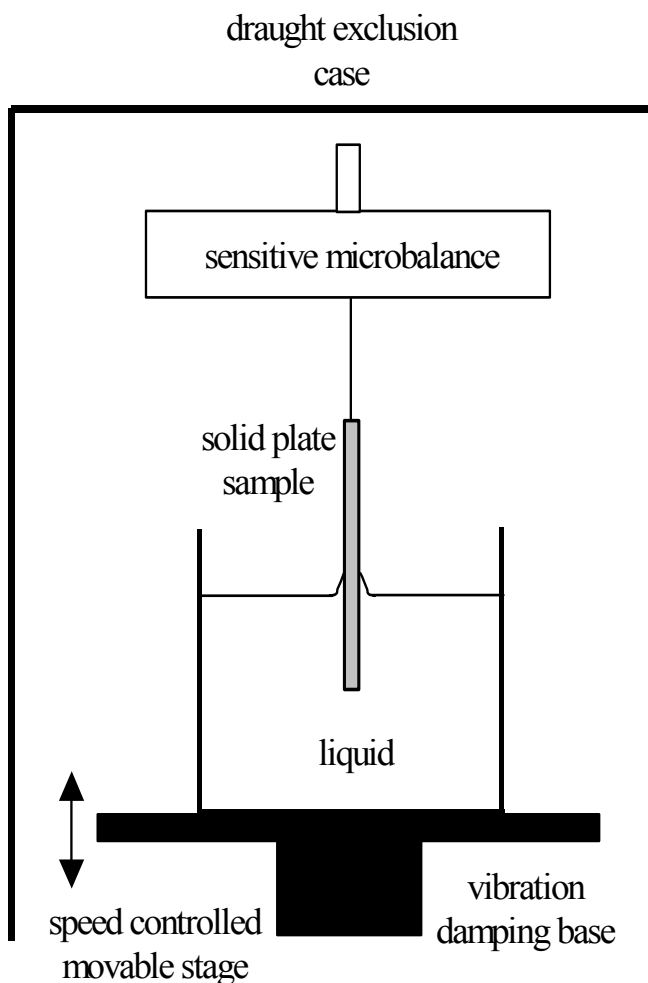


Figure 13: Wilhelmy plate method for measuring dynamic contact angle.

A Cahn Dynamic Contact Angle was used to measure the advancing θ_{adv} and receding θ_{rec} dynamic contact angles, and contact angle hysteresis ($\theta_{adv} - \theta_{rec}$) of samples less than 3g in weight. The analyzer employs the Wilhelmy plate technique (Figure 13) to measure forces exerted as the solid/liquid boundary is moved along the sample surface. Contact angle hysteresis is used to characterise surface heterogeneity and roughness. A FTA (First Ten Ångströms) 200 Dynamic Contact Angle Analyzer was used for sessile drop measurements. The sessile drop measurement process was automated, thus reducing measurement uncertainty.

Although the results obtained using the two methods were not identical, the results obtained on the anodised aluminium samples using distilled water and glycerol probes displayed consistent trends for each treatment. The sessile drop method measurements clearly indicate that the treatment identified as “optimised” (i.e. full clean + barrier layer) has the lowest contact angle, and hence improved wettability compared with the other surface treatments. Over-anodising the aluminium surface is counter-productive (i.e. contact angle similar to light clean and mill finish surfaces).

Table 9: Contact Angle Measurements (degrees) for Anodised Aluminium (distilled water/glycerol)

Treatment	θ_{adv}	θ_{rec}	$\theta_{adv} - \theta_{rec}$
Dynamic Method			
Mill finish	89.5/91.9	51.3/27.0	38.2/64.9
Light clean	84.5/84.8	0.0/0.0	84.5/84.8
Full clean	81.6/86.1	0.0/0.0	81.6/86.1
Full clean + 25 nm barrier (optimised)	53.2/65.7	36.0/28.5	17.2/37.2
Light clean + 25 nm barrier	74.2/80.4	0.0/33.6	74.2/47.8
Full clean + 25 nm barrier + 75 nm anodised film	85.5/89.1	0.0/0.0	85.5/89.1
Sessile Drop Method			
Mill finish	$96.0 \pm 6.7/97.0 \pm 4.1$		
Light clean	$98.3 \pm 7.3/97.2 \pm 4.2$		
Full clean	$53.7 \pm 4.3/76.8 \pm 3.5$		
Full clean + 25 nm barrier (optimised)	$32.4 \pm 6.2/42.1 \pm 1.6$		
Light clean + 25 nm barrier	$83.3 \pm 4.2/74.1 \pm 1.7$		
Full clean + 25 nm barrier + 75 nm anodised film	$85.4 \pm 2.8/86.7 \pm 4.1$		

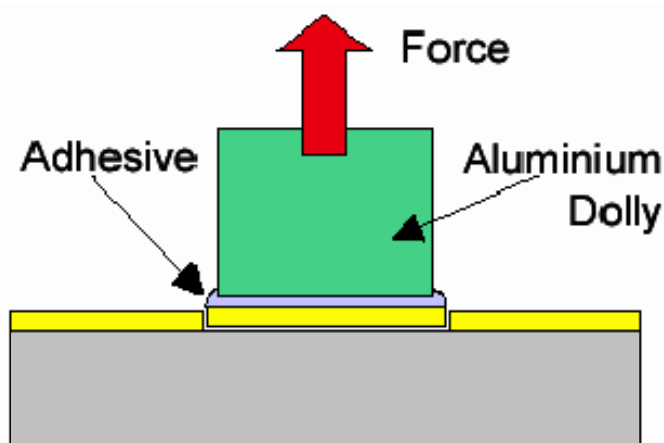


Figure 14: Pull-off test [14].

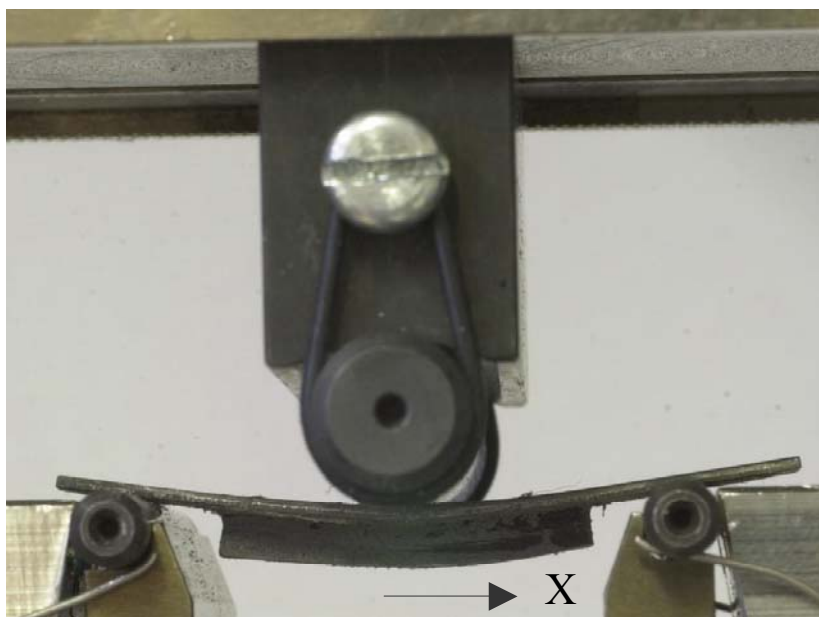


Figure 15: Three-point bend test [14].

Mechanical tests have been carried out at NPL [14], although at a later date than the contact angle measurements presented in Table 9, on the same anodised aluminium samples. The pull-off test (Figure 14) and a three-point bend test (Figure 15) were used to assess the adhesion strength of a single-part toughened epoxy adhesive to the various surfaces. The strength data is presented in Table 10. Comparing the strength results with sessile drop contact angle measurements (Table 9) it can be seen that adhesion strength tends to increase as the contact angle decreases; although ranking using the two different mechanical approaches is not identical.

Table 10: Adhesion Strength Data [14]

Treatment	Pull-Off Strength (MPa)	Three-Point Bend Strength (MPa)
Mill finish	10.7 ± 0.8	4.3 ± 0.4
Light clean	13.0 ± 0.5	4.9 ± 0.6
Full clean	14.8 ± 0.4	5.8 ± 0.4
Full clean + 25 nm barrier (optimised)	14.3 ± 0.7	5.3 ± 0.4
Light clean + 25 nm barrier	14.0 ± 0.5	4.9 ± 1.0
Full clean + 25 nm barrier + 75 nm anodised film	13.3 ± 1.3	4.8 ± 0.8

Tables 11, 12 and 13 compare contact angle measurements for different substrates and surface treatments using sessile drop and dynamic methods from published literature. Table 13 also includes surface energy values (see [6]). These results further demonstrate the sensitivity of contact angle methods to changes in surface treatments.

Table 11: Static Contact Angles for Surface Treated Aluminium [11]

Surface Treatment	Average Contact Angle (degrees)
As received (untreated)	61.0
Solvent Cleaned	80.0
Alkaline Etched	6.7
Standard FPL etch	<5

**Table 12: Contact Angles for Various Surface Treated Plastics
Military Handbook – 619B**

Material	Contact Angle (degrees)			
	Untreated	Plasma	Flame	Chemical
Polypropylene (PP)	87	22	87	60
Polyethylene (PE)	71	18	-	75
Poly vinyl chloride (PVC)	90	35	-	79
Polycarbonate (PC)	75	33	-	76
High Density PP	87	42	38	54

Table 13: Dynamic Contact Angles and Surface Energies for Mild Steel [11]

Surface Treatment	Contact Angle (degrees)		Calculated Surface Energy (mJm^{-2})		
	θ_{adv}	θ_{rec}	γ^d	γ^p	γ^{total}
As received (untreated)	90.5	31.1	32.1	1.8	33.9
Alumina gritblast	86.9	30.2	50.4	0.5	50.9
Acid Etch	60.1	31.3	38.1	13.0	51.1
Zinc Phosphate Conversion	53.0	40.9	40.3	16.1	56.4

Contact angle measurements were also carried out at NPL [15] on corona discharge treated injection moulded discontinuous glass fibre-reinforced polypropylene with a glass fibre weight content of 50%. The material was 4 mm thick. Surface treatment was carried out using a Sherman Treaters GX10 corona laboratory bench-top unit with a 280 mm wide U-channel metallic electrode. The composite specimens were cleaned thoroughly beforehand with isopropanol and stored in dessicators, supported on an edge, both before and after treatment until needed. Both sides of the specimen were treated identically and within the same region of the treatment area to avoid the introduction of uncontrolled error due to either varying field strength along the length of the electrode or changes in the height of the base-plate with position.

Table 14: Experimental Design Matrix for Corona Discharge Treated Composite [15]

Run	Treatment Time (min/m)	Input Power (kW)	Electrode Separation (mm)
1	0.20	0.75	5.5
2	0.40	0.50	5.5
3	0.20	0.75	5.5
4	0.40	1.00	5.5
5	0.20	0.75	5.5
6	0.04	0.50	5.5
7	0.20	0.75	5.5
8	0.04	1.00	5.5
9	0.20	0.75	5.5
10	0.04	0.75	4.5
11	0.40	0.75	4.5
12	0.20	1.00	4.5
13	0.20	0.50	4.5
14	0.20	1.00	6.5
15	0.04	0.75	6.5
16	0.20	0.50	6.5
17	0.40	0.75	6.5

The key controllable process factors investigated were [15]:

- Treatment time (0.04 – 0.4 min/m)
- Input power (0.5 – 1.0 kW)
- Electrode separation (4.5 – 6.5 mm)

Table 14 shows an experimental design (3 factor Box-Benken) matrix used to assess the effect of the key process factors on contact angle and to determine the optimum process settings (i.e. lowest contact angle achieved). A design of experiments (DoE) approach was used to devise and analyse the test matrix. Each run consisted of two specimens cut from different mouldings giving two sets of nominally identical specimens. The Cahn dynamic contact angle analyser was used to measure the contact angle on the samples with a distilled water probe.

The optimum surface treatment, as predicted using DoE, occurs when the input power is 1 kW and the treatment time is 0.36 min/m. The contact angle associated with these conditions is 52.34°. The closest conditions to these settings was Run 4 (see Table 14 and Figure 16), which gave a contact angle of 51.48° for a treatment time of 0.4 min/m and an input power of 1 kW. The results shown in Figure 16 indicate that contact angle tends to decrease with the intensity of treatment (i.e. treatment time x input power). Varying the electrode separation had minimal effect on the results.

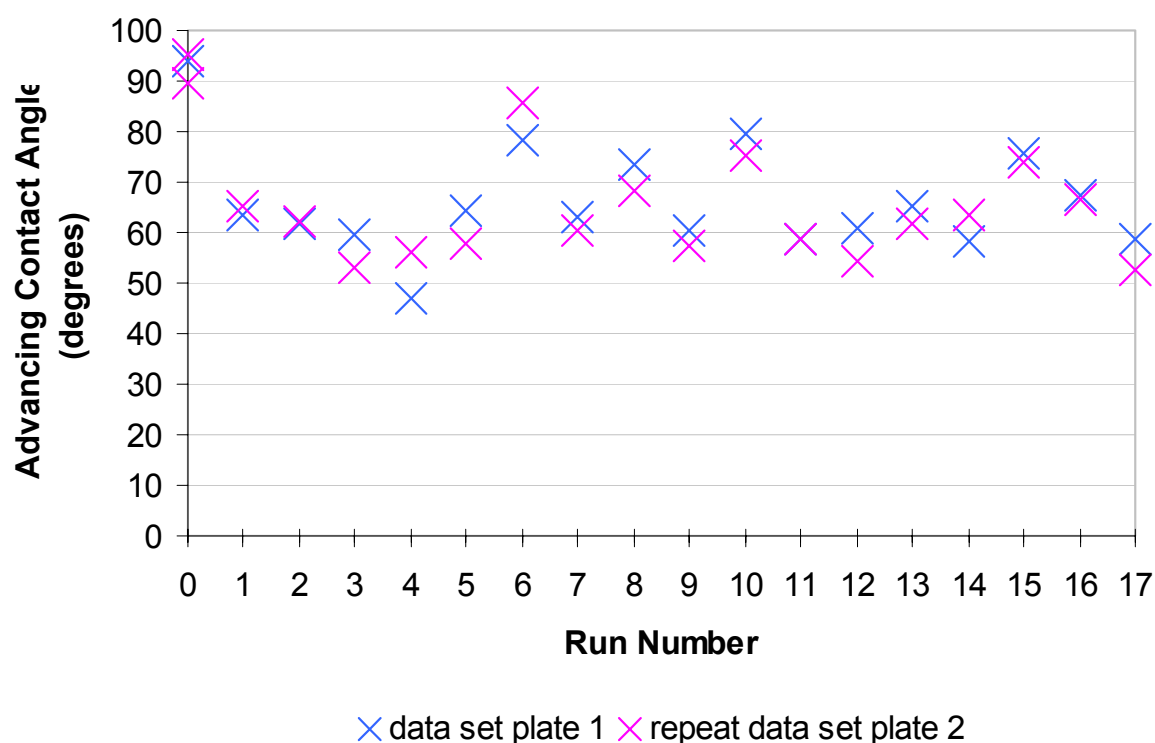


Figure 16: Contact angle results for corona discharge treated glass fibre/polypropylene.

Care needs to be taken in preparation, storage and handling of contact angle specimens to prevent damage or contamination of the surfaces. Specimens need to be flat, with parallel faces and edges and free of surface or edge defects (e.g. scratches or burrs) and protected from contamination.

5. MICRO-HARDNESS

Vickers micro-hardness tests were carried out on CAE aluminium specimens. The test machine, which is fitted with a diamond tipped indenter, measures a comparative Vickers micro-hardness. The weight used for testing was 500 g. Differences in micro-hardness were minimal, ranging from 65.5 HV (Hardness Vickers) for the untreated material to 66.7 for 10 minutes exposure and 68.2 HV for 60 minutes exposure. Associated uncertainty was ± 2 HV.

Table 15: Hardness Measurements for Surface Treated Aluminium and Titanium [11]

Surface Treatment	Micro-Hardness (Vickers Hardness Number)	Ultra-Micro Hardness (N/mm ²)
Aluminium		
As received (untreated)	80-110	1,400
Phosphoric Acid Anodising (PAA)	65-84	2,900
Chromic Acid Anodising (CAA)	79-135	19,000
Titanium		
As received (untreated)	258-352	10,800
Sodium Hydroxide Anodising (SHA)	234-248	800
Chromic Acid Anodising (CAA)	322-369	12,500

It is evident from the work at AEA Technology (Table 15) on surface treatments of aluminium and titanium [15] and from the work at NPL on CAE aluminium that micro-hardness tests can be used to differentiate between types of treatment (e.g. between soft and hard surfaces), but not between levels of treatment. The associated scatter in hardness can be high thus making differentiation between levels of treatment virtually impossible, particularly as differences in surface hardness are relatively small. In addition, the indenter penetration needs to be less than 10% of the surface layer thickness to avoid the influence of the substrate on results, which is impossible to achieve with micro-hardness measurements. Standard hardness tests are unsuitable for assessing differences in surface layer properties.

6. SURFACE RESISTIVITY

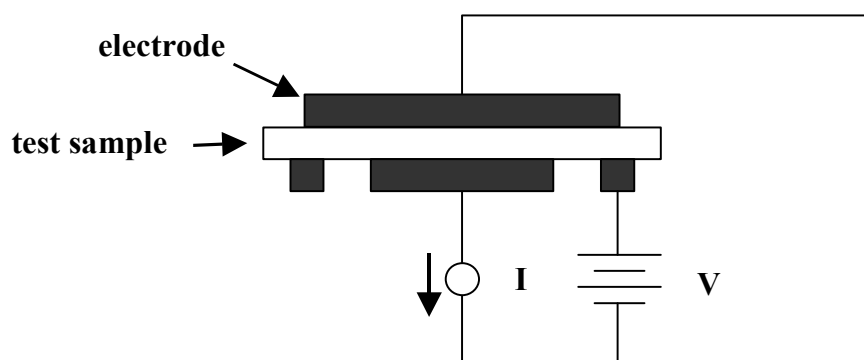


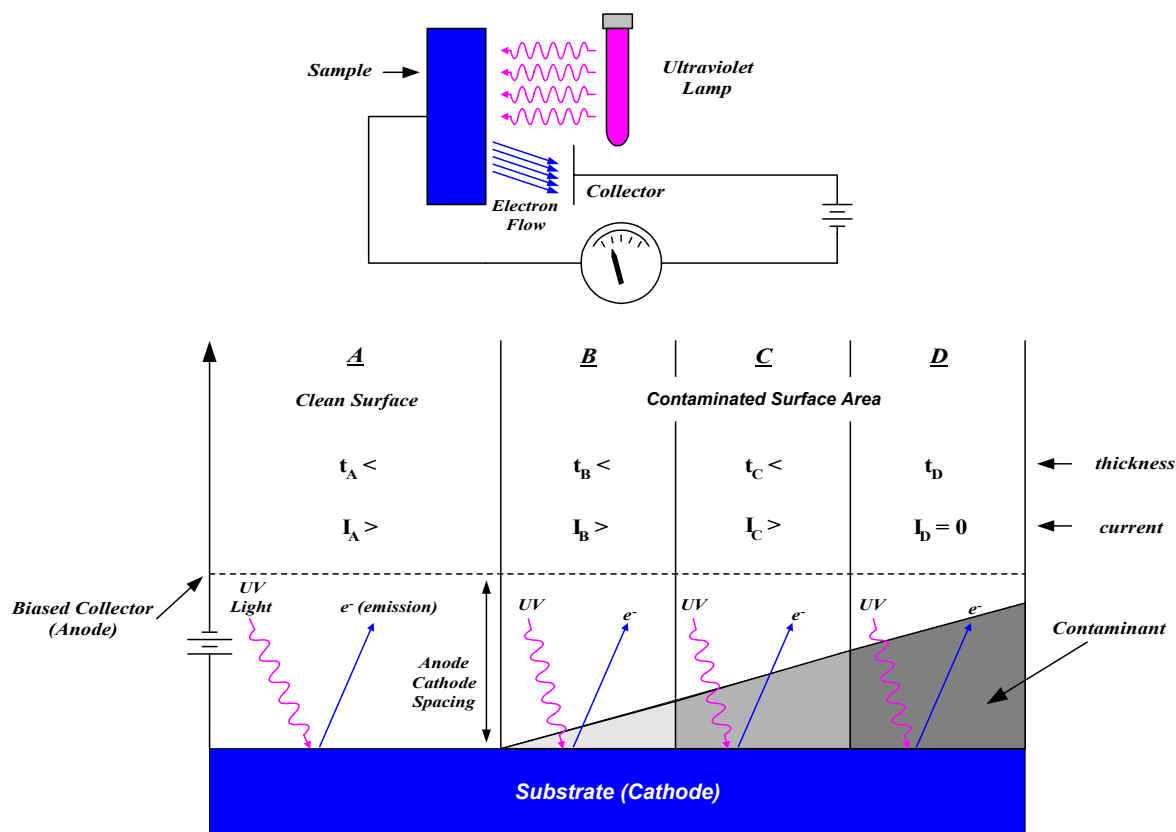
Figure 17: Surface resistivity equipment.

Surface resistivity measurements were conducted on CAE aluminium samples using an Industrial Development Bangor Ltd Model 482 surface resistance meter (see Figure 17). Flexible contour electrodes with a diameter of 75-80 mm were used to inspect 100 mm square specimens. The technique proved easy to implement and could readily be adapted for on-line inspection.

The technique proved insensitive to the different levels of CAE treatment. The resistance for the untreated 5251 aluminium was 1.5×10^7 ohms and between $5-8 \times 10^5$ ohms for the different levels of exposure to CAE solution. Hence, the technique can be used to differentiate between untreated and CAE treated material, but not between levels of treatment. The resistance of the oxide layer, formed as a result of chemical treatment, tends to breakdown under prolonged exposure to applied voltage.

7. OPTICALLY STIMULATED ELECTRON EMISSION (OSEE)

Optically stimulated electron emission (OSEE) has proved a useful tool for monitoring surface contamination and optimisation of surface treatments for metallic substrates. It is highly sensitive to very low levels of contamination, and has been successfully used for determining surface characteristics in multi-stage processing. OSEE operates by illuminating the area of inspection with ultraviolet (UV) radiation in the presence of a direct current (DC) electric field (see Figure 18). The UV radiation liberates electrons in the area of inspection by the photoelectric effect. The free electrons are collected on the positively charged anode with the magnitude of the resultant current being strongly related to the level of surface contamination. Contaminants absorb the UV radiation, thereby reducing the number of electrons emitted from the substrate, thus the greater the current the cleaner the surface. OSEE is particularly suited to studying contamination build-up following surface treatment, and could be used to determine maximum time allowable between treatment and application of an adhesive (i.e. open time).



Where I is Photo Emission current and t is thickness of contaminant

Figure 18: Principle of Optically Stimulated Electron Emission (OSEE).
(courtesy of Alcan International Ltd).

Figures 19 and 20 show results from line trials on an aluminium alloy produced at Alcan's plant in Warren, Ohio (USA). The study used a three stage cleaning process. Stage 1 gives a heavy etch, Stage 2 is a very light surface clean, and Stage 3 is a rinse. In Figure 19, the instrument is initially reading mill-finish material. Then Stages 2 and 3 are switched on, and the metal is lightly cleaned, giving an increase in signal. When Stage 3 is switched off, the signal drops, indicating incomplete rinsing. In Figure 20, the full acid etch is initiated, giving a large rise in signal. Switching off Stage 3 gives only a very small decrease in signal (after a very heavy etch), but switching Stages 2 and 3 off, reduces the signal. Switching back to the full clean restores the signal to the original curve. Switching off the etch Stage 1 again reduces the signal. As the surface cleanliness increases, the decrease in signal is reduced (i.e. smaller drop).

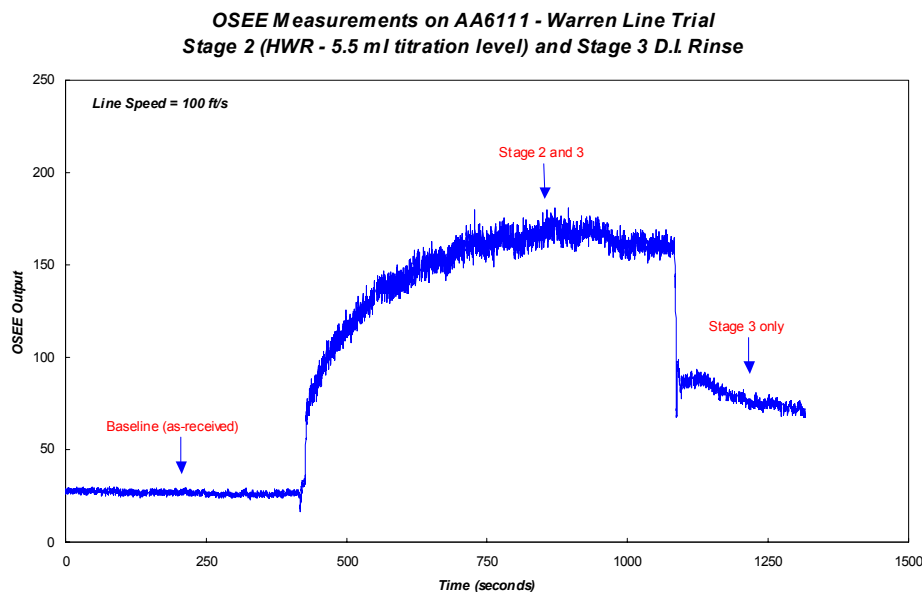


Figure 19: OSEE signal from AA6111 T4 aluminium surface after a light clean and rinse. (courtesy of Alcan International Ltd).

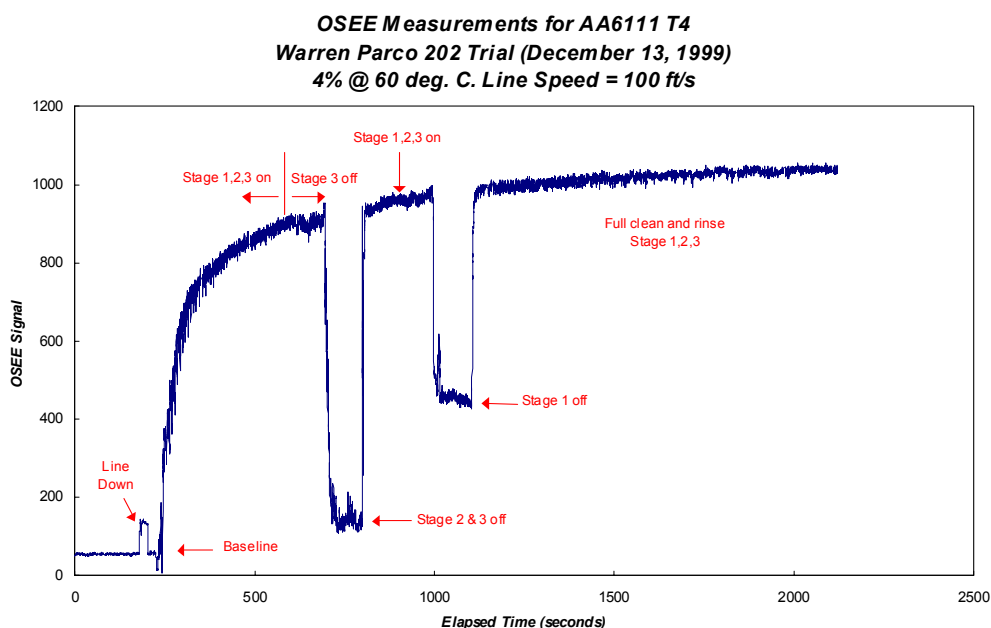


Figure 20: Signal dependence on level of active cleaning for AA6111 T4 aluminium. (courtesy of Alcan International Ltd).

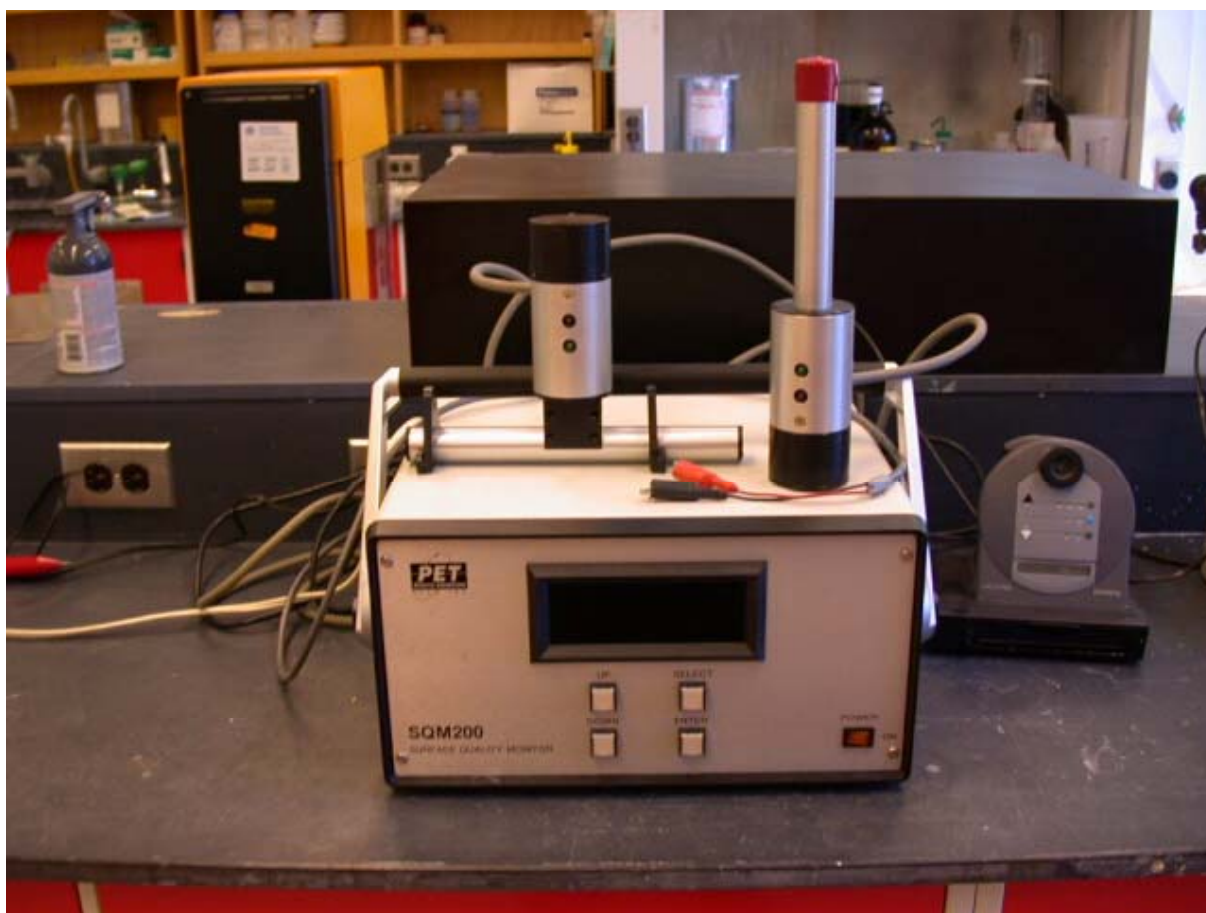


**Figure 21: Portable optically stimulated electron emission (OSEE) unit.
(courtesy of Alcan International Ltd)**

Alcan (Ontario) inspected samples of the six different surfaces using a portable OSEE unit as shown in Figure 21. This instrument is suitable for both hand-held and on-line inspection (scan facility), and requires minimal operator training. A total of six measurements were taken for each condition and the results averaged. The units of measurement for the technique are based on a voltage relative to the condition exhibiting the highest output, which will depend on the nature of the substrate, cleanliness, etc., as well as the gain used to amplify the signal.

In general, as the cleanliness of the metal increases, the OSEE reading will increase due to a decrease in the attenuation of electrons by organic contaminants (see Figure 22). However, as the thickness of the oxide layer increases, the OSEE will decrease due to an increase in electron attenuation by the oxide layer. The results for the anodised treatments examined tend to correlate with these trends. As observed by Alcan in the past, the mill-finished material exhibits the lowest output due to the heavy oxide and organic contaminants on the metal surface. The highest readings were obtained for the lightly cleaned material, which is followed closely by the full electrolytic etch. Once the barrier and/or anodised film is applied, the OSEE output drops dramatically due to the increase in electron absorption by the thin films. There are minimal differences in the readings obtained for **full clean + 25 nm barrier film** ("optimised" system), **light clean + 25 nm barrier** and **full clean + over-anodised** - since the UV source is of a fixed wavelength so a large portion of the electrons are absorbed.

Note that the contaminants or thin films on the surface, depending on their own photoemission characteristics can either enhance or attenuate the inherent emission from the surface as well. It also should be mentioned that there could be considerable variability in measurements depending on the uniformity of the surface with respect to cleaning and/or film thickness.

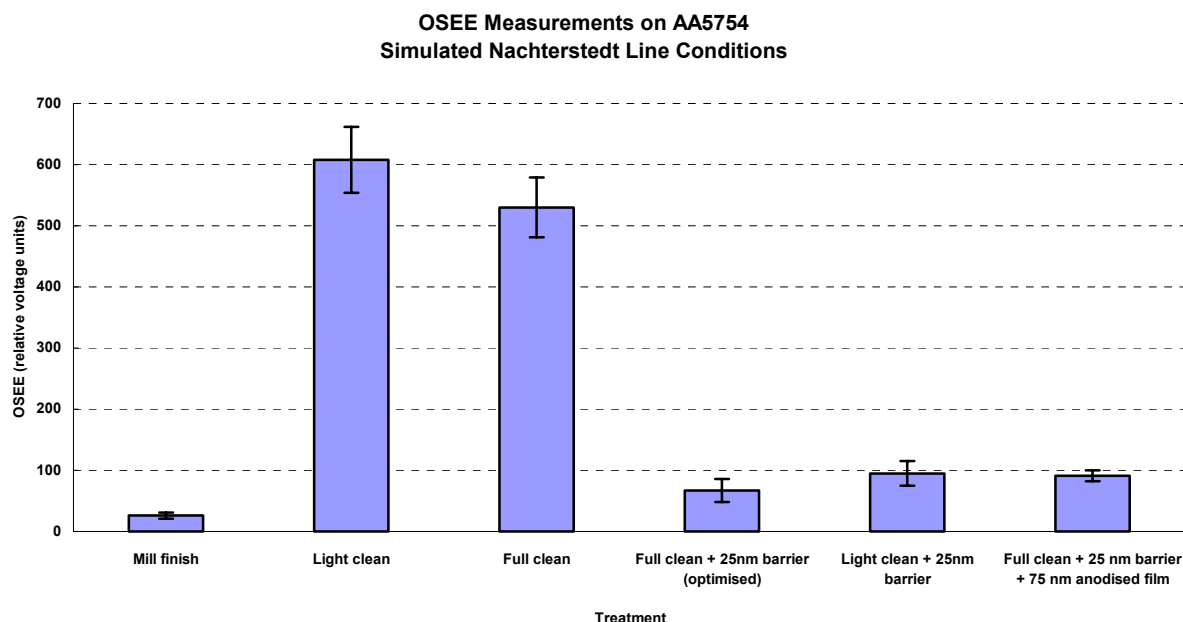


Figure 22: OSSE measurements on anodised aluminium (courtesy of Alcan, Ontario).

In summary, OSEE is best suited for on-line inspection to determine the level of cleanliness or degree of treatment. OSEE is unable to provide absolute measurements of surface activity for different treatments or ageing times. The technique is only able to detect barrier layers/cleaning levels through changes relative to initial substrate surface measurements (see Figures 19 and 20). Hence, calibration is required for each surface to be assessed. Efficacy is compromised when contaminants fluoresce. OSEE is a non-contact, non-destructive technique that provides quantitative data. It is fast and relatively inexpensive, and straightforward to operate. The technique can be used to assess different methods of cleaning or the effectiveness of different cleaning agents.

8. DISCUSSION AND CONCLUDING REMARKS

Most of the techniques studied proved useful in determining changes in surface properties for different levels of treatment, although the range of application of these techniques to the systems studied was generally limited (see Table 16). The results clearly establish colorimetry as the most versatile technique for detecting changes in surface morphology. It was possible to quantify changes in reflectivity and relate these changes to levels of treatment or various stages in production of multi-layered systems. It is also adaptable for on-line inspection. Ellipsometry can be used to accurately determine layer thickness of multi-layered systems, provided the analyst has a good knowledge of the technique and optical properties of individual layers within the system. The sessile drop method proved far more reliable than the Wilhelmy plate technique in differentiating between surfaces with good and poor adhesion. The latter requires considerable care in specimen preparation, whereas there are no special preparation requirements for the sessile drop method.

The portable units used for measuring surface roughness, surface resistivity and gloss required minimal operator training and were relatively inexpensive. OSEE is an on-line production tool for inspecting surface quality of metal substrates, but is limited in its use for determining the surface activity of aged materials (i.e. off-line).

The corona discharge trials demonstrated the methodology and logic behind planning and conducting a matrix of tests in a systematic manner using DoE approach. Combined with surface characterisation techniques, such as colorimetry and sessile drop method for measuring contact angle, this approach enables production engineers/researchers to assess the effects and non-linearity of key processing factors and possibly optimises process conditions.

Table 16: Suitability of Characterisation Techniques for Different Surface Treatments

Characterisation Technique	Surface Treatment				
	Grit-Blasted	CAE	Anodised	Oil Lubricated	Corona* Discharge
Micro-hardness	No	No	No	No	No
Contact Angle	Yes	Yes	Yes	No	Yes
Profilometry					
Contact	Yes	Yes	Yes	No	No
Optical	Yes	Yes	Yes	No	No
AFM	Yes	Yes	Yes	No	No
Gloss/Reflectivity	Yes	Yes	Possibly	No	No
Colorimetry	Yes	Yes	Yes	Yes	No
Ellipsometry	No	Yes	Yes	No	No
OSEE (on-line)*	Yes	Yes	Yes	No	No
Surface Resistivity	No	No	No	No	No

* Corona discharge treatment of glass fibre-reinforced polypropylene.

ACKNOWLEDGEMENTS

This work forms part of the programme for “Measurements for Materials Systems” funded by the United Kingdom Department of Trade and Industry, as part of its support of the technological competitiveness of UK industry. The authors would like to express their gratitude to AG Electro-Optics Limited, Alcan International Limited (Banbury, UK and Ontario, Canada), BP (Sunbury), Corus, Industrial Development Bangor Limited, J A Wollam Co. Inc., Sherman Treaters Ltd, and to colleagues at the National Physical Laboratory, particularly Dr Giles Aldrich-Smith, Miss Elena Arranz, Dr Greg Dean, Mr Bruce Duncan, Mr Sam Gnaniah, Mr Richard Mera and Mr Richard Shaw.

REFERENCES

1. Kinloch, A.J., “Adhesion and Adhesives - Science and Technology”, Chapman and Hall, 1987.
2. Adhesives and Sealants, Engineered Materials Handbook, Volume 3, ASM International, 1990.
3. Harris, A.F. and Beevers, A., “The Effects of Grit-Blasting on Surface Properties for Adhesion”, International Journal of Adhesion and Adhesives, 19(6), 1999, pp 445-452.
4. Handbook of Adhesives and Sealants, E M Petrie, McGraw-Hill Handbooks, 2000.
5. Broughton, W. and Gower, M., “Preparation and Testing of Adhesive Joints”, NPL Measurement Good Practice No 47, 2001.
6. Broughton, W.R. and Lodeiro, M.J., “Review of Surface Characterisation Techniques for Adhesive Bonding”, NPL Report MATC(A)66, 2002.
7. Broughton, W., Lodeiro, M., Shaw, R., Arranz, E. and Gnaniah, S., “Assessment of Surface Characterisation Techniques for Adhesive Bonding”, NPL Measurement Note MATC(MN)24, 2002.
8. Lodeiro, M.J, Broughton, W.R., and Gnaniah, S., “Optimisation of Corona Discharge Surface Treatment for Improved Adhesive Bonding using Design of Experiments”, NPL Measurement Note MATC(MN)24, 2002.
9. Cook, M.P. and Thomas, K., “Evaluation of Gloss Meters for Measurement of Moulded Plastics”, Polymer testing, Volume 9, 1990, pp 233-244.
10. Cook, A. and Duncan, B.C., “The Performance of Gloss Meters on Curving Surfaces”, NPL Report DMM(A)111, 1993.
11. Bull. S.J., “Characterisation of Materials Prior to Adhesive Bonding”, MTS Adhesive Programme Project 4, Report 5, AEA Technology, 1996.
12. Tompkins, H.G., “A User’s Guide to Ellipsometry”, Academic Press, 1992.
13. Woollam, J.A., “Ellipsometry, Variable Angle Spectroscopy”, Encyclopedia of Electrical and Electronics Engineering, Wiley, 2000, pp 109-117.
14. Duncan, B., Arranz, E., Crocker, L. and Urquhart, J., “Tests for Strength of adhesion”, NPL Measurement Note MATC(MN)49, 2003.
15. Lodeiro, M.J., Broughton, W.R. and Gnaniah, S., “Optimisation of Corona Discharge Surface Treatment for Improved Adhesive Bonding using Design of Experiments”, NPL Measurement Note MATC(MN)25, 2002.