THE USE OF OPTICALLY STIMULATED ELECTRON EMISSION FOR THE DETECTION OF SURFACE CONTAMINATION

C. J. ALLEN, C. KERR AND P. WALKER
SCT Materials, AWE, Aldermaston, Berkshire

INTRODUCTION

When metals, semiconductors, and some polymers are exposed to high energy radiation such as ultra-violet, some electrons at the surface will absorb the photon energy and escape from the surface. This phenomenon is known as optically stimulated electron emission (OSEE). At a metal boundary surface the potential energy of an electron approaches zero and thus functions as a barrier to the escape of electrons. In order to escape from the surface an electron requires additional energy over that associated with its velocity component perpendicular to the barrier surface. This energy may be provided by the processes of thermionic or field emission, by secondary emission from primary electron, ions, atoms or photons [1]. In the process described, the energy is provided by UV radiation and the emitted electrons are collected across an air gap by a biased collector and measured as a current. Not all the escaping electrons will be collected, some will be deflected back to the surface, combine with oxygen or diffuse as free electrons. The typical current level is $10^{-10} – 10^{12}$ amperes [2]. Any surface layer present, depending on its own photoemission characteristics will either enhance or attenuate this current.

These changes in current can be used to detect the presence, position and thickness of a surface layer whether organic, oxide or other inorganic, and makes the OSEE technique particularly valuable for assessing the degree of contamination of a surface. Relatively non-emitting materials, and therefore attenuating, include hydrocarbon oils, greases and silicones, which are all common contaminants harmful to the attainment of strong adhesive bonds, good adhesion of surface coatings and the achievement of effective pretreatment.

The fact that a contaminant may be emitting rather than attenuating does not necessarily rule out the possibility of using OSEE, as even emitters may change the strength of the measured signal. Metal powders and fragments can be located by their enhanced emittance over a low emittance background.

Equipment

The equipment described is the Model OP1010 Surface Quality Monitor manufactured by Photo Acoustic Technology, Inc. of Newbury Park, California and is known as PATSCAN. The equipment is illustrated in Figure 1 and consists of an IBM PC Computer with high resolution monochrome monitor with a high resolution graphics capability (A), a control unit (B), a sensor with vertical height adjustment (C), and a 150 x 150mm scanning stage with NEAT Controllers (D).

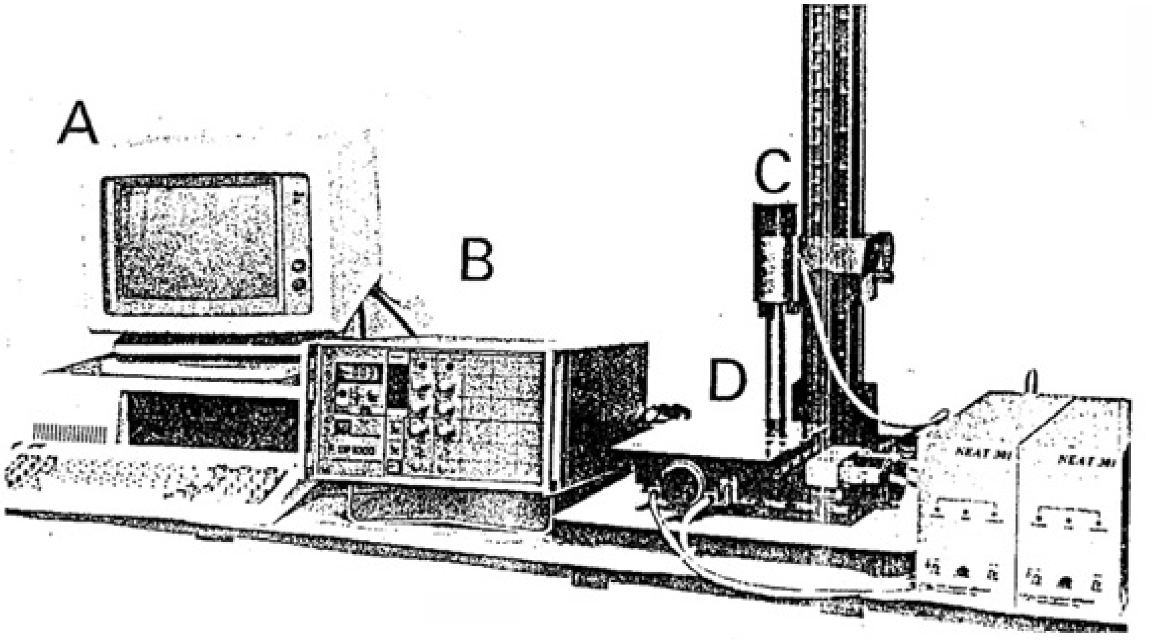

Figure 1. PATSCAN Model OP1010 Surface Quality Monitor.

The scanning stage may be commanded to control the direction, speed and scanning interval in the X and Y direction and may be halted or reversed as required. The sensor(s) contain an ultra-violet lamp, a detector, detector biased circuitry and amplification electronics. The aperture size can be altered with suitable fitments to reduce the area inspected. A rotary switch enables the amplifier gain to be set as required and signal lights indicate if readings are within a pre-set window.

The control unit houses the UV lamp power supply, DC power supply, the electronic circuit boards and various displays.

The PC/monitor containing dedicated PATSCAN software enables the user to control the motions of the scanning stage in terms of speed, area covered, number of data points etc. In the graphic display mode a three dimensional image of the data collected may be manipulated as required. The X and Y positions, axis, speed etc. are on continuous display.

FACTORS AFFECTING EQUIPMENT PERFORMANCE

There are several factors known to influence the use of PATSCAN, the most important of which are discussed below.

Sensor Distance

The sensor output is markedly dependent on the distance of the sensor from the test substrate, and three factors are important [3], (i) as the sensor distance increases, the UV intensity decreases, and fewer secondary electrons are released, (ii) electron losses due to collision increase with distance, and (iii) collection efficiency decreases due to a decrease in the electric field strength. The effect of these accumulative effects on sensor readings is shown in Figure 2 for three aperture sizes on a PATSCAN type probe. Gause [3] suggest a maximum distance of 6.35mm while data from Smith [4] indicates a distance of 1.2mms for the same percentage current drop using an unspecified probe. Clearly this is a parameter to be established for individual probe and aperture settings.

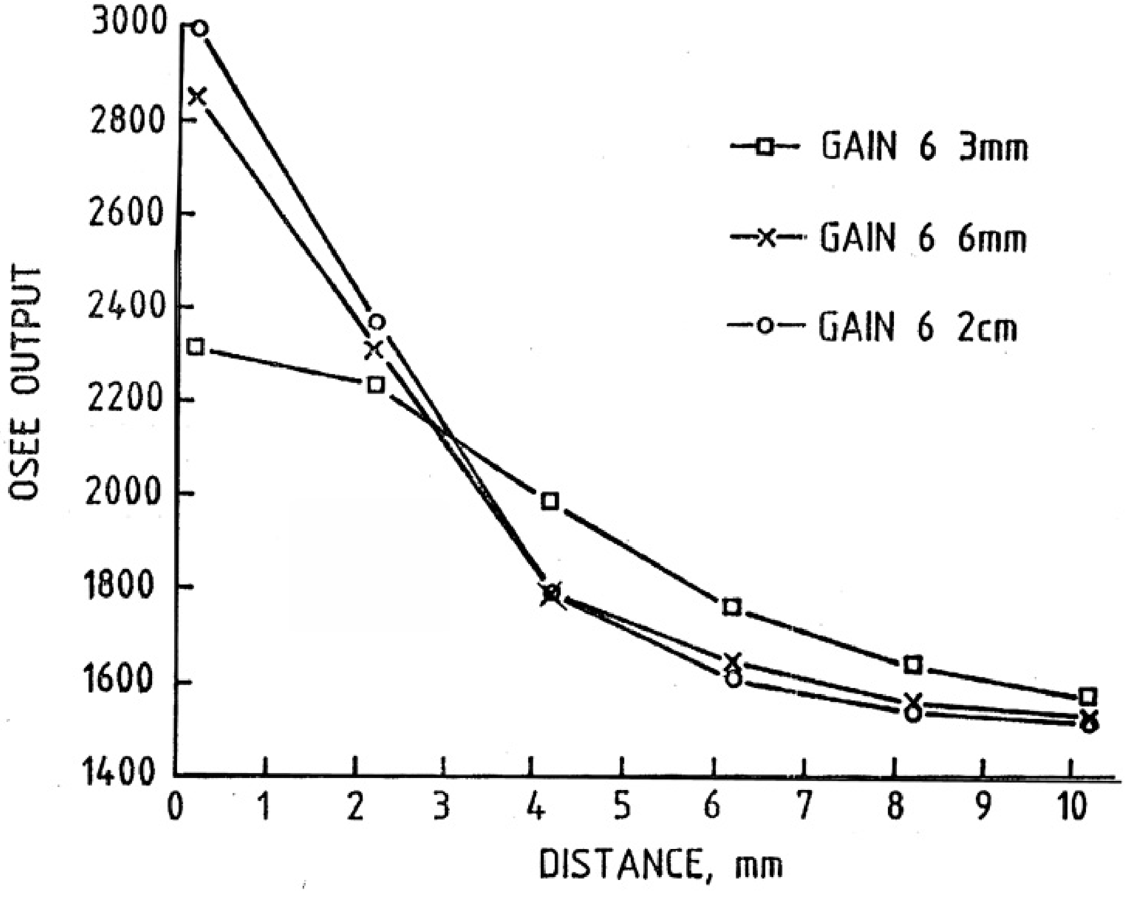

Figure 2. Effect of sensor distance on OSEE signal.

Scan Time

Scan time i.e., duration of exposure of the test surface to UV light can be important as the peak current reading may fall with even short time exposure due to electron stripping of the surface layer, most noticeable on some organic emitters.

On a contaminated surface, the measured OSEE may increase with exposure time due to the disassociation of the organic molecules under intense UV irradiation [5]. In practice this variable is eliminated by the recording of the peak OSEE response and a constant short exposure time.

Scan Interval

The scan interval i.e., distance between measured areas is only important in terms of the completeness of the examination. Large intervals require the use of a large aperture probe and small intervals a small aperture probe. For identification of local areas of contamination, small scan intervals are recommended if a detailed picture is to be obtained. The equipment described is capable of adjustment over the range 0.03 to 20mm.

UV Wavelength and Intensity

Short wavelength radiation produces higher energy electrons than long wavelength, and the former are more readily collected by the sensor. The rate of electron emission from a surface is dependent on the lamp intensity which is governed by the current passed. The probes used contain a low pressure mercury vapour lamp emitting over the range 185 to 600nm, the current is preset for maximum lamp life and is not adjustable.

Detection Limits

The lower detection limit for the measurement of contaminant layer thickness is claimed to be 1-2Å [2]. There is effectively no upper limit, as even when the OSEE signal is extinguished by the presence of a thick contaminant layer, the presence of the contaminant is readily detected by cleaning the surface and remeasuring. A layer of silicone resin (RTV 102) 240Å thick has been shown to extinguish the OSEE signal [4].

Operating Modes

The equipment may be used in either of two operating modes, the choice of which is dependent on the particular application to which the equipment is being put.

Peak Detect Mode

This mode is used when establishing upper and lower settings if the equipment is to be used on an accept/reject basis, as for example when being used as an inspection tool on surface having unknown characteristics.

Scan Mode

This mode is recommended when characterizing surfaces, identifying contaminated areas, or being used as a research tool. It can also be used for inspection purposes in this mode when large areas or moving surfaces are being investigated.

RECORDING OF DATA

Data may be recorded in three ways:

(a) numerical hard copy (tabular data)
(b) plotted graphic data (also displayed)
(c) normalised plotted graphic data (also displayed)

(a) Numerical Data; in this case block numerical data on the current measurements is provided. The presence of contamination arising from a fingerprint on a clean aluminium surface is shown in Table 1. The scan area is 15 x 12mm and the scan step 0.15mm. The lowest OSEE signal values coincide with the area of maximum pressure and therefore contamination level.

TABLE 1

Numerical printout for a fingerprint on clean aluminium

2999	2999	2999	2999	2999	2805	2999	2999
2999	2999	2999	2587	2237	2117	2810	2999
2999	2999	2328	2122	1961	1931	2299	2999
2999	2999	1986	1901	1827	1862	2694	2999
2999	2156	1755	1710	1693	1811	2784	2999
2999	2230	1667	1649	1653	1834	2784	2999
2999	2460	2056	2188	1653	2522	2810	2999
2999	2999	2350	2463	2410	2622	2999	2999
2999	2999	2999	2999	2999	2999	2999	2999
2999	2999	2999	2999	2999	2999	2999	2999

(b) Graphic Data: Figure 3 is an example of a three-d print-out which shows a scan of a heavily fingermarked aluminium surface, the scan area is 150 x 120mm and the scan step 1.5mm. The area of contamination by the fingers shows as a series of apparent depressions reflecting the lower OSEE signal values from the contaminated areas.

(c) Normalised Graphic Data: In this case the OSEE signal data from original uncontaminated surface is subtracted from that of the contaminated surface, point by point, before printing. Figure 4 shows the data from the same panel as Figure 3 but treated in this manner. The effect is to show the contamination as a series of raised areas more closely representative of the actual situation.

This latter approach to data record requires data for a clean substrate to be obtained at the same scan interval and gain setting before contamination, and is therefore not universally possible. Methods (b) and (c) are the most useful allowing the contaminated areas to be located and accurately pin-pointed. The choice between (b) and (c) must be a personal one and the present authors have different preferences.

DISPLAY OPTIONS FOR GRAPHICS

Graphic data can be displayed and printed in several forms. The elevation angle i.e. the angle of tilt from the horizontal can be changed over the range 0-90°, the quadrant, i.e. the side of the three dimensional graph viewed, can be selected and the vertical height can be enhanced. A zoom option is also available for selecting and magnifying small areas.

The visual effect of changing the quadrant viewed is shown in Figures 5 and 6 which show Quadrants 1 and 4 of a heavily contaminated chromic acid etched aluminium panel, the data is normalised.

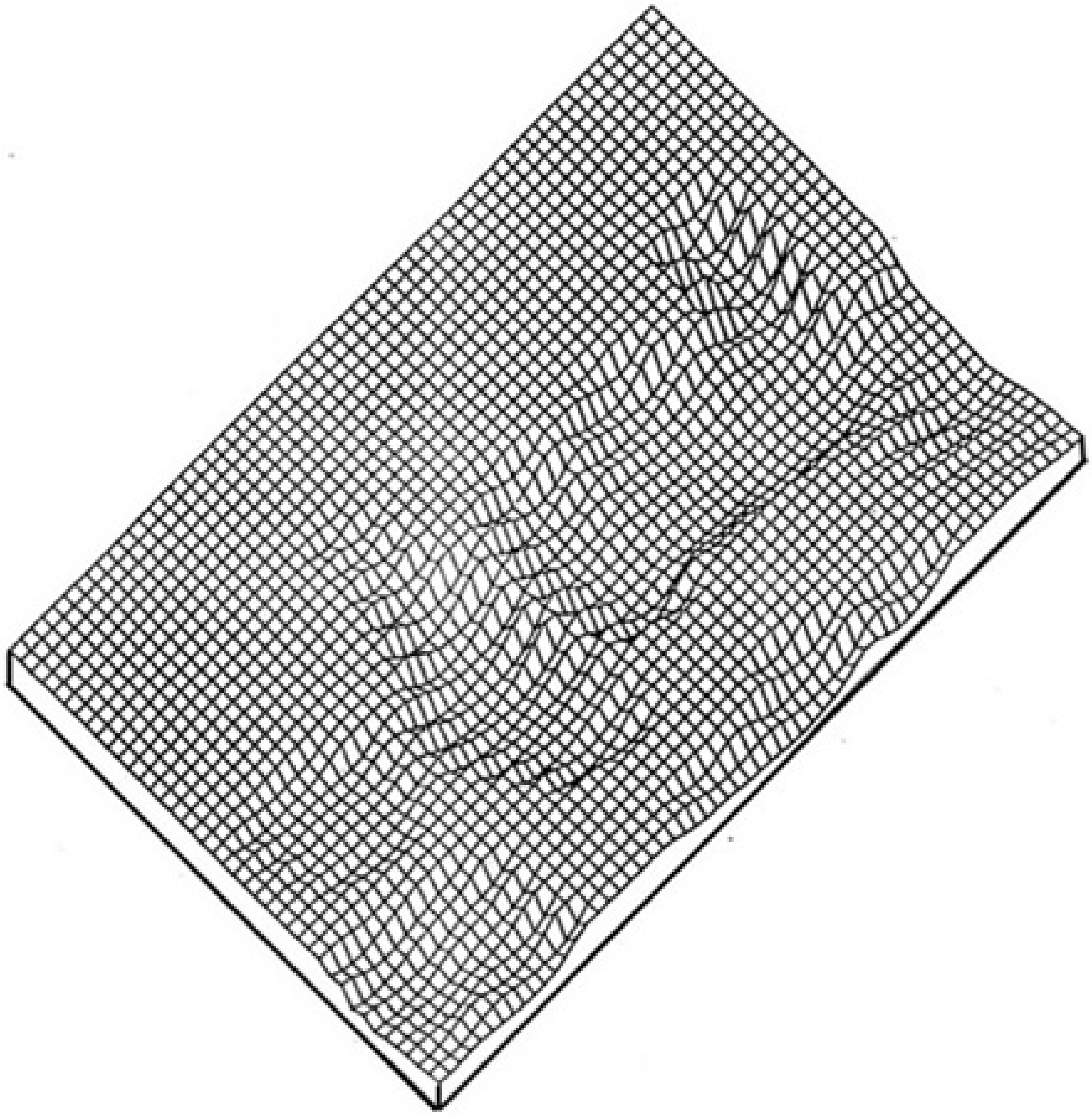

Figure 3. 3D Print-out of a heavily fingerprinted surface.

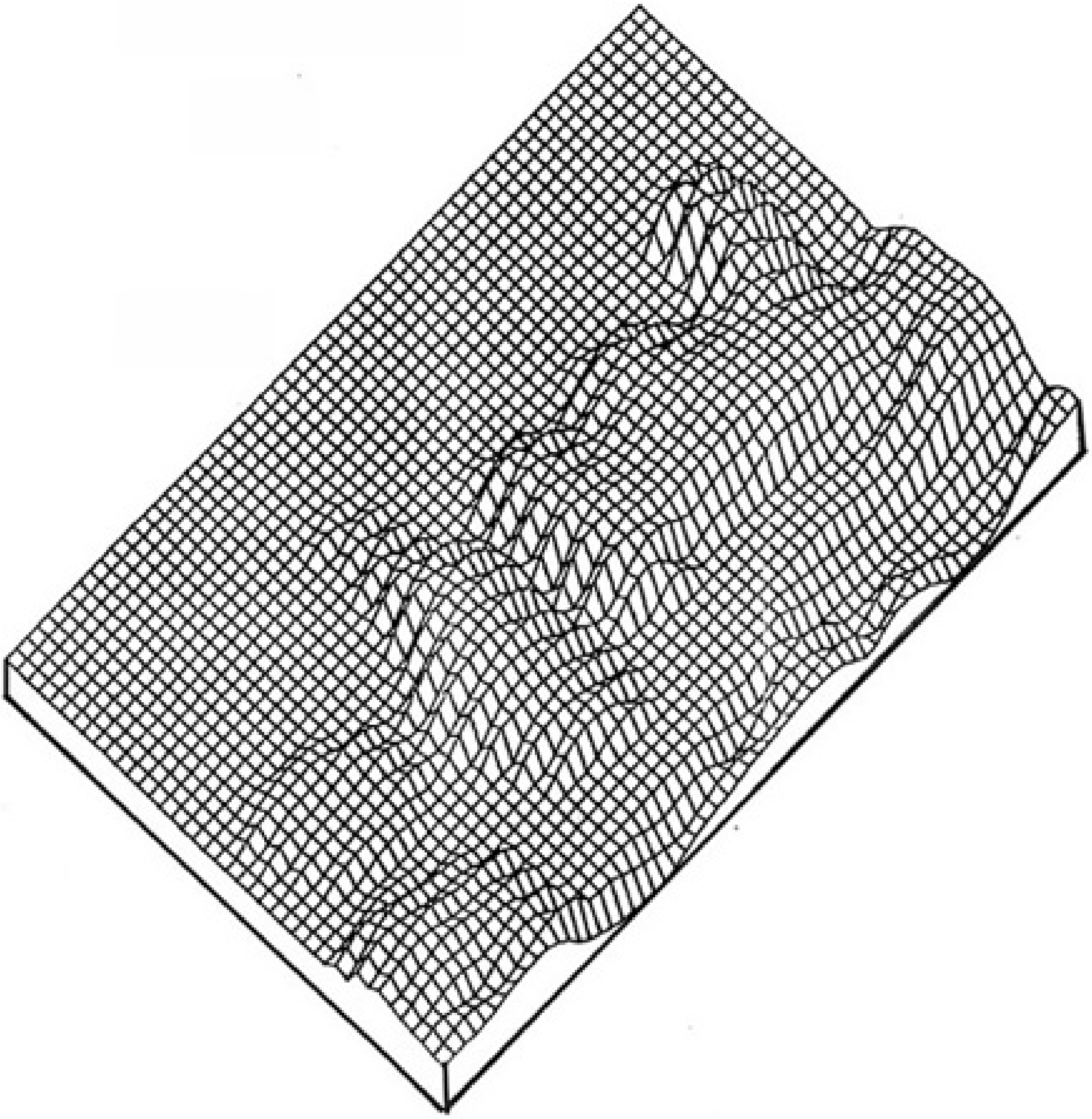

Figure 4. Normalised graphic print-out of a heavily fingerprinted surface.

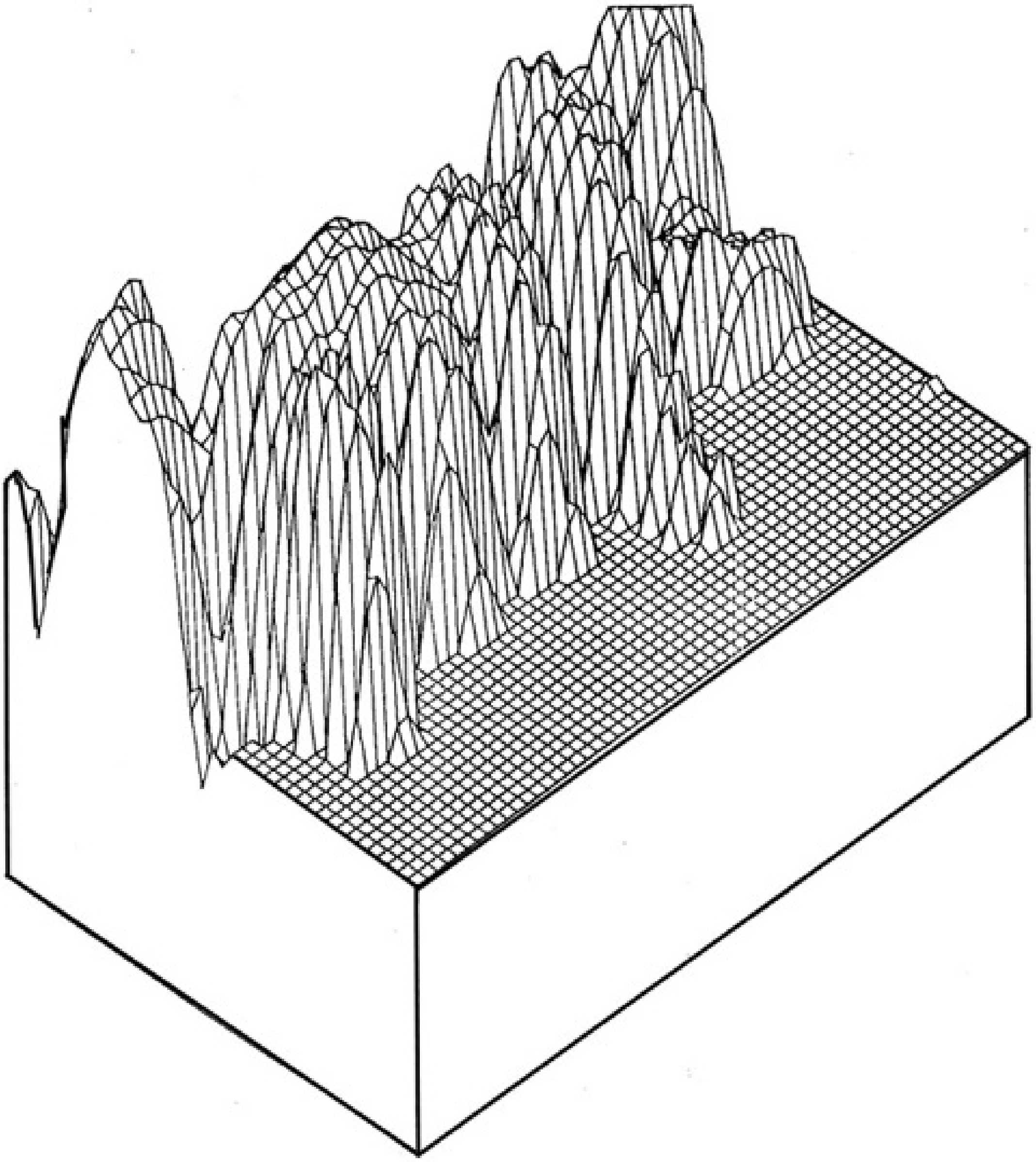

Figure 5. Quadrant 1 normalised print-out

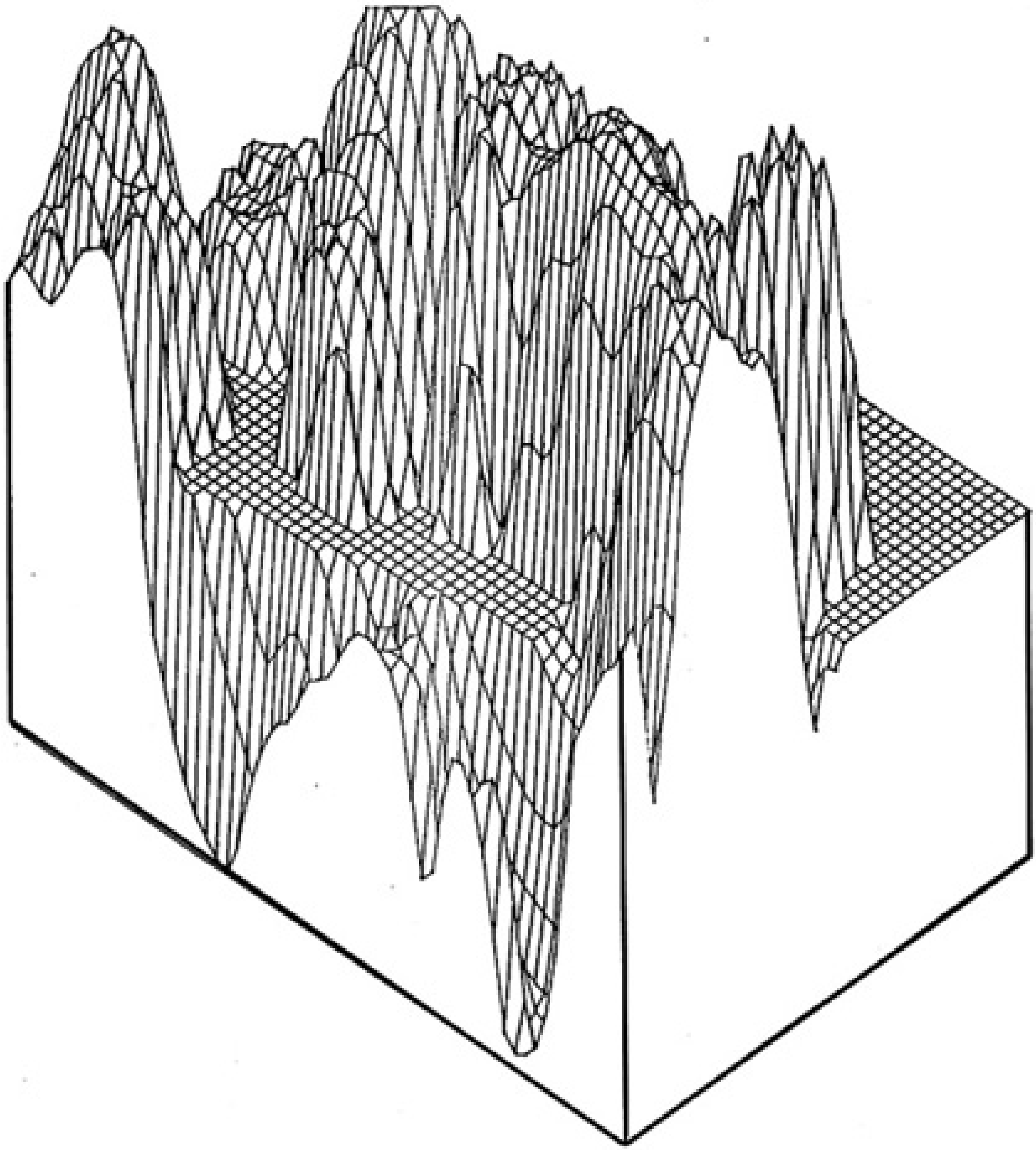

Figure 6. Quadrant 4 normalised print-out.

Surface Investigated by OSEE

Sensor response depends on the photoelectron work function of the material relative to the maximum usable UV energy reaching the surface. If a material has a work function less than 5 eV it should produce a measurable photocurrent [3]. Surfaces investigated by other workers are shown in Table 2.

TABLE 2

Surfaces investigated by OSEE

Emitting Surfaces	
Most Metals	[3,4]
Semiconductors	[5]
Graphite/Epoxy Composites	[3,4]
Glass/Epoxy Composites	[3]
Some Epoxide Paints	[4,5]
Some Polyurethane Paints	[5]
Magnetic Discs	[2]
Pencil Marks (Red)	[2]
Photo Resists	[4]
Nickel Oxide	[6]

Non-emitting Surfaces	
Poly tetrafluorethylene	[3]
Nickel	[6]
Glass	[3,5]
Magnesium Fluoride	[3]
Aluminium Oxide	[3,4,5]
Copper Oxide	[4]
Hydrocarbon Greases	[2,5]
Silicones	[2,3,4,5]
Fingerprints	[3]
Chromate Coatings	[3]
Silicon Dioxide	[2,4]
Ceramics	[5]
Photoresists	[2]
Contact Adhesives	[4]
Adhesive Residues	[4]
Cellulosic Paints	[5]
Polyethylene	[5]

Uses of OSEE

The PATSCAN equipment may be used for a wide range of purposes including:

- Inspection:
    - efficiency of cleaning processes
    - presence of contamination
    - uniformity and quality control of anodic and chromate films
    - detection of flaws.

- Research:
    - detection of contamination
    - identifying suitable solvents for cleaning
    - correlation of bond strength with cleanliness of surface
    - identification of sites of failure

Practical Investigations Using OSEE

Detection of Contaminants

Figure 7 shows the graphic data (not normalised for a carbon fibre reinforced plastic composite deliberately contaminated with silicone fluid, hydraulic oil and orange juice. The area scanned is approximately 120 x 20mm and the scan step 2.0mm, the position and extent of each of the three contaminants can be seen clearly. The maximum and minimum OSEE signal values were 1646 and 995.

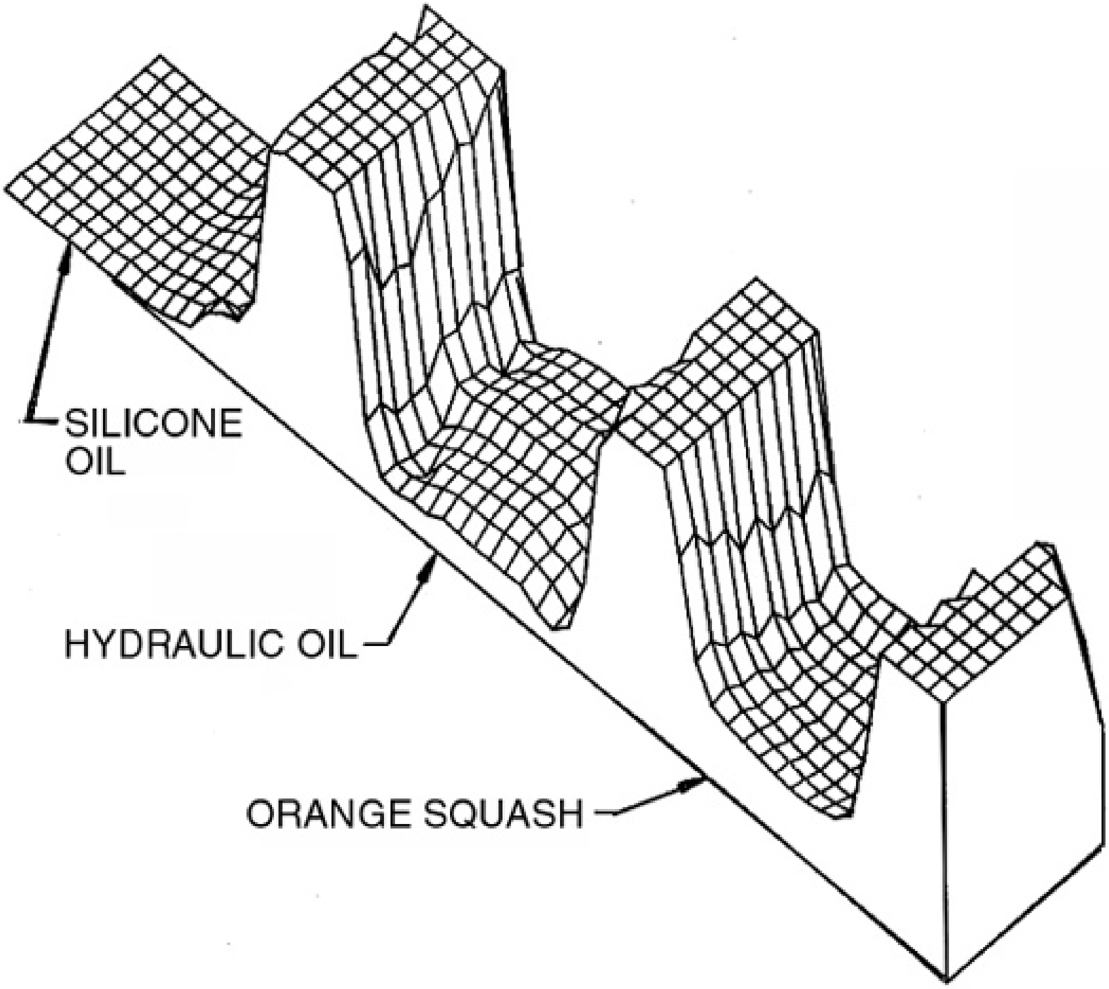

Figure 7. Non-normalised print-out of a contaminated CFRP surface.

The graphic data for an abraded degreased panel deliberately contaminated with silicone grease and a PTFE spray is shown in Figure 8. Once again the data is not normalised and the scan area is 90 x 60mm and the scan step 1.5mm. Four distinct areas can be identified, the PTFE sprayed area on the extreme left of the panel, on immediately adjacent area showing a decreasing contamination level, a silicone grease contaminated area and the clean panel on the right: The interesting feature here is that the silicone contaminated area shows a sharp demarcation between the contaminated and non-contaminated areas, the PTFE spray does not. This indicates the dangers attendant on the use of release agents applied by spray as they may contaminate large areas. The maximum and minimum OSEE signals were 1726 and 1499.

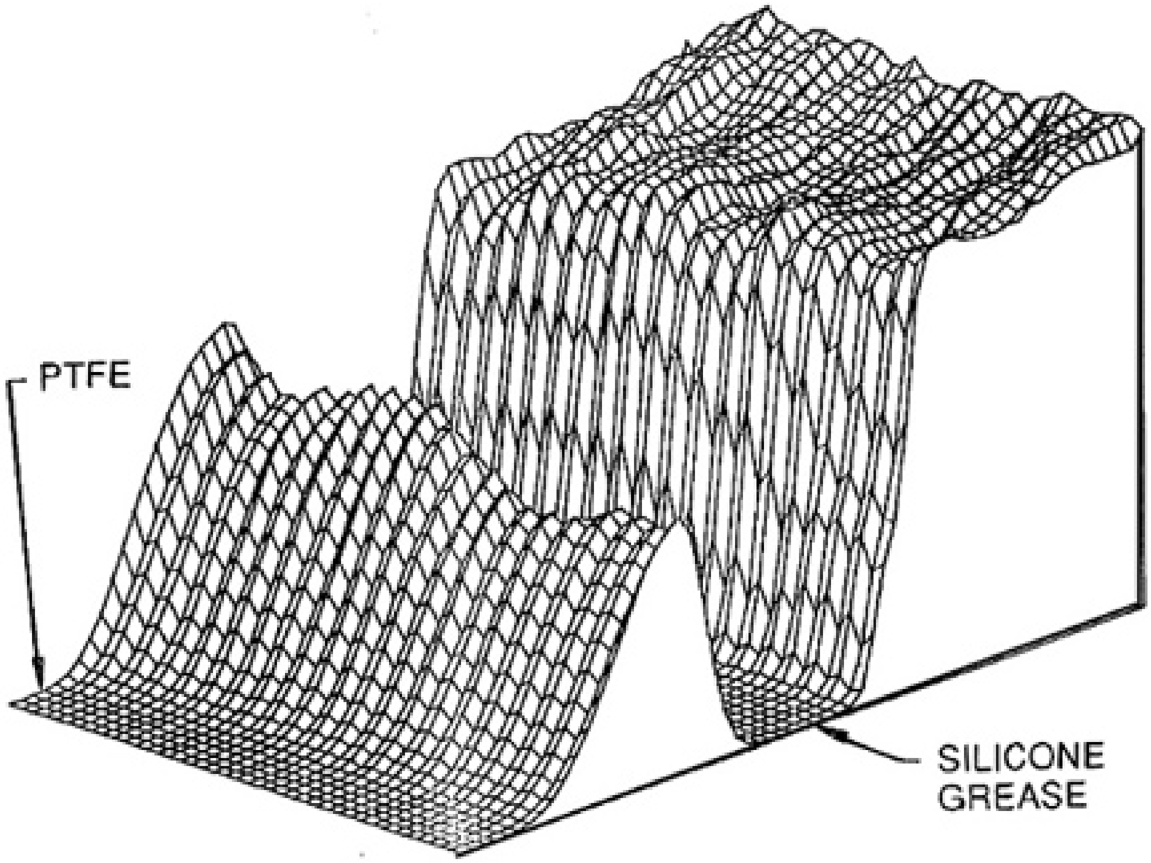
PTFE
SILICONE GREASE

Figure 8. Non-normalised printout of a contaminated aluminium surface.

Figure 9 shows normalised graphic data for a clean aluminium panel deliberately contaminated with stripes of a mould release agent Releasil 7 and molybdium disulphide. The scan area is 90 x 60mm and the scan step 1.5mm, and the maximum and minimum OSEE signals 1492 and 905 respectively. Both contaminants were applied by finger and the graphics indicate that the $Mo\ S_2$ was in the form of a uniform thickness non-spreading layer, the Releasil 7 showed signs of spreading and non-uniform film thickness.

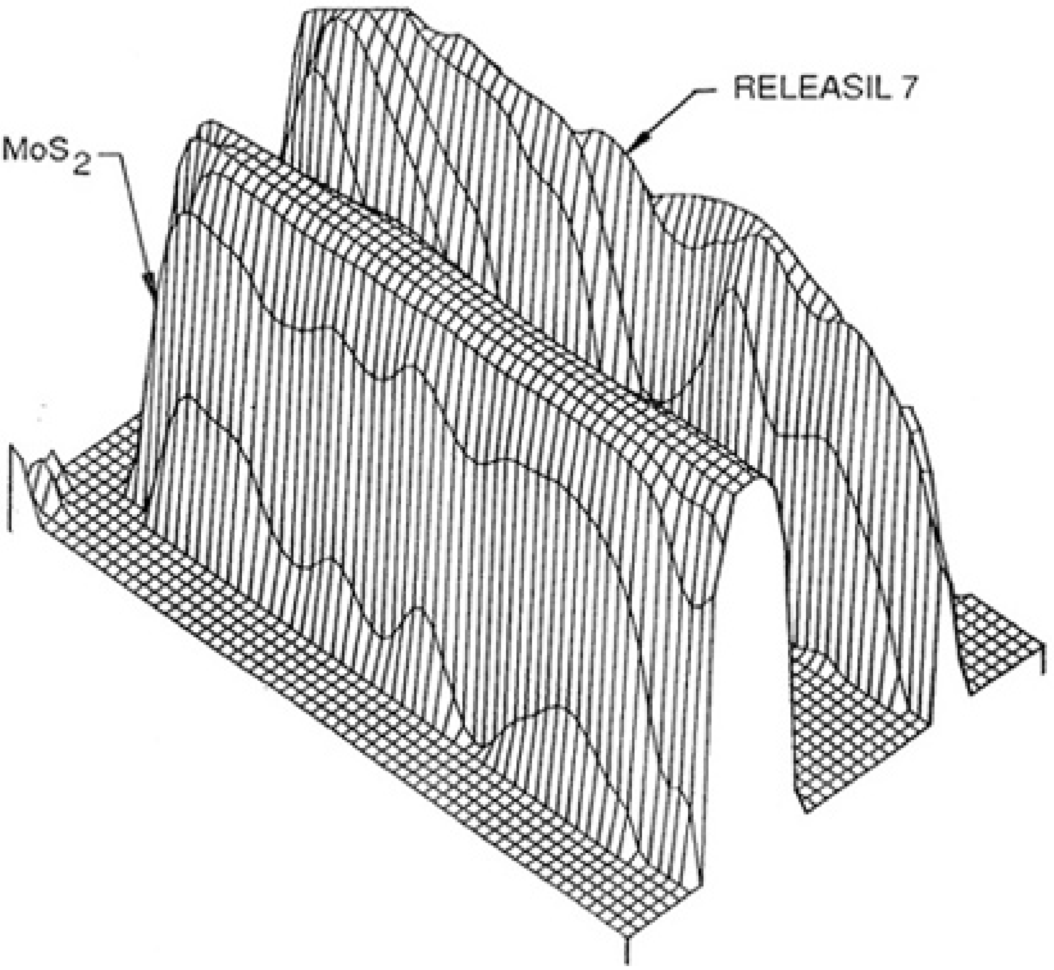

Figure 9. Normalised print-out of an MoS_2 and Releasil contaminated panel.

Efficiency of Solvent Cleaning.

Figure 10 shows the non-normalised graphic data for a clean abraded aluminium panel which has been contaminated with a silicone coil and subsequently solvent cleaned. Five distinct areas can be identified. On the extreme left the clean surface can be seen with a slight trace of contaminant in the center, the area of contamination marked “oil”, followed by 1 and 2 wipes and finally spray; the solvent used was acetone. It can be seen that it is not until the panel has been given three successive solvent treatments that most of the contaminating silicone oil has been removed.

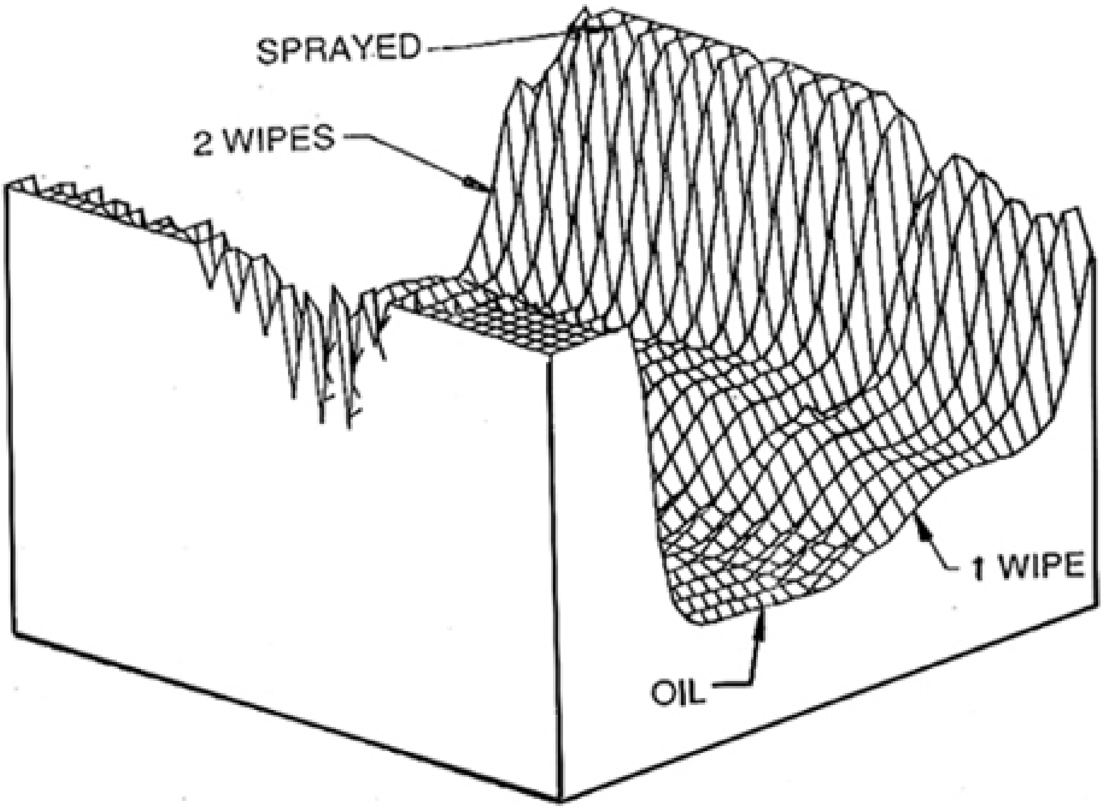

Figure 10. Effect of solvent cleaning on the OSEE output from a silicone oil contaminated panel.

The efficiency of solvent cleaning processes using toluene for the removal of hydrocarbon oil contamination from a mild steel panel is shown in Table 3. The separate panels were given the accumulative treatments shown, thus panel 2 was given one solvent wipe and panel 6 given the treatments for 2-5 inclusive plus vapour degrease. The OSEE signal output increased with increasing level of cleaning and the bond strength of a two pack epoxide adhesive as determined by the torque shear method, [7] also increased with improved cleaning.

TABLE 3
Effect of solvent cleaning on OSEE signal and bond strength

Cleaning Process		OSEE Signal		Bond Strength
		Minimum	Maximum	MPa
As received	(1)	1512	1521	Zero
1 Solvent Wipe	(2)	1511	1575	8.7
2 Solvent Wipes	(3)	1557	1637	12.9
3 Solvent Wipes	(4)	1584	1704	16.8
Solvent Spray	(5)	1676	1758	19.3
Vapour Degrease/ Solvent Spray	(6)	1696	1924	22.7

The scatter of results was extremely high and it would have been interesting to correlate the local OSEE signal with the measured individual bond strength readings.

Aging Of Prepared Surfaces

Changes in a prepared surface with time may be important when adhesively bonding or coating materials which grow an oxide film or suffer other changes such as migration of low molecular weight species to the surface or collect contamination by static attraction. The change in the OSEE signal of an abraded aluminium panel with time is shown in Figure 11, where the OSEE output is plotted against time of exposure, the maximum and minimum outputs are shown.

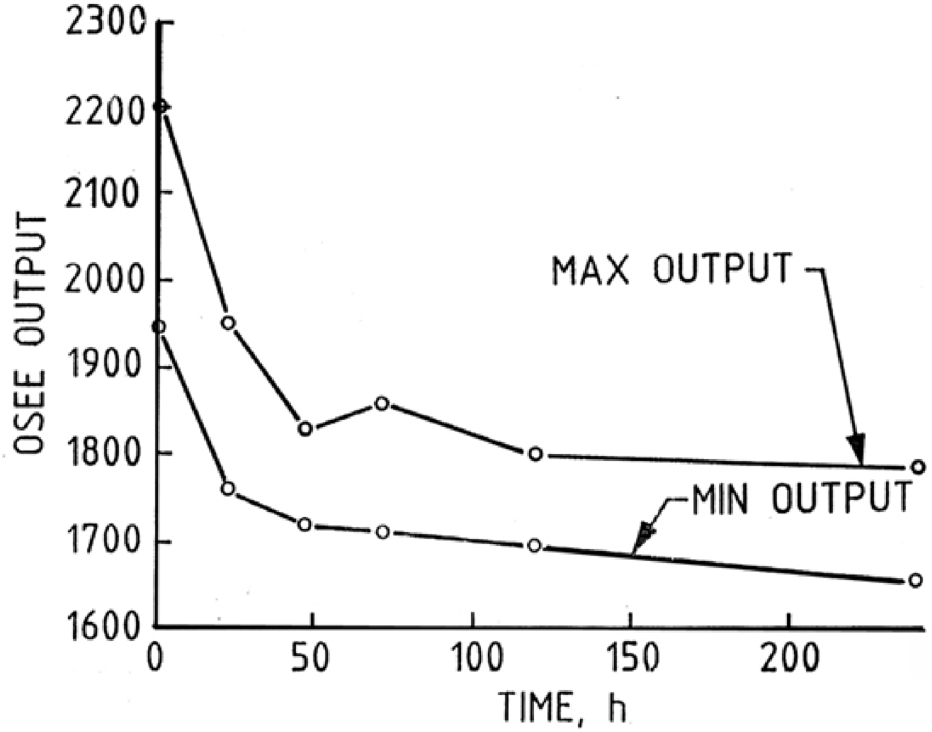

Figure 11. Effect of ageing on the OSEE output from an abraded aluminium panel.

The OSEE signal diminishes rapidly over the first twenty-four hours as the thickness of the non-emitting oxide film increases. There is little further change in output after fifty hours ageing.

Detection of Scratches

The graphic data for a scratched aluminium panel is shown in Figure 12 where the scratches have penetrated through the non-emitting surface oxide layer resulting in an enhanced OSEE signal ouput from the scratches. The scan area is 90 x 60mm and the scan step 1.5mm.

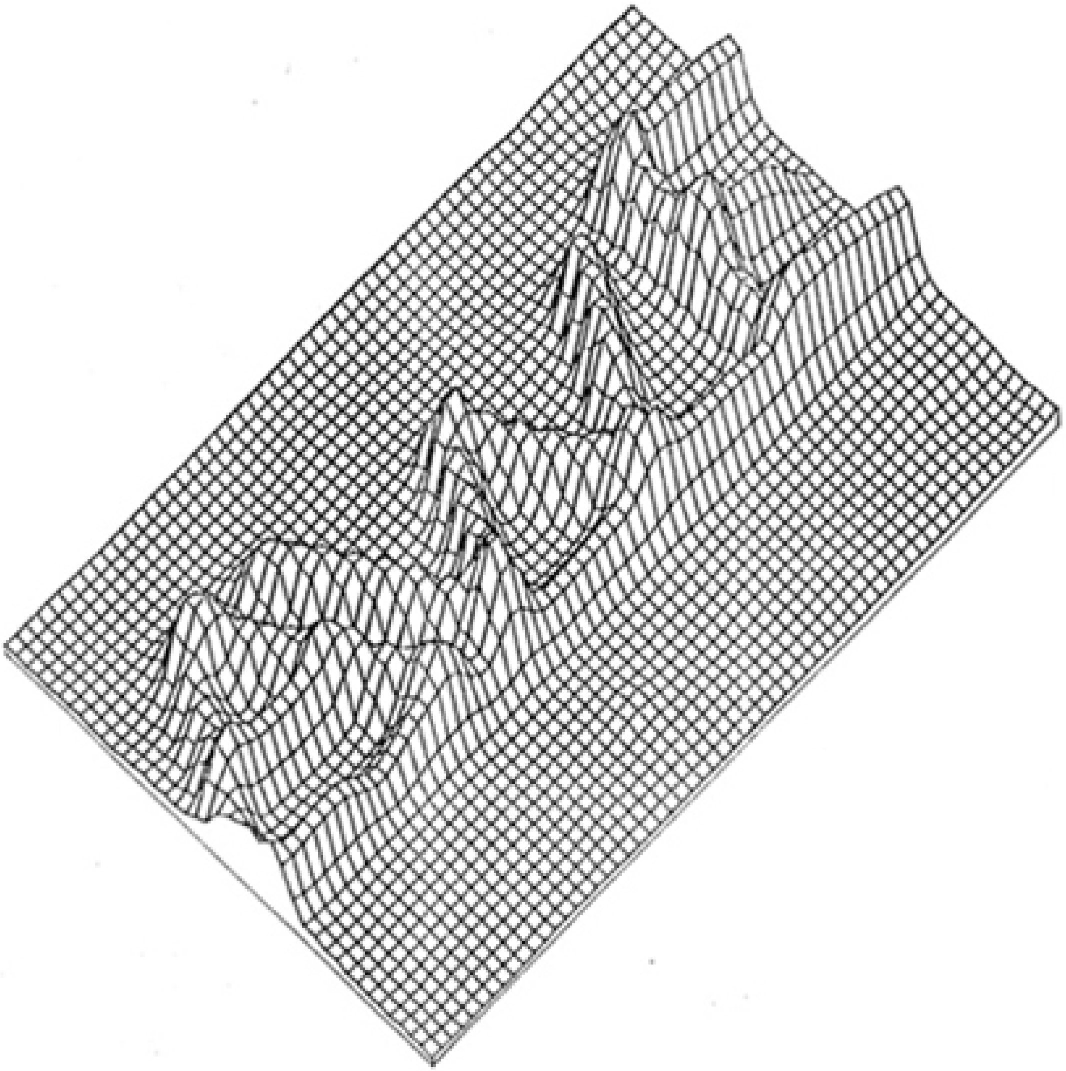

Figure 12. Detection of scratches.

CONCLUSIONS

It has been demonstrated that OSEE is a useful tool for the detection of contamination on substrates prior to bonding, with the capability of being able to scan the entire area, OSEE also provides information on the distribution of contaminants over the surface and is capable of producing both graphic and numerical data. The technique has shown that solvent cleaning processes can be inefficient resulting in a distribution of contamination over an area rather than its complete removal. The method should provide a useful tool in the solution of problems involving contamination of substrate.

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