Alternative surface modification processes in metal finishing and electronic manufacturing industries

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Title - Alternative surface modification processes in the metal finishing and electronic manufacturing industries. A review of the literature

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Biography

Andy graduated from Portsmouth Polytechnic in 1986 and shortly after he joined British Aerospace working in their PCB facility. In 1989 he moved to Shipley Europe (now Rohm and Haas Electronic Materials) where he developed electroless and electroplating processes publishing several papers and patents along the way. In 2002 Andy completed a PhD at Loughborough University and in 2006 he joined the Coventry University Sonochemistry Centre and is now Head of Materials Processing. Andy is a Chartered Chemist, a Member of the Royal Society of Chemistry, a Member of the Institute of Metal Finishing and a Member of the Institute of Circuit Technology.

Abstract

The metallization of non-conductive materials is an important manufacturing process which is utilized throughout the metal finishing and electronics industry. One of the most critical stages in the metallization process is the surface modification of the non-conductive substrate as this will often determine the subsequent adhesion. This paper reviews the traditional wet chemical surface modification processes employed in metal finishing and electronic manufacturing and reveals that many of these are characterised by the use of hazardous chemistry. With environmental and health and safety legislation becoming stricter ‘greener and cleaner’ processes are becoming more desirable and this review will show that over the past 30-40 years several alternative approaches to surface modification have been investigated. Few of these processes have been commercialised but, with legislative pressures building, it is now perhaps time to revisit some of these less conventional techniques.

Key words

Surface, modification, electroless, electroplating, PCB, ultrasound

Introduction

The metallisation of non-conductive materials by electroless plating has had an enormous number of applications for at least the last 40 years. It has enabled the properties of a plastic/polymer (cost, mouldability, dielectric, weight etc) to be combined with those of a metal (conductivity, aesthetic appearance, strength etc). For this reason it has become an important process in the automotive, aerospace and electronics industries as well as in the domestic market. Indeed, with the advent of plastic/printed electronics this demand is likely to grow still further as any material that can be printed could become an electronic circuit whilst the metallisation of glass and ceramics is important for the manufacture of the next generation of displays and photo-electric cells.

For the plating of any non-conductive material to be effective it is critical that there is good adhesion between the substrate and the coating and this has traditionally been achieved by surface modifying the surface of the material. In this stage of the metalisation process the surface of the material might be significantly altered and become roughened or textured to form a mechanical bond between the substrate and the subsequent coating. Alternatively (or concurrently), the treatment might alter the surface chemistry of the material allowing for a chemical bond to be formed with the deposited metal.

This paper will briefly review some of the traditional surface modification processes employed in the metal finishing and electronics industry. However, it will mainly concentrate on alternative surface modification processes with particular attention to those developed as a pre-treatment to electroless plating.

Traditional Surface Modification Processes

The Metal Finishing Industry

One of the most commonly utilized plastics in the metal finishing industry is acrylonitrile-butadiene-styrene (ABS) and the use of chromic acid either on its own or, more usually, dissolved in sulphuric acid, is probably the most commonly employed etch for this material although early solutions also sometimes contained phosphoric acid[1]. Formulations range from 25-585 g/l Chromium (VI) oxide in 70-20 % by volume sulphuric acid[2] or up to 900 g l^{-1} Chromium (VI) oxide in water[3] although elevated temperatures are necessary to obtain high chromium concentrations. Many studies[2,3,4,5,6] have shown that when this material is placed in the chromic acid bath the butadiene particles in the polymer matrix are oxidized leaving a pitted morphology. The subsequent coating then becomes anchored in these pits providing a mechanical/physical bond[4,2] although some workers suggest chemical bonding is also important[5]. It is now typical to use a solvent prior to chromic acid etching[7] which swells the resin and produces a more uniform morphology. The final stage in chromic acid etching of ABS is the neutralisation of hexavalent chrome residues which must be removed to avoid poisoning of the subsequent electroless plating line. Solutions of reducing agents such as hydrazine or sodium bisulphite have been employed for this task[1].

There have been some studies into the use of chrome-free etching formulations. For example Teixeira et al[8] investigated some based around sulphuric or nitric acid with hydrogen peroxide. However they found that the ABS panels had to be brushed prior to processing to obtain acceptable adhesion.

The Electronics Industry

The advent of double and multi-layer printed circuit boards produced a requirement to make connections between the circuit on one side of the board to those in other layers[9]. Holes are therefore drilled in the boards, but the walls of these 'through holes' are composed of the di-electric laminate and have to be made conductive to enable the circuits to be connected and for this reason they are commonly electroless copper plated. The surface modification techniques used in printed circuit board (PCB) manufacture have a dual purpose. Not only must they texture the hole wall laminate to enable good adhesion between the substrate and the electroless copper but also the process must 'desmear' the drilled hole. During the drilling of through holes in a circuit board the drill bit becomes very hot[10] and may exceed the glass transition temperature (Tg) of the laminate material. In this way epoxy is transferred to the drill bit and is 'smeared' on to subsequently drilled hole walls. This is particularly problematic when drilling multi-layer boards (MLBs) as the epoxy can be smeared across the inner-layers of these boards inhibiting electrical connection. It is therefore important that the surface modification process not only textures the epoxy laminate but also removes any smeared epoxy from the inner-layers.

One of the early methods of desmearing PCBs was by immersing the board in concentrated sulphuric acid[10,11,12]. This was clearly an extremely hazardous procedure, difficult to control and produced a 'glassy' morphology to the hole walls which made electroless copper adhesion problematic[11, 12]. Chromic acid was also used[10] (up to 1000 g l^{-1}) but, although quite effective, the main issue in this case was the difficulty in removing all traces of hexavalent chrome from the very porous texture produced[11]. In the early 1980's most of the PCB industry converted to using 'swell and etch' desmear processes[11,12]. In these techniques the boards are first immersed in a hot, alkaline solution containing one or more solvents[13] and this leads to the 'swelling' of the resin. After rinsing the boards are then placed in a hot, alkaline permanganate solution which 'etches' the laminate removing any smeared epoxy and leaves the laminate with a honeycomb type texture[11]. The final step of the process is neutralisation which removes any manganese residues[14] from the hole walls. It is claimed that these 'swell and etch' processes cause significant reductions in PCB through hole defects such as hole wall pull away, blistering and blow holes whilst dramatically improving the peel strength of the electroplated deposit (Figure 1). In recent years there has been a move to high Tg laminates[15] which are more chemically inert and this has required the use of more aggressive desmear conditions e.g. more aggressive and concentrated solvents.

Polyetherimide type plastics have been commonly utilized for the manufacture of Moulded Interconnect Devices (MIDs) and although concentrated sulphuric acid has been used for the surface modification of these materials[16], swell and etch processes similar to those for desmearing have tended to predominate[17,18] and this is also true with respect to the photo-imageable dielectrics employed for sequential build-up (SBU)[19]. PTFE, Polyimide and Liquid Crystal Polymers (LCPs) are all materials

which have useful properties for the electronics industry. PTFE is an extremely difficult substrate to surface modify and methods using tetrahydrofuran (THF) and naphthalene species[20] are disclosed. It has also been problematic to obtain good adhesion on Polyimide materials and the use of strongly alkaline treatments[21, 22] is normally required to bring about ring opening of the polymer and make it hydrophilic whilst sulphuric and chromic acid methods are reported for LCPs[23]. Poly(ethylene terephthalate) (PET) is another polymer utilized in electronic manufacture and was etched using a nitric acid/ permanganate solution by Domenech et al[24] whilst Gan et al[25] employed a sulphuric acid / permanganate formulation on the same material.

Finally, dielectric ceramics and glass are finding uses in a range of electronic devices e.g. optical circuits and waveguides. These materials are also chemically inert and therefore wet surface modification methods tend to use fluorinated acids e.g. a mixture of tetrafluoroboric acid and nitric acid[26] or potassium dichromate, sulphuric acid and hydrofluoric acid[27] both formulations being developed for the surface modification of lead zirconium titanate.

These wet chemical surface modification techniques have tended to predominate in both the metal finishing and electronics industries due to the fact that they can be easily fitted into the pre-treatment line before electroless plating and for reasons of cost. However, it can be seen that they tend to be characterised by the use of hazardous chemistry, high temperatures (and therefore, high energy costs), long immersion times and the need for copious rinsing (high water usage). When these processes were developed in the 1960's and 70's legislation was not as rigorous whilst energy costs were relatively low. Despite the fact that much research has been performed on alternative surface modification techniques over the last 30 years few have been adopted by the industry. However, in today's climate of more stringent environmental and health and safety legislation and the demand for the carbon footprint of production processes to be reduced, there is perhaps a need to re-evaluate some of this work.

Alternative Surface Modification Techniques

Plasma

Plasma surface modification techniques tend to be quite aggressive and are very efficient at removing significant amounts of material in a relatively short time (e.g. 2 minutes on ABS[28], Figure 2) compared to traditional techniques and, with the correct morphology, good adhesion can also be obtained. They tend therefore to be more frequently employed to surface modify inert materials such as Polyimide[29,30], LCPs[31], PET[32], Polyvinylidene fluoride (PVDF)[33, 34]etc.

Plasma treatment will not only roughen the polymer substrate [29,31,32,33] but, depending on the atmosphere used (argon, oxygen, ammonia, nitrogen etc), can introduce functional groups to the surface of the material[29,31,32,33]. This will affect the wettability of the surface[31] (Figure 3) and subsequent catalysation prior to electroless processes [29,32,34,35] since palladium and tin have strong affinities for nitrogenated and oxygenated surfaces respectively, and these are the main components of electroless catalyst formulations. Improved adhesion is generally achieved when plasmas are

utilized which contain nitrogen species [29,31,32] by a combination of chemical and mechanical affects.

Some desmearing of PCB's has been performed by plasma techniques for a number of years but when used with conventional FR4 type laminates it is claimed[11,12] that they leave behind an 'ash' which must be removed and, depending on the nature of the plasma, may also introduce fluorinated species onto the surface which can make subsequent electroless plating problematic. However Lee et al[36] showed that FR4 holes drilled conventionally and with a laser could be effectively desmeared using an air mesh plasma technique and also demonstrated a large drop in contact angle.

Sonochemistry

When ultrasound is applied to an aqueous solution a process known as acoustic cavitation occurs[37] and this phenomenon brings about a number of affects which have been utilized for surface modification. For example, microjetting (due to bubble collapse at or near a solid surface, Figure 4) can mechanically erode a surface whilst efficiently transporting reactants to and products (and debris) away from the substrate. In addition, acoustic cavitation can generate extremely localised high temperatures and pressures which can alter the chemistry of the surface of the polymer as well as generating radical species which can bring about oxidation of the material.

It has been reported that ultrasound can surface modify materials such as ABS[38], PVC[39], polyethylene[40, 41] as well as piezoelectrics such as lead zirconium titanate[42]. Zhao et al[38] used an ultrasonic horn in water and found that the adhesion of electroplated copper to ABS was always better compared to equivalent chromic acid etching times whilst weight loss and roughness (Figure 5) were higher when treatment times of more than 30 minutes were used. XPS measurements also indicated a chemical change to the surface and these workers found similar results with PVC[39]. However, ultrasound can also be used in conjunction with wet chemical treatments e.g. persulphates[40] and other mild oxidizing agents[41] where it has been shown that under sonication polyethylene materials can be surface modified and become more hydrophilic as determined by contact angle. More aggressive formulations were employed (e.g. tetrafluoroboric acid / nitric acid) to etch lead zirconium titanate[42] and the application of ultrasound produced a linear increase in weight loss.

Kathirgamanathan[43] demonstrated that no chemical pre-treatement was required if ultrasound was applied during the electroless plating of polyethylene microporous membranes, adequate adhesion apparently being obtained.

The PCB industry has used ultrasonics to enhance the desmear process for many years and it is particularly useful in horizontal equipment[44] where it has been shown to improve the topography, debris removal and the adhesion of subsequent metallisation in through holes.

Photocatalysis

In the photocatalytic process titanium dioxide particles are dispersed in an aqueous solution. They are then irradiated with UV light of an appropriate wavelength which causes the generation of radicals (e.g. hydroxyl, perhydroxyl etc) on the surface of the

particles. These, and other oxidative species, then attack the surface of the substrate and surface modify it. This technique was used as a pre-treatment before electroless copper plating for ABS[45] and on glass epoxy resin[46]. Despite the fact that the treatment caused the amount of active oxygen on the surface of both materials to increase and, on the epoxy, a significant drop in contact angle occurred (Figure 6), adhesion was typically slightly less than when a traditional chemical surface modification process was employed. Bessho et al[47] showed that by optimising the titanium dioxide concentration and UV light intensity, very low contact angles could be achieved on a SBU substrate. Using these optimised conditions they surface modified the material and produced adhesion equivalent to a chemical process although the roughness was much lower. These workers produced similarly promising results on ABS[48].

Electrochemistry

Work by Brewis et al[49, 50] demonstrated a procedure whereby the Ag (II) ion was generated electrochemically from a solution of Ag (I) and nitric acid. The polymer was then immersed in this solution and surface modification occurred due to the highly oxidative nature of Ag (II) and/or by hydroxyl radicals formed by the oxidation of water by this species. It was shown that the amount of active oxygen on the surface of the treated materials increased and that good levels of adhesion could be achieved. It was, however, also demonstrated that good adhesion could be obtained by simply contacting the polymer material with the polarized anode in nitric acid in the absence of silver ions.

Similar work was performed by Graves et al[51] who reported that the morphology obtained after surface modification of ABS by electrochemically generated Ag(II) (after solvent swell) was equivalent to that obtained with a chromic acid etch and they also claimed equivalent adhesion values. In a further development of this process the workers proved that silver ions became trapped within the morphology of the substrate and that if these were reduced to metallic silver, catalysation of subsequent electroless plating could be enabled.

Gaseous Sulphur Trioxide

In this process the substrate is exposed to an atmosphere of sulphur trioxide and air and it has been shown[52] that a microporous texture results on various grades of ABS generating good adhesion (Figure 7) on this and other polymers (polystyrene, polyphenylene etc). Similar findings were reported on ABS by Roubal[53] who also demonstrated the effectiveness of the treatment on PVC materials. Polyimide has also been surface modified using this technique[54] and although treatment in concentrated sulphuric acid produced better adhesion the gaseous method was thought to be more convenient and processing times were significantly lower than the standard potassium hydroxide techniques.

Ozone and UV Ozone

The use of Ozone to surface modify a range of plastics including ABS was disclosed by Jobbins et al[55] as an alternative to chromic acid etching and showed that effective electromagnetic interference (EMI) shielding could be achieved when polymers were

etched and then electroless nickel plated using this technique. A UV/Ozone process[56] was employed to surface modify polyethylene (PE) and polyetheretherketone (PEEK). And the process caused the wettability of both materials to improve whilst increasing the oxygen content on the surface.

Other techniques

Ehrbar et al[57] reports the use of Corona discharge to surface modify a range of commercially available polymers. Although they were able to metallise most of the 22 plastics tested, good adhesion after electroless copper plating could only be obtained on four. PTFE was surface modified by ArF laser in an hydrazine atmosphere[58] and the workers were able to produce a surface with reduced contact angle which could be metallised with electroless copper and nickel to give satisfactory adhesion. The surface of a polycarbonate polymer was mechanically surface modified by blasting the surface with various grades if silicon carbide, boron carbide or aluminium oxide. Although the materials could be roughened and electroless plated after the treatment the results was not as good as chemical etching[59].

Conclusions

It is quite clear from this review that several alternatives to traditional wet chemical surface modification in metal finishing and electronic manufacturing have been investigated. Plasma processes have certainly found a niche when treating very inert materials but is a very expensive alternative for more conventional substrates. It is also not a process which can be readily placed into a wet chemical process sequence (e.g. electroless copper or nickel). This is also true of the laser process described although one could imagine how a corona discharge technique might be incorporated into a horizontal line. Both the sulphur trioxide and ozone methods would be problematic due to the exhaust gases produced.

The traditional wet chemical processes have been successful over the years because they are cheap and can fit easily onto the front end of an electroless process line. However, for them to work effectively they must inevitably contain highly oxidizing species which tend to make them hazardous. Three of the alternative techniques stand out as they can be used in water. The sonochemical processes are a combination of mechanical and chemical attack of the substrate surface whilst the photocatalytic method generates radical species when the solution is irradiated with UV light. In both cases, when the source of energy is turned off (either the ultrasound or UV) the solutions will once again become non-hazardous. This is true to a lesser extent for the UV/Ozone process although the water will become ozonated which could present waste disposal issues. The electrochemical techniques also generate oxidizing species although the chemistry is somewhat more hazardous (nitric acid / silver nitrate). However, once again, the radical species will decay away when the current is turned off and any residual silver (II) can be electrochemically reduced back to silver (I).

Perhaps these latter processes suggest a way forward for surface modification. Instead of using highly oxidizing, hazardous chemistry these techniques indirectly generate transient oxidizing species which, once the material has been treated, will rapidly decay away returning the solution to its benign state.

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Figure 1. Effect of Desmear Type on Peel Strength
Data taken from Deckert et al, Reference 11, Table 3

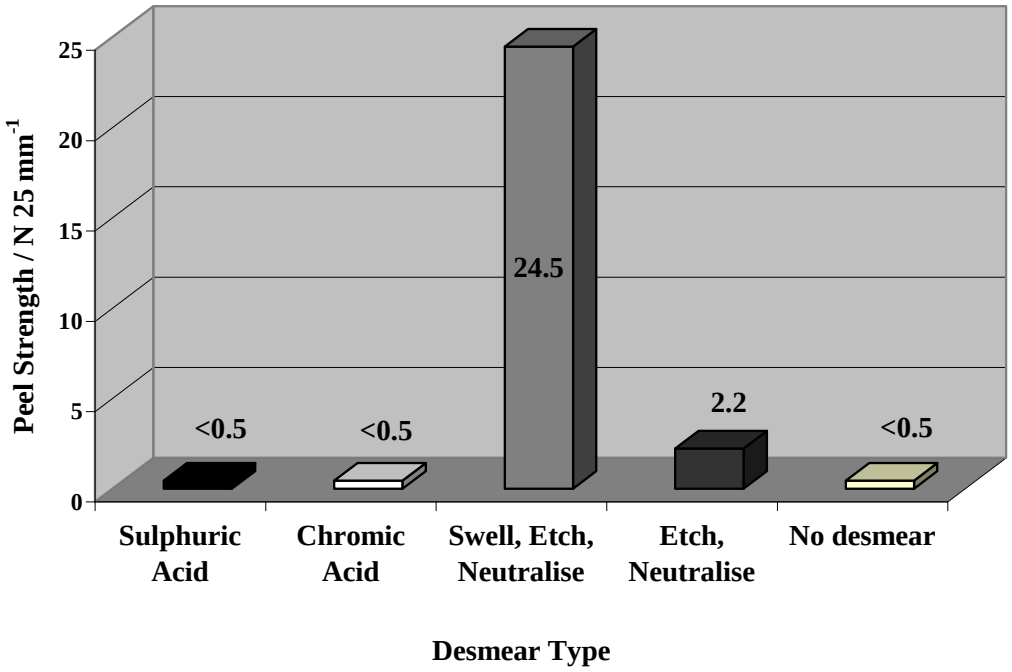

Figure 2. Effect of Etch Time on Weight Loss produced by Oxygen Plasma and Chemical Etching on ABS
After Villamizar et al Reference 28.

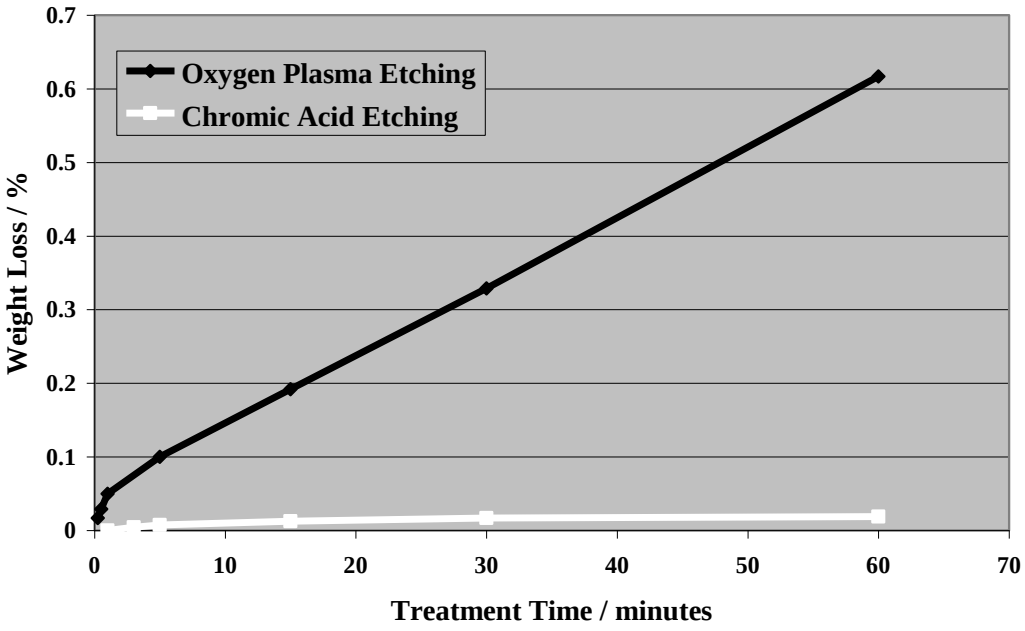

Figure 3. Contact Angle of Water for LCP Films Treated by Nitrogen Plasma with Various rf Powers.
Data taken from Asano et al Reference 31, Table 1.

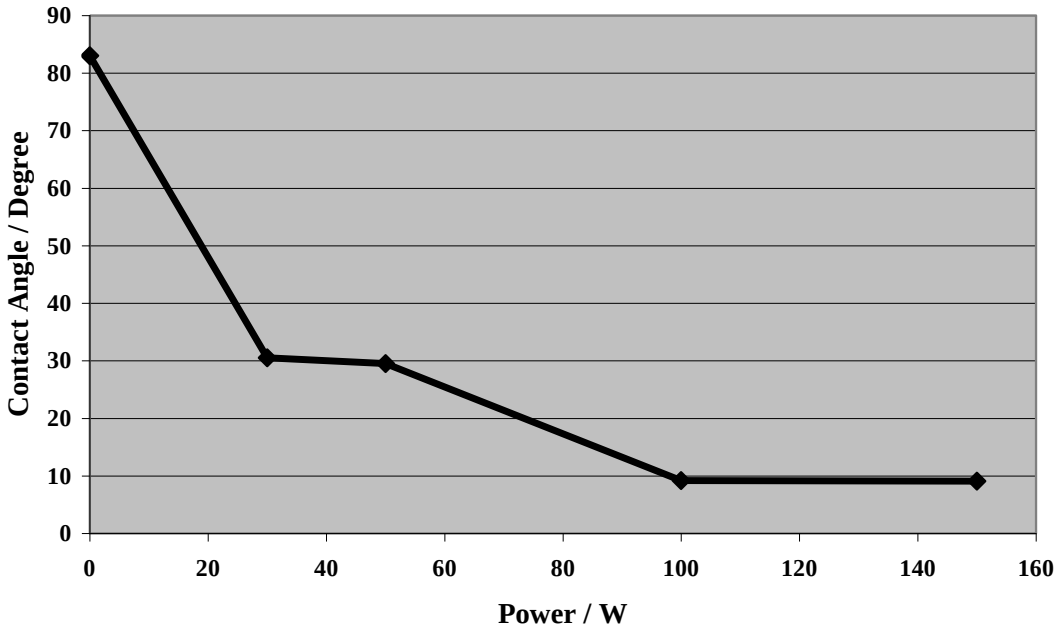

Figure 4. Micojetting at a solid surface.
Prof. Crum, University of Seattle.

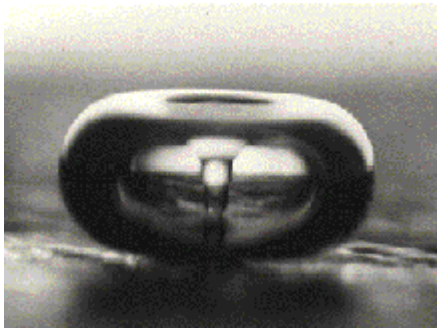

Figure 5. Surface Roughness of ABS versus Etching Time
Data taken from Zhao et al, Reference 38, Table 3.

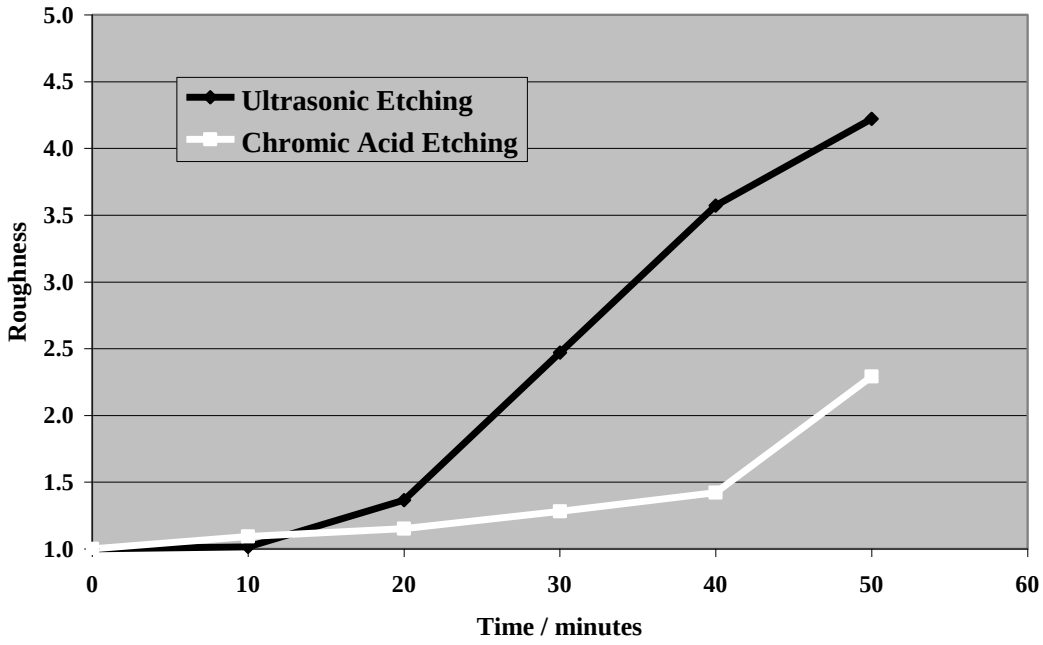

Figure 6. The Change in Contact Angle for Glass Epoxy Resin after the Photocatalytic Reaction in TiO_2 solution.
After Kim et al, Reference 46.

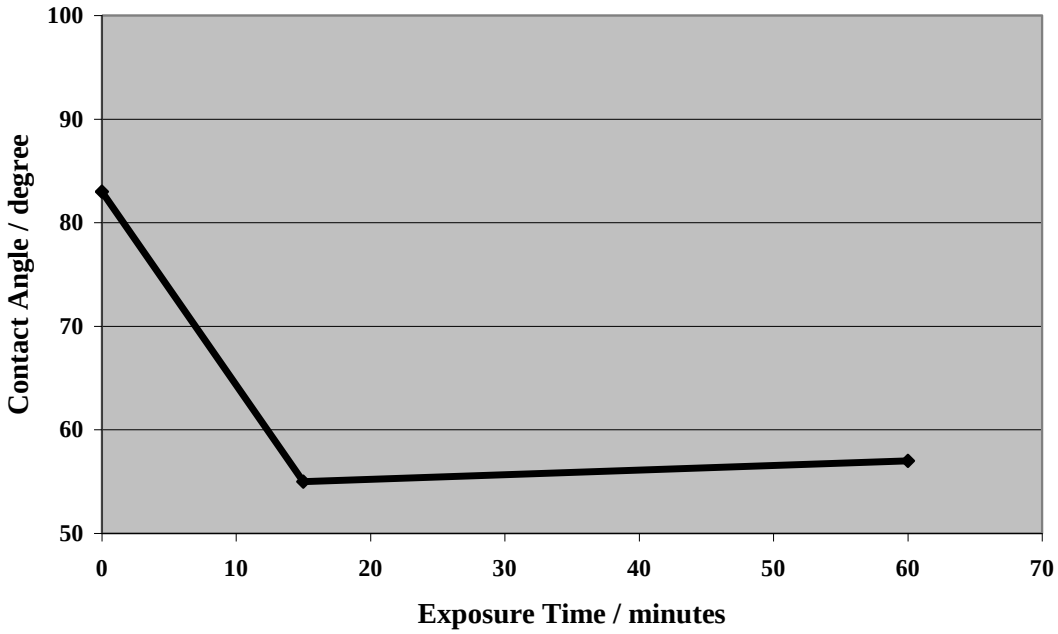

Figure 7. Adhesion of Electrodeposit as a Function of Sulphur Concentration on ABS Surface
Data taken from McCaskie et al Reference 52, Table 1.