

Society for Adhesion and Adhesives

Adhesion and Adhesives

Greener techniques

One-day Symposium 24th April, 2002

**Society of Chemical Industry, Belgrave Square,
London**

This one-day symposium is one of an on going series organised by the Society for Adhesion and Adhesives.

Society for Adhesion and Adhesives Committee

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The next symposium is due to be held at the SCI on Thursday 5th December 2002.

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Programme

- 10.00** **Registration and coffee**
- 10.30** **Environmental issues with adhesives and solvent-reduction strategies**
Stephen G Abbott, SATRA Technology Centre, Kettering, UK
- 11.00** **Adhesives based on polyurethane dispersions for footwear sole bonding**
Wolfgang Amdt and Dr Heinz-Werner Lucas, Bayer AG, Dormagen, Germany.
- 11.30** **Solvent-free adhesives - meeting the environmental challenge**
Andrew N Crabtree, Bostik Findley Ltd, Leicester.
- 12.00** **Discussion**
- 12.15** **Lunch**
- 14.00** **Corona and plasma pretreatments of composite materials,**
B R K Blackman and A J Kinloch, Imperial College
- 14.30** **An evaluation of alternatives to chromic acid anodising,**
G W Critchlow, Loughborough University
- 15.00** **Organosilane based surface treatments for metallic alloys,**
S R Davis, N Porritt, S J Shaw, D A Tod and S Torry, QinetiQ
- 15.30** **Electron Beam Technology - A Tool for the Future?**
Bruce Dance TWI, Cambridge.
- 16.00** **Discussion followed by Tea**

S	Abbott	Satra	S
K W	Allen	Oxford Brookes University	
K B	Armstrong	Consultant	
W	Arndt	Bayer AG	S
R	Barter	Hexcel	
J	Bishopp	Consultant	
B	Blackman	Imperial College	S
M	Bowditch	Consultant	
J G	Broughton	Oxford Brookes University	
J	Comyn	Loughborough	
H A	Cowe	Trenchant	
A	Crabtree	Bostik Findley	S
G	Critchlow	Loughborough	S
R	Dahm	Loughborough	
M E	Fakley	Permabond	
C	Hobman	QinetiQ	
G M	Kavanagh	QinetiQ	
A J	Kinloch	Imperial College	
H	Lawson	Alcatel	
S	Millington	QinetiQ	
T	Mitchell	TWI	S
J	Palmer	Sealocrete	
N	Porritt	QinetiQ	S
S	Shaw	QinetiQ	
Mr	Tan	Imperial; College	
D	Tod	QinetiQ	
P H	Winfield	Oxford Brookes University	
P	Wylie	QinetiQ	

S Speaker

ENVIRONMENTAL ISSUES WITH ADHESIVES AND SOLVENT REDUCTION STRATEGIES

Stephen G Abbott
SATRA TECHNOLOGY CENTRE
Kettering, UK

Health and safety in the workplace

The term 'environment' is usually associated with the world outdoors, but can be considered to include the air in the workplace and in the home.

Apart from specific hazards such as the flammability of solvents and risk of burns with hot melts, adhesives in general tend to produce potentially harmful vapours and may be harmful to skin and eyes. Depending on the quantities used, mechanical extraction of vapours may be necessary; skin and eye contact must be prevented by gloves and goggles wherever risks of contamination or splashing are possible.

Control of environmental pollution

Concerns relating to pollution include:

General contamination of the environment - air, soil, water - by toxic or harmful substances. These include adhesive constituents such as solvents, reactive monomers and curing agents.

Damage to the ozone layer in the upper atmosphere, especially by the chlorofluorocarbons (CFCs) and chlorinated solvents. Ozone layer damage allows an increase in harmful UV radiation from the sun.

The 'greenhouse effect' due to increased atmospheric levels of gases, such as carbon dioxide from combustion of fuels and methane from biological sources. This effect restricts the re-emission of solar radiation and leads to global warming.

Interactions of gases in the atmosphere leading to 'chemical smogs' and 'acid rain'.

Volatile organic compounds (VOCs), such as solvents in adhesives and surface treatments, participate in complex chemical reactions in which light energy converts oxygen in the air to ozone. Although the ozone layer in the upper atmosphere is beneficial, nearer the ground ozone is harmful to biological processes at concentrations as low as 0.1 parts per million. It is a major contributor to the photochemical smog formed when pollution levels, sunlight intensity and geographical conditions are favourable. The smog aggravates respiratory complaints and assists in acid damage to vegetation.

The widely dispersed sources of VOCs means that control measures aim to embrace even small scale users.

In the UK The Environmental Protection (Prescribed Processes and Substances) Regulations define various prescribed processes, including Di-isocyanate processes; Coating processes and printing; Manufacture of dyestuffs, printing ink and coating materials; Processes involving rubber. Operators of these must apply for

authorisation and meet specified conditions including maximum emission levels for pollutants.

The European Commission (EC) Solvents Directive imposes a similar regime throughout the EU, with full compliance from 2007.

Controlling VOC emissions

In the UK prescribed adhesive coating processes - those using more than 5 tonnes per year of solvents at a location - are subject to local authority air pollution control.

Regulations set a concentration limit of 50 mg/m^3 (as carbon) in vented exhausts and target reductions in fugitive emissions. Shoe factory emissions typically exceed this limit by a factor of 5-50. An alternative mass balance regime allows exemptions, for example a maximum solvent usage of 20 g/pair of shoes against former typical values of 30-45 g. Limits based on solvent mass per unit area coated are available for other adhesive users such as furniture manufacturers and rubber fabricators. The EC Solvents Directive sets similar requirements.

The control regimes have encouraged the substitution of solvent preparations by water-borne or hot melt systems and this is the preferred option. However, these may have drawbacks such as the need for specialist application equipment, extended drying times or closely controlled working times, limited tack and variable bonding performance.

For demanding applications, such as shoe sole bonding or rubber fabricating, low-solvent adhesives are not always sufficiently versatile to fully displace solvent-borne adhesives; moreover, solvent-based cleaners and pretreatments continue to be necessary.

Some adhesive using processes are likely, therefore, to require solvent arrestment measures. Adsorption on carbon beds is feasible but mainly suited to processes using a single solvent of low water solubility which can be recovered by steam stripping. More generally, the mixed cocktail of adhesive solvents is best handled by thermal or catalytic incineration or biotreatment.

Catalytic combustion

Catalytic combustion enables solvent vapours to be flamelessly oxidised or 'burnt' at lower temperatures than thermal incineration. However, the polluted air stream has to be heated to the minimum temperature for combustion of the solvents concerned, which is usually in the range $250\text{-}350^\circ\text{C}$. Heat from combustion of the solvents can be utilised to preheat the pollutant stream, although the solvent concentration needs to be high if the process is to be 'self sustaining'.

SATRA studies have confirmed that catalytic combustion can satisfactorily handle the mixed solvents from adhesives in shoemaking. A pilot unit was demonstrated in factories, arresting solvents from coating shoe uppers and soles. High solvent loadings, mainly butan-2-one (methyl ethyl ketone), of over 4000 mg/m^3 , were reduced to well below the regulatory limit of 50 mg/m^3 .

Catalytic combustion is a highly effective means of arresting solvent vapours. However, capital and energy costs are relatively high, unless these can be minimised by reducing air

flows and increasing exhaust solvent concentration and temperature. This is difficult to achieve in adhesive bonding of batch components by dispersed solvent emitting processes. The process is best suited to coating processes which are continuous and are coupled with a drying oven, to produce a solvent-rich warm exhaust.

Biotreatment

Biological treatment of organic pollutants by microorganisms on a suitable moist support medium is established for controlling odours, but emissions of mixed solvents present a challenge through differing solubilities and rates of breakdown.

SATRA developed a project to demonstrate biological control of VOC emissions at a footwear factory. This company was keen to continue using proven solvent-borne adhesives due to the challenging service conditions to which their products are exposed. Processes for cleaning and applying adhesive to soles produced an exhaust carbon concentration of 150-900 mg/m³, deriving from both water soluble (acetone, methyl ethyl ketone) and low solubility (hexane, toluene) solvents. A pilot demonstration unit was constructed combining a biotrickling filter to handle the more soluble solvents and a biofilter to deal with less soluble species.

After a commissioning period VOC removal efficiency was consistently 85-95%, and the unit proved tolerant of breaks in working and peak solvent loadings. Cost calculations for a full-scale process indicated capital and operating cost savings of 30% and 55% respectively, compared with catalytic incineration. The trial confirmed that biotreatment is an ideal means of controlling near ambient temperature exhaust of moderate solvent loading, as in many adhesive bonding processes. A full scale unit subsequently installed at the trial site has given satisfactory service.

Other environmental issues

Disposal of factory waste is being increasingly controlled. Adhesive users should aim to restrict the amount of waste generated, for example by ensuring that containers are as completely emptied as possible in use. Post-consumer waste is a growing concern especially in relation to short life products such as packaging; however, any adhesive used forms a low proportion of the total volume and is unlikely to attract specific attention providing it is fully cured and non-hazardous.

Adhesive bonding is a relatively low energy user and may compare favourably with other assembly processes such as welding, although the energy used to produce the adhesive itself must be taken into account.

Consumer-led pressures for recycling, ecolabelling and renewable resources present further challenges to the adhesives industry, although the adherends, rather than the adhesive, continue to be the predominant concern of the environmental lobby.

Conclusions

The main environmental issues faced by adhesive producers and users are emissions of pollutants and disposal of waste. Solvent-containing preparations are increasingly constrained and will only be used long term where essential for performance. Solvent usage on other than a moderate scale may require measures to arrest emissions.

Abstract

Adhesives based on polyurethane dispersions for footwear sole bonding

Wolfgang Arndt, Dr. Heinz-Werner Lucas, Bayer AG, Dormagen, Germany

Bonding is nowadays the most important joining process in shoe production. Various parts of the shoe, made of many different materials, are joined together by bonding during the production process. The shoe industry has traditionally used solvent-based adhesives for this, but a number of new regulations and other requirements have already resulted in partial substitution by solvent-free systems. However, there are still certain processes in which solvent-based adhesives dominate, in particular in the bonding of shoe soles.

Developments in the last decade have led to a marked improvement in the quality and increased practical application of aqueous polyurethane adhesive dispersions in the bonding of soles. This has made it relatively easy to substitute solvent-based adhesives without making any compromises on quality. The technical demands made on adhesives for bonding shoe soles are very high indeed. Not only must they be suitable for many different applications and substrates and guarantee a permanent, load-resistant bond between the materials, they must also satisfy the demanding requirements of the consumer from an optical point of view, for example. Any discoloration of the adhesive, especially with light-colored soles in the fashion and sports shoe segments, is unacceptable.

Standard EN 1391 describes the technical specifications and thus provides a guideline for the minimum requirements concerning peel strength and other properties. There are also specific, as yet non-standardized requirements on shoes for particular applications, for example the resistance properties of working and safety shoes under changing temperatures. Because most shoes are nowadays manufactured in Asia, the climatic conditions during transport of the shoes through tropical regions also has to be taken into account. All these requirements are satisfied by adhesives based on polyurethanes. The adhesives are flexible and are noted for their good adhesion to many materials as well as their high chemical resistance. By crosslinking with isocyanate hardeners, their long-term resistance can be increased significantly.

The adhesive systems of this kind on the market are still predominantly solvent-based. During shoe production, the bonding of soles is a process that needs the largest amount of adhesive. On the other hand, it is generally impossible to recover the solvents in this industry and optimum air exchange tends to be very difficult to achieve due to the workplace circumstances. For this reason, attention will continue to focus on the replacement of solvents in this sector. End-users and consumer associations are increasingly calling on the shoe industry and their suppliers to comply with the Responsible Care commitment and to improve hygiene at the workplace in low-wage countries. The growing pressure has since led to a significant intensification of environmental legislation. Within the European Union, Directive 1999/13/EC on the limitation of emissions caused by volatile organic solvents will become effective in 2005. This specifies a gradual lowering of emission threshold values according to a defined schedule. Practical experience has shown that it is only possible in children's shoe production to consistently fulfill these regulations without taking any additional measures.

A comparison of the bonding properties of solvent-based adhesives and adhesive dispersions shows that the distinct trend from solvent-based to water-based systems can in no way be explained only by the stricter emission thresholds. Instead, we can conclude that the equal or even improved properties of the water-based products can actually raise the already high quality standard of production

SOLVENT FREE – MEETING THE ENVIRONMENTAL CHALLENGE

There is ever growing pressure on adhesive producers, and users alike, to make products with as little negative impact upon the natural world as possible, to leave the whole natural environment as little disadvantaged by product manufacture and use as possible. At the same time pressures in society demand facilities, fabrications, and conveniences with ever higher performance capability, in the context of a market economy.

This talk aims to review some of the Solvent Free adhesives available to users, and how they are progressing towards meeting the environmental challenge, whilst also meeting new technical levels.

The issue of solvent emissions, or flammability/toxicity hazards, for example, has been around for decades, and the demise of solvent based adhesives, (SBA), was allegedly imminent 25 years ago.

Current situation

FEICA statistics for adhesive use in 1999, show SBA ~ 12% of the market, by weight, in Europe, agreeing with another source that ~130,000 t of solvent was used by the industry. Many 'greener' options appear to exist already, but there is pressure from the Solvent Emissions Directive to reduce this further.

The statistics show that SBA tonnage, though slightly declined in 1999, was still very similar to that four years earlier. One can assume people are comfortable with their adhesive choice, there has been little pressure to change, or change is undesirable in some way. Some SBA users incinerate solvent and some capture the solvent emissions. Such users are currently unlikely to change, having made significant capital investment, unless forced to.

The choices for someone wanting to use a solvent-free adhesive, will be from polymer dispersions & emulsions, hot melt adhesives, reactive adhesives, natural polymers, and those based on water soluble polymers. The first two are the main subject of this talk.

POLYMER DISPERSIONS & EMULSIONS

Water based dispersions and emulsions constitute approx. 40% of the European adhesive sales by weight, and the most commonly used type world wide. This arguable makes them the first candidates as prime solvent-free challengers. For a start, on switching to WB from SB, one may transport ~1/3 of the volume of adhesive, the number of containers may be ~1/3. There is a saving on packaging waste, and less adhesive waste.

Since the 1970s there has been steady development by polymer and resin producers to refine, modify, and tailor their products.

WB products are available to bond a wide range of surfaces, but the areas of challenge are still the low energy surfaces like polymer film and metals, and in matching some of the higher performance characteristics of SB formulations. The major players include, polyvinyl acetate, ethylene vinyl, VAE, acetate, acrylic, SBR, polyurethane.

PVA formulations are good for bonding cellulosics, and so are very widely used in packaging and woodworking. Higher water resistance is now available, and there are remoistenable grades with low odour and taste. Copolymerisation between vinyl acetate monomer and ethylene produces the VAE copolymers, which, by variation of the proportions of the two monomers a wider range of flexibility and adhesion results, in comparison with PVAs..

Plasticisers are commonly used in these formulations, and these will be subject to new labelling regulations from mid-year, driving manufacturers to reformulate to safer environmental options. Also affected by relabelling are biocide containing formulations.

WB acrylic adhesives- Developments have been made in improving heat resistance of PS grades, and in extending adhesion to a wider range of metals and polymers. Crosslinking

to reduce fogging in vehicles interiors, and are also used in filter medium bonding, where extractable chemicals must be at a minimum.

POLYESTERS

Crystalline polyesters have sharp melting points and retain their properties close up to the melting point. HM polyesters are applied as powders, film or web, or by melt applied coatings. Powder adhesives, in lamination of foam to fabric for upholstery, eliminate flame lamination, which releases unwanted VOCs. Nets or webs are a very clean use of adhesive.

Polyesters have wide adhesion, outstanding and long lasting adhesion to plasticised PVC. They have excellent heat resistance, excellent water and hot wash resistance, good oil resistance, and excellent electrical properties.

PET film extruders are increasingly working to coextrude the film with adhesive grades to give heatseal coatings, rather than SB coat. New grades are being developed for this.

Polyester adhesives allow all polyester laminates/compounds for automotive components e.g. headliners, giving an easier recycle option.

Low melting polyesters range extension – for melt, powder and web - will degrade when wasted.

Water dispersible polyester, used in formulation of adhesives which will disperse in water but not in ionic solutions (body fluids). It allows for better separation of components when it comes to recycling e.g. labels from bottles, 'paper' nappies.

EXTENDING HOT MELT PERFORMANCE

The next extension is for an HM adhesive to become thermosetting after application, giving enhanced bond characteristics, e.g. increased heat resistance, chemical/solvent resistance, better ageing resistance, higher bond strength. One option is reactive PU hot melt (HMPU). When warmed, then applied, it will cool to give sufficient green strength, and then react with moisture to give ultimately a fully reacted polymer. The choice of backbone polyol is a major determinant of the initial hot melt properties. HMPUs now find use in many applications, in Automotive, exterior and interior, construction, textile, woodworking, product assembly, medical, and others. In many of these, HMPU supplant SB adhesive use.

Additional benefits brought by HMPU are good wash and dry clean resistance, and autoclavable and sterilisable bonds. There is still significant growth potential in HMPUR.

SPUR – Silylated PU technology. Where there may be concerns about the use of isocyanate, SPUR technology provides an isocyanate free, curing polymer. These may be viewed as similar to the HMPU described above, reacted with an amino-silane to produce a silane terminated prepolymer, which is also moisture curing.

SPUR products, and indeed the similar silyl terminated polyethers (MS polymers) have found extensive use as construction sealants, where the silylated group extends the scope of adhesion. This technology is not yet widespread within HM adhesives, but may grow.

PAR. An area recently developing, PAR links the silylation just described with HM polyamides described earlier. PAR – reactive polyamide, brings Silylation encapping to dimer acid based hot melt, to join polyamide benefits with higher heat resistance.

This brief and selective review of solvent free adhesive shows how the adhesives industry has developed a wide range of technology, capable of addressing the current environmental concerns, whilst still extending product capability, to meet the growing technological demands of the day.

systems are available to give temperature and solvent resistance, and specific adhesion. Key applications are in pressure sensitive tape and adhesive coating for labelling, where SB grades still feature. Flooring adhesives and sealants also utilise WB acrylics.

SBR adhesives are lower priced generally, but also relatively lower performance. They have their place in elastomer formulations, and often in blends with rubber and tackifiers, used in fabric bonding. As such they are an alternative to SB adhesives used in these applications.

Polyurethanes, are higher performance products, often matching their SB equivalents in adhesion and performance, now that experience in use has developed. Solvent elimination in footwear manufacture has been quite successful, and also in automotive and lamination.

Water borne polychloroprene adhesives have taken some niche applications from solvent based equivalents, for contact adhesive applications, and some specialist rubber bonding.

HOT MELTS

Hot melt adhesives contain no solvents and require no drying. Their use has grown significantly in the past twenty years. With a 50 – 80% smaller mass requires transporting, and storage space. On application of the adhesive, the energy consumption is more often lower for hot melts than either solvent or water based, if active drying is used.

From a technical viewpoint the fast setting of hot melt bonds normally gives an advantage over the other two, allowing shorter application to bonding times, and usually with little bond maturing time required at the end of the line. From a health and safety viewpoint, the hazard of SBA, flammable, and irritant or harmful, is swapped for a high temperature hazard. Both can be minimised in the workplace, though the HM usually has fewer issues to deal with.

A list of polymers used in hot melt adhesives would include polyethylene, amorphous polypropylene, ethylene copolymers, block copolymers, polyamide, polyester, and urethane. EVA based hot melt adhesives hold the biggest section of the market, a majority of them in bonding to paper, fabrics, wood and some plastics. The normal upper service temperature of 60 – 80°C, and the drive behind technological advances will be to reduce cost, for a relatively commodity market.

Thermoplastic elastomers, constitute the next significant group, and are important pressure sensitive hot melts (or HMPSAs). This two phase nature allows the chemist to target modification to one phase or the other, making additions that will affect either block, or both.

Amorphous polyolefins, now made by direct synthesis, find use in sealants and adhesives, paper and in film and foil lamination. APOs offer good thermal stability, excellent adhesion, wide formulating capability, and excellent water resistance.

POLYAMIDES

With polyesters, these are classed as high-performance hot melt adhesives, having higher strength than EVAs and a wider range of service temperatures, and certain superior performances such as chemical or wash resistances. They are found in use bonding plastics, glass, wood, leather, foam, fabric, rubber and some metals, such as aluminium, and copper.

Dimer Acid-based Polyamides are derived from renewable natural feedstock, either from oilseed crops, or from trees. Characteristics of dimer acid based polyamide include a sharp melting point, excellent adhesion to many substrates including treated polyolefins, good chemical and oil resistance, and a moisture vapour barrier.

Copolyamides, or 'Nylon-type' polyamides, have melting points upwards of ~100°C. These adhesives are useful in bonding more polar surfaces, or where solvent resistance is required. They are used in bonding fabrics, offering dry clean resistance, wash resistance, and steam resistance. They are supplied in powder, pellet, web and film form. Grades are now available

Corona and Plasma Pretreatments of Composite Materials

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Fibre composites based upon *thermoplastic* polymeric matrices containing continuous fibres of carbon or 'Kevlar' are being increasingly used in engineering structures. Engineering applications frequently require that they be joined to components fabricated from similar fibre composites, or to other types of materials, and the use of structural adhesives, typically based upon epoxy resins, offers many advantages compared with other methods of joining.

The present paper describes in detail the mechanics and mechanisms of the adhesion of fibre composites; based upon *thermoplastic* poly(ether-ether ketone), poly(aromatic-amides), poly(phenylene sulfide), etc, matrices and, for comparative purposes, *thermosetting* epoxy matrices. The thermoplastic composite substrates were pretreated by light abrasion and solvent cleaning, followed by either an oxygen-plasma or corona pretreatment. The adhesives were a room-temperature curing epoxy paste and a hot-curing epoxy film. The surface topography and chemistry of the composites have been characterised using contact angle measurements and X-ray photoelectron spectroscopy, both before and after using the pretreatments. Joints were then prepared using the epoxy adhesives and the adhesive fracture energies, G_c , of the joints were measured.

It is shown that good adhesive bonding of the thermoplastic composites can be achieved only if a plasma or corona pretreatment is used prior to bonding. For the oxygen-plasma and corona pretreatments employed, the adhesive fracture energy, G_c , for the thermoplastic composite joints increased steadily with the intensity of the pretreatment until a plateau value of G_c was reached. On the other hand, the thermosetting-based epoxy composites needed only light abrasion and solvent

cleaning to give high values of G_c . Without the oxygen-plasma or corona pretreatment, the thermoplastic composite joints failed at the adhesive/composite interface at a very low applied load. The oxygen-plasma and corona pretreatments lead to an increase in the surface concentration of polar, oxygen-containing groups, resulting in both increased wetting by the epoxy adhesive on the thermoplastic composite substrate and greater intrinsic adhesion across the adhesive/composite interface. The enhancement in intrinsic adhesion was reflected in the locus of failure of the joints moving away from the adhesive/composite interface, and in far higher values of G_c .

Finally, two major aspects of the observed results, with wide applicability to many adhesion problems, have been analysed in detail. First, the need to apply a critical intensity of surface pretreatment to the thermoplastic fibre composite to prevent interfacial failure, and hence give relatively high values of G_c , has been interpreted by relating the chemical composition of the surface of the composite to the corresponding value of the polar force component of the surface free energy. It is thereby shown that the fundamental requirement is that a critical value of the surface polarity has to be attained. Secondly, after this critical value is reached, it is shown that the locus of joint failure may then be accurately predicted from a knowledge of the stress field in the joint and the experimentally measured interlaminar fracture stress of the fibre composite substrates.

An Evaluation of Alternatives to Chromic Acid Anodising

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A review of the literature reveals a broad range of treatments for the adhesive bonding of aluminium and its alloys. The most successful and widely adopted treatments include; chromic acid etching and anodising (CAE and CAA), and, phosphoric acid anodising (PAA). These treatments provide highly micro-rough surfaces suitable, if fully wetted, for "interphase" formation. In addition, and particularly with the anodic oxides, a barrier film is produced which is thought to prevent hydration and loss of joint strengths through this mechanism.

The requirement for more environmentally-benign surface treatments to the hexavalent chromium based processes previously mentioned has led to many investigations into alternatives.

In the present study a non-chromated alternative oxidation treatment has been optimised for the adhesive bonding of both clad and unclad 2000 series and unclad 7000 series alloys.

A range of surface analytical techniques (AES, XPS, AFM, SEM, STEM) have been used to study the changes imparted to the surface by the "standard" and optimised oxidation treatment.

Adhesion levels have been established using the Boeing wedge test. In addition, salt spray and linear polarisation tests have been carried out to assess the corrosion performance of the optimised oxidation treatments.

The CAA process has been used throughout this study as a baseline to the standard and optimised oxidation treatment.

This study has shown that the optimised non-chromate containing anodic oxide provides similar chemistry and surface structure to the familiar CAA. Resultant adhesion levels are also comparable to that of the CAA as measured using the wedge test.