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Low Cost Aluminium Closures

by

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Low cost aluminium closures are a new design of closure (hood, door or tailgate) for automotive vehicles. A closure is made from an outer and inner panel and other components such as: hinges, latches, strikers and reinforcements. A low cost aluminium closure has a pre-coated aluminium outer panel joined to a zinc coated steel inner panel with additional components made of zinc coated steel. Low cost aluminium closures offer the potential to reduce weight, manufacturing complexity and improve corrosion resistance. The purpose of this research is to demonstrate that low cost aluminium closures can at least equal the performance of the existing all zinc coated steel closure architecture in terms of corrosion resistance, structural durability, manufacturing feasibility and part cost.

Low cost aluminium closures have been shown to be at least as corrosion resistant as the existing all zinc coated closure and the structural durability of low cost aluminium closures meets the specified performance level. The existing hem flange adhesive is suitable low cost aluminium closures and an optimised two part epoxy has been evaluated and would be recommended for use on large closures where increased handling strength is required. Manufacturing feasibility has been investigated and low cost aluminium closures can be manufactured in Ford of Europe production plants with minimal changes to existing production lines. The part cost of low cost aluminium closures has established and taking into account the cost reduction associated with weight saving low cost aluminium closures can be manufactured for significantly less than the existing closure.

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1.0 Introduction

Low cost aluminium closures are a new type of body closure architecture for automotive vehicles. Body closures are hoods, doors and tailgates and are termed closures because they enclose the vehicle body and are attached mechanically to the main vehicle body by hinges. Closures are assembled from sheet metal stampings, castings, fasteners and other components such as crash reinforcements, hinges, locks and electrical systems. Low cost aluminium closures use organically pre-coated aluminium and zinc coated steel sheet to form a reduced weight closure with the potential to improve corrosion resistance and reduce manufacturing complexity.

The automotive industry is a challenging business and manufacturing environment. The business and economic constraints the automotive industry operates under will be discussed briefly in this section along with the challenges of mass production. The operating environment for automotive vehicles will be described and the importance of robust design and manufacturing techniques on manufacturing and in service performance will be highlighted. Current use of aluminium for the manufacture of automotive vehicles will be examined and as well as the reasons why aluminium has not been more widely adopted discussed.

The architecture of low cost aluminium closures will be described and the economic advantages of the low cost aluminium closure concept examined with reference to current all steel vehicle manufacturing processes. The weight reduction potential and corrosion considerations surrounding a mixed material system will be introduced. The hypothesis and aims and objectives of this research will be stated together with an overview of the structure of this dissertation.

1.1 The Automotive Industry

Today's automotive industry is a fiercely competitive environment and automotive manufacturers must produce high volumes of high quality vehicles that meet (and hopefully exceed) customer expectations to maintain and increase their market share. They must do this cost effectively and also meet a myriad of legislative requirements for safety, fuel economy, exhaust emissions and end of life disposal of vehicles (amongst many other requirements).

1.1.1 Mass Manufacture

Most automotive manufacturers are in the business of mass manufacture. Vehicles are very complex mechanical and electrical systems and the economics of mass manufacturing allow the cost of such complex systems to be kept within the reach of consumers. Organisations such as Ford Motor Company Limited, produce multiple vehicle lines at volumes of approximately one hundred thousand vehicles per line per year, this equates to one vehicle coming off the end of the production line every five minutes. The processes, materials and resources required to manufacture one vehicle every five minutes make mass manufacturing environments extremely challenging. Materials must arrive correct and on time at the start of the production line and all the plant and assembly processes must function together to ensure the smooth flow of parts and material to all parts of the line. Quality control procedures are essential to ensure that parts made at different times and by different processes fit together and function correctly.

Closures are made up of an inner and outer panel and a number of other components. The inner and outer panels are stamped from sheet material in the press shop using high load press installations to conform a sheet metal blank (trimmed metal sheet) to the required contour of the main draw die by a combination of drawing and stretching. Subsequent passes through the press consolidate the features through restrike, trim the part and pierce holes where required.

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The stamped panels are moved to a sub-assembly line where the inner and outer panels are joined together using a combination of adhesive bonding and mechanical clinching. The adhesive bond is sometimes given an induction curing process to give the closure handling. Depending on the closure architecture other components may have been fixed to either the inner or the outer panel before they were joined together and after assembly further components will be joined to the closure, such as strikers, welded fasteners and hinge reinforcements. The fully assembled body in white closure will join the vehicle body, termed body in white (a traditional term for a vehicle body structure) before the vehicle is painted. Closures are removed from the painted vehicle for electrical fit out and trim and then rejoin the vehicle in final assembly.

Quality control of raw materials and manufacturing processes ensure that closures are dimensionally accurate and meet the strength and stiffness requirements specified by the vehicle designers. In-plant inspection procedures (and quality requirements placed on suppliers) ensure that most deviations from specified quality levels are detected before the vehicle leaves the plant but unfortunately not all faults can be or are detected. Some faults will escape into the field and these may be serious enough for a vehicle to be recalled to a dealership for repair or rectification of the fault may be carried out at the next routine service interval. Robust material selection procedures and manufacturing techniques minimise the risk of faults occurring in the plant and escaping into the field and are an essential method of controlling the variability of manufacturing inputs and processes.

1.1.2 Robustness in Manufacture and Use

Every manufacturing process increases the variability of a raw material as it is made into the final component and mass manufacturing industries use robust design to produce high quality products economically. Taguchi defines robustness as a product or process that can function well against background noise (Grove and Davis (1992)). Noise refers to any cause of variation whether it originates in the manufacturing process, the customer's method of use or the environment.

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Figure 1.1 Over Engineering



Figure 1.2 Robustness Failure

Figure 1.1 shows graphically an over engineered situation. In an over engineered situation the variation due to inner noises is controlled to a statistical distribution that will never overlap the expected outer noise distribution (Davies (1997)).

Demand Function		Capacity Function
Inner Noise		Outer Noise
Piece to Piece	Dimensions	Customer Usage
Variation	Change in	Operating Environments (Climactic or
	Dimensions (Wear	Road Conditions)
	Out)	
	Change in	Internal system and component
	Mechanical	interactions
	Properties	
	(Fatigue)	

Table 1.1 Inner and Outer Noise Types

Robust design aims to bring the demand and capacity functions as close together as possible without robustness failures occurring when the curves overlap as in figure 1.2. Consider a door assembly that is at the upper end of its dimensional specification, when this component is exposed to noises in service, for example high temperatures on a hot summers day the door may expand and jam shut, this would be a failure. Vehicle manufacturers use robust design to optimise costs and minimise failures. However, the effective use of robust design relies on a thorough understanding of the outer noises affecting a system and being able to control the statistical distribution of inner noises to an appropriate level.

One method of controlling inner noises is to reduce the number of manufacturing processes needed to produce a component or assembly. Pre-coated aluminium allows manufacturing complexity to be reduced by eliminating at least one highly variable process (over hem sealing see section 2.4.2) and the manufacturing method used to pre-coat the aluminium sheet is highly repeatable and robust (pre-coating is applied continuously on line at the sheet rolling mill).

1.1.3 Operating Environment for Automotive Vehicles

Automotive vehicles operate in a demanding environment. They are driven by customers of different sizes and driving styles in every type of climate. The same vehicle may have to withstand the arid environment of North Africa, the marine environment of the west coast of the USA or the cold climates of Northern Europe. Each of these different environments places different demands on the vehicle and in the case of this research, closures. The primary issue associated with closures experiencing different climates is corrosion. In marine and cold climates salt (sodium chloride) from sea water and de-icing salts used in icy and snowy regions (sodium chloride and calcium chloride) act together with moisture from the air and rain fall to form an aggressive corrosion environment. In arid climates salt and moisture are not an issue but the abrasive nature of sand and possible high winds may be problematic for paint appearance. All environments are challenging to closures with respect to stone chipping and after paintwork has been chipped marine and cold climates exploit any damage to paint work and corrosion often initiates at the site of the stone chip.

Vehicle owners vary greatly in the way they treat their vehicles when they drive them and also in general use. For example when a door is closed the force exerted on the door by one owner may be much greater than by another. As such, doors must be designed to withstand all reasonable "door slams" and should not need large forces to close them fully. Some vehicle owners may take great care of their vehicles regularly washing and waxing the body work which can help protect the vehicle from corrosion by reducing salt build up on the body work. The vehicle manufacturers cannot rely on all vehicle owners being so attentive and so vehicles must be designed to withstand reasonable salt loadings and resist corrosion for the warranty period of the vehicle to fall in line with customer expectations.

Customer expectations are a very important consideration. Although a small amount of visible red rust may be acceptable without compromising the structural performance of the vehicle it is unlikely to be acceptable to the customer. Therefore it is often the customer requirements that dictate design specifications and these specifications are used in robust engineering design to meet customer expectations throughout the life of the vehicle.

1.1.4 Aluminium Vehicles

Steel has been the metal of choice for mass production of automotive vehicles and relatively small amounts of aluminium have been used in the manufacture of vehicles. The aluminium content of vehicles has increased from approximately 64 kg to 130 kg per vehicle in the past 10 years (Osborn (2005)), in approximately the same time period (1987 to 2000) vehicle curb weight has increased by 12% (German (2002)). Usage of aluminium has increased by 103 %, so the increase in aluminium could not

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be accounted for by overall curb weight increases. Aluminium has been used successfully in powertrain applications to manufacture engine blocks and can give considerable weight savings over equivalent cast iron blocks. The use of aluminium for alloy wheels and heat exchangers has also increased the aluminium content of vehicles.

Aluminium vehicle bodies are less well developed and only a few vehicles bodies are produced entirely of aluminium. Audi was one of the first companies to produce an aluminium vehicle body (the A8 and later the A2) using a space frame design that utilises two and three-dimensional extrusions and cast nodes. Jaguar has produced a conventional unibody (sheet metal construction) vehicle, the Jaguar XJ and the XK Coupe is about to be produced from aluminium using a combination of space frame and unibody architecture. Kelkar et al (2001) have suggested that a complete redesign of the steel automobile body is necessary for aluminium to make significant inroads into the vehicle body material market. They concluded that space frame technology has greater potential to produce an economically competitive aluminium vehicle and that significant challenges still exist for aluminium to be widely incorporated into mass production vehicles. The main areas of concern were joining parts together, stamping body panels and the base material cost of aluminium compared to steel.

Chart 1.1 shows the incentives vehicle manufacturers and aluminium producers have to increase the aluminium body content in vehicles. Body in White accounts for 28% of the mass of the vehicle and it would give aluminium producers an extensive new market. Vehicle manufacturers would have the opportunity to reduce weight in order to meet ever more stringent fuel economy and emission targets. For aluminium to be used in large quantities to manufacture vehicle bodies a number of events must take place:

- The price per kilogram of aluminium must converge on the price of steel.
- Manufacturers must make a strategic decision to make vehicle bodies from aluminium (like Audi and Jaguar) and employ suitable design techniques to make the design economically viable.

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3. Aluminium producers and manufacturers must work together to solve the technical challenges of joining and stamping aluminium in mass production volumes.

Mason (2003) conducted a study into manufacturing hoods from aluminium for Ford of Europe and found that due to the material cost of aluminium it was not economically feasible to manufacture even one component (on an otherwise entirely steel vehicle) entirely from aluminium. The current difficulties associated with producing all aluminium components or vehicles on grounds of cost and technical challenges have led to a novel design of closure to selectively utilise aluminium and produce a low cost aluminium closure.





1.2 Low Cost Aluminium Closures

LandRover has used steel and aluminium together for many years by combining a steel chassis with an aluminium body. In cases where the steel chassis is not electrically isolated from the aluminium body, galvanic corrosion can occur and the aluminium will corrode preferentially to the steel. If a robust method of electrically isolating steel from aluminium was available and the part design allows for joining to be carried out without welding or fasteners i.e. adhesive bonding, then there would be minimal risk of galvanic corrosion occurring and steel could be used alongside aluminium successfully in a vehicle body.

Alcan (now Novelis) presented a new type of automotive aluminium sheet to Ford of Europe in 2001. Pre-coated aluminium sheet (shown schematically in figure 1.3), then termed electrocoat replacement (ECR) was marketed to Ford as a way of removing the need for electrocoat (one of the initial paint layers applied to a vehicle).



Figure 1.3 Pre-coated Aluminium

Electrocoat paint systems are expensive to install and run, as prior to electrocoat the vehicle body is cleaned, rinsed, given a phosphate pretreatment (to increase zinc coating weight and improve electrocoat paint adhesion), electrocoated and then the electrocoat paint is baked before final paint layers are applied. This process takes approximately 1 hour for a vehicle to complete and a paint system without electrocoat would undoubtedly be more efficient. ECR aluminium sheet would have been an excellent opportunity if Ford of Europe were making all aluminium vehicles. Jaguar were starting to produce the XJ in aluminium but the development process had not been conducted with ECR aluminium sheet and the paint line for the XJ is common to the XJ and the S Type (which is an all steel construction), so there would have been no advantage in using ECR sheet for the XJ.

Despite the initial application being unsuitable, ECR sheet was considered to have advantages for other body applications. The organic pre-coating gives increased formability and the electrical isolation provided by the coating meant it was suitable for direct substitution for a steel stamped outer panel in a closure. A hood was the most suitable closure to trial the concept as the outer panel of a hood is adhesively bonded to the inner panel. An additional advantage of pre-coated aluminium is that it forms durable adhesive bonds, unlike untreated aluminium sheet.

1.2.1 Component Architecture

A pre-coated aluminium outer panel would be stamped in existing tooling designed for stamping steel and assembled with the existing zinc coated steel inner panel, steel hinges, reinforcements and other steel components. Figure 1.4 shows the low cost aluminium hood concept on a hood. The pre-coating would be used on the inside of the outer panel to ensure electrical isolation from the inner panel in conjunction with the hem flange adhesive as shown in figure 1.5. A hem flange is the joint that is formed when an inner panel is joined to an outer panel during the assembly of a closure.

It is not thought that any significant changes would be needed in either the stamping, assembly or paint processes. The initial work conducted by Alcan (Carr et al (1997)) showed compatibility with automotive adhesive systems and paint processes. Their work also showed improved formability of pre-coated aluminium sheet when compared to uncoated aluminium sheet of the same alloy grade.



Figure 1.4 Low Cost Aluminium Closure Concept (Hood)



Figure 1.5 Low Cost Aluminium Hem Flange

1.2.2 Economics, Weight Reduction and Corrosion Considerations

As with all businesses the economic feasibility of any new product must be demonstrated. Mass production environments are especially challenging for new products as even a small increase in part cost has serious implications for a vehicle production line manufacturing one hundred thousand vehicles a year. Low cost aluminium closures aim to address the economics of using a premium material (aluminium) by making the most efficient use of this premium material and by reducing manufacturing complexity. Further long term economic advantages may be gained by the potential to improve corrosion resistance and competitive advantages may be gained from the reduction in vehicle weight.

1.3 Hypothesis

The hypothesis to be tested in this thesis is:

Low cost aluminium closures can at least meet the performance of the existing all zinc coated steel closure in terms of corrosion resistance, structural durability and economic and manufacturing feasibility, so that the opportunity for weight reduction and decreased manufacturing complexity can be realised.

1.4 Aims and Objectives

The aims of this research are to test the hypothesis stated above by assessing corrosion performance and structural durability of a low cost aluminium closure. A business case will be formulated to investigate the economic and manufacturing implications of low cost aluminium closures.

The objectives of this research are to manufacture a number of low cost aluminium closures in a mass production environment and to test the corrosion resistance of these closures using accelerated laboratory and accelerated proving ground tests. The structural durability of the closure will also be assessed using an accelerated proving ground test. The corrosion resistance of small sections of assembled closures will be investigated using electrochemical techniques and where possible electrochemical results will be correlated with the corrosion performance of the full size demonstrators. The structural durability of the metal substrates used to form a hem flange will be assessed using single lap shear joints adhesively bonded together with automotive hem flange adhesives. The joints will be tested in tension to assess the effects of environmental degradation. The overall objective will be to produce a corrosion resistant closure that performs equivalently to all zinc coated steel closure with an optimised adhesive system for bonding steel to aluminium.

1.5 Overview of Dissertation

This dissertation will first address the economic and manufacturing implications of producing a low cost aluminium hood within a Ford of Europe production plant on an existing vehicle. The literature covering all aspects of low cost aluminium closures will be reviewed and discussed. From the environments they will operate in to the corrosion mechanisms seen on zinc coated steel and the stress distributions of single lap shear joints. Conclusions drawn from the literature will be summarised, an experimental design described and the materials and methods used in this research will be detailed. Results and discussions will be divided into to two sections:

- Structural Durability of Low Cost Aluminium Closures
- Corrosion Performance of Low Cost Aluminium Closures

An overall discussion and conclusions will draw together the important observations and discoveries and relate them back to the business case (presented in section 2). Finally recommendations will be made as to the suitability of low cost aluminium closures for use on future Ford of Europe vehicles and what further work is required to allow this new technology to be implemented.

2.0 The Business Case for Low Cost Aluminium Closures

Low cost aluminium closures have the potential to offer weight reduction and improved corrosion resistance when used to replace conventional all steel closures. The technical demands of manufacturing an all aluminium car body are considerable and these demands increase when aluminium is used in conjunction with other metals, however Jaguar and Audi are currently manufacturing all aluminium vehicle bodies successfully.

The business implications of producing mixed material closures needs careful consideration to ensure that the performance of closures meets the standard required and that the component can be economically and successfully manufactured.

The risk of producing an entirely new component in a mass production environment should not be underestimated and the manufacture of a low cost aluminium closure must fit into current manufacturing processes with minimal disruption and the need for only minor changes. This business case aims to address some of the performance and manufacturing issues that producing low cost aluminium closures may present. In a business case of this scope it would be impossible to address all possible processes affected by producing an entirely new component, but it should serve as a good starting point for a more in depth study into the overall implications of producing a low cost aluminium closure.

2.1 Performance of Aluminium Closures

Aluminium has been used by a number of manufacturers to produce vehicle bodies effectively and with the application of the correct design practices it is possible to meet the functional demands of a closure. Closure is a general term for doors, hoods and tailgates and closures have specific functional demands as summarised by Lahaye et al (2000):

- Dent resistance: High strength after paint baking for high dent resistance if maximum weight saving is required.
- Stiffness: Combination of inner and outer panel should give a component with high torsional rigidity.
- Design aspects: High formability for stamping and flat hem capability.
- Paint appearance: High standard of paint finish required for exterior body panels ("A" Class Finish).
- Corrosion: For aluminium good corrosion resistance is focused on low filiform corrosion (FFC) susceptibility.

This list above is not exhaustive, but gives a number of points to consider when selecting aluminium for use in a closure. Dent resistance can be classified in two ways, static and dynamic and is an important functional demand as it can influence customer perception of body panel quality. It is also important for a body panel (outer panel) to have good dent resistance during manufacture as it minimises the risk of in plant damage and in service dents and dings. Aluminium alloys selected for outer panel applications have a bake hardening response to give adequate dent resistance, the heat input required to bake harden the sheet comes from one of the paint oven bake cycles and is specific to each manufacturer. The bake cycle for electrocoat paint used by Ford of Europe is approximately 180 °C and on average vehicles will see that temperature for 30 minutes. Automotive aluminium alloys (and bake hardenable steel grades) are developed to bake harden at temperatures commonly seen by vehicles on production paint lines. Gauge selection of the aluminium sheet must compensate for the reduced strength of aluminium when compared to an equivalent steel sheet and the strength criterion used in this business case:

$$YS_{alu \min} \times t_{alu \min}^{2} \ge YS_{steel} \times t_{steel}^{2}$$
[2.1]

(YS = Yield Strength (MPa), t = Thickness (mm))

The two most common aluminium alloys selected for outer panels in Europe are AA6016 (AlMg0.4Si1.2) and AA6111 (AlMg0.7Si0.9Cu0.7) and both of these alloys have a bake hardening response giving them appropriate mechanical properties after bake to meet the functional demands of closures. Typical mechanical and functional properties are shown in table 2.1. The up-gauge required to meet the strength criterion in equation [2.1] (for example a 0.65 mm steel outer panel with YS = 235 MPa would require an aluminium panel of AA6016 to be a minimum of 0.81 mm thick (YS_{AA6016} = 150 MPa)) means that the stiffness of an equivalent strength aluminium outer panel is usually superior to the steel panel.

Property	Alloy		
	AA6016	AA6111	
Yield Strength T4 (MPa)	< 130	< 170	
Yield Strength T6 (MPa)	> 150	> 200	
(185 °C for 20 minutes)			
Flat Hemming Capability	Mild roughening	Severe cracking	
Spring back	Less	More	
Copper Content (wt %)	0.1	0.7	
Filiform Corrosion	0.5 – 0.9	1.4 - 5.2	
Susceptibility on Two Different			
Paint Systems			
(Length of filament			
delamination (mm))			

Table 2.1 Mechanical and Functional Properties of AA6016 and AA6111 (Layahe et al. (2000))

Part	Substrate	Coating	Gauge (mm)
Hood Outer	BHZ 260 ZC	55A55AHD	0.65
Hood Inner	DX54D	60G60GHD	0.65

Table 2.2 Production Materials for a Typical All Zinc Coated Steel Closure

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The grades of steel used in a typical Ford of Europe closure are given in table 2.2 and the yield strength of the outer panel material is 235 MPa, as used in the calculation above. AA6111 can allow for further down gauging enabling more weight to be saved, as the higher T6 yield strength gives improved dent resistance due to the increased copper content giving an improved bake hardening response.

2.2 Manufacturing Considerations for Aluminium Closures

2.2.1 Stamping Aluminium

Automotive aluminium alloys used for forming outer panels are generally less formable than their steel counterparts and this is due to the mechanical properties of aluminium allowing lower strain to failure and increased spring back on equivalent forming operations used for stamping steel. Spring back occurs when a panel is stamped to shape and then on withdrawal from the die the elastic portion of the total deformation is recovered by the stamped part. Unfortunately spring back in automotive panels is unpredictable due to the three dimensional nature of the stresses and strains applied to the panels during stamping and it is often only truly understood when a die set is tried out for the first time. As die sets are made from hard tool steels or cast iron any modifications required to produce a part to the correct dimensions by minimizing spring back are costly and time consuming.

When designing a part (outer panel) and the corresponding stamping tool (die set) with aluminium in mind the problems with formability can be minimized with intelligent contouring of dies and optimizing the strain imparted at each stage of stamping. Due to the complex nature of stamping operations computer aided modeling is still of limited use and this is especially true of aluminium where spring back is an important factor. Often the skill and experience of the stamping engineers is required to manufacture a die set to overcome spring back. Complex stamped parts such as the hood (bonnet) of the Jaguar XJ have been successfully stamped in aluminium but often require more passes (than the same part made of steel) to achieve the correct profile and more die development time is needed. When designing a part to be stamped from aluminium an appropriate design that is possible in aluminium is needed. The overstrike required (to minimize spring back) to produce a part of the correct dimensions first time must be accounted for by the stamping engineer in the die design.

2.2.2 Hemming Aluminium

Formability of the base alloy in closures also plays an important part in the hemming (clinching) performance. Poor formability will result in cracking of the sheet at the hem radius and lead to unacceptable visual appearance of the hem. Also, spring back after clinching can mean that hems are more open making subsequent sealing operations more difficult. As such aluminium is not suitable for the primary hemming technique (flat hemming, shown in figure 2.1) used by automotive manufacturers. During flat hemming the outer panel is clinched flat around the inner panel, also known as a 180 ° hem because the metal has been formed around 180 °. Aluminium cannot withstand the deformation required to produce a flat hem and so alternative hemming techniques are required.

Rope hemming and compressed radius hemming are two techniques used in manufacturing aluminium closures. Rope hemming requires less deformation than flat hemming but does not give a good visual appearance to the customer due to the large radius of the hem. Compressed radius hemming presents the customer with a sharp edge as with flat hemming but is less demanding on the total deformation required, figure 2.1 shows flat, rope and compressed radius hems schematically. Flat hemming AA6016 results in mild roughening that after painting results in a satisfactory paint appearance, however in areas of three dimensional deformation such as cowl edge corners flat hemming may still be too much of a challenge for AA6016. AA6111 is likely to crack during even a simple flat hemming operation, after paint this would lead to an unacceptable cosmetic result.

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Figure 2.1 Flat, Rope and Compressed Radius Hems

2.2.3 Paint Appearance and Processing of Aluminium

Paint appearance is critical to customer satisfaction and 6xxx series aluminium alloys allow an "A" Class paint appearance to be achieved. Other more formable aluminium alloys, such as 5xxx series used for inner panel applications show surface defects called stretcher strain markings or Lüders bands that show through after painting giving an unacceptable paint appearance. 6xxx series alloys do not exhibit these "Type A" defects and so are preferable to 5xxx series alloys from a paint appearance as well as a structural performance. When 6xxx series alloys are roll textured they can achieve similar paint appearances to steel outer panels. Roll texturing can be created by two different techniques as described by Benati et al. (2002): Electron beam texturing (EBT), where a controlled beam strikes the roll in a deterministic manner, creating highly repetitive textures and electrodischarge texturing (EDT) where the electro discharge machine randomly erodes small areas on the roll surface. Glossy paint appearance is achieved and problem paint appearance issues such as "orange peel" are minimized. Surface texture can also improve the formability of the material, Lahaye et al. (2000) reported a significant reduction in galling (loss of surface metal oxides during stamping, resulting in die contamination and defects on the stamped surface) when surface texture had been applied.

2.2.4 Corrosion Properties of Aluminium

The corrosion properties of aluminium present different concerns to those seen on steel. Aluminium does not corrode in the same way as steel due to its tenacious oxide layer that will repassivate the surface if it is damaged and will act to protect the underlying metal. As such, aluminium will not corrode at cut edges and no red rust corrosion products will be observed. Cosmetic corrosion of aluminium under paint films with thread like morphology is known as filiform corrosion and although superficial results in poor customer satisfaction. It is well known that copper content in aluminium alloys increases the risk of filiform corrosion and therefore AA6016 is a better choice of material if corrosion resistance is considered important. It is also well known that rework of aluminium panels with abrasive media can also increase the risk of filiform corrosion.

Other functional demands lead from those listed above; in Europe crash resistance and pedestrian protection are very important attributes for any new vehicle. A study was conducted by Mason (2003) on the feasibility of all aluminium hoods in response to an increase in head impact criterion (part of the assessment of pedestrian protection of new vehicles) and in that report aluminium hoods (with inner, outer panel and all hinges and strikers) were found not to be economically feasible at that time.

Aluminium can meet the functional demands for closures, as demonstrated by many manufacturers including Jaguar and Audi. However, in general aluminium has not been used for closures on high volume production vehicles in Europe. As a result of the work done by Mason (2003) a new concept was required to meet both the functional and economic demands of using aluminium in high volume production vehicle closures, low cost aluminium closures.

2.3 Low Cost Aluminium Closures

The low cost aluminium closure concept (as described in section 1.2 and illustrated in figure 1.4) selectively uses pre-coated aluminium in the outer panel. The pre-coating is applied to the inner side of the outer panel. The demonstrator selected for this work was a Ford Focus CMax Hood. The Ford Focus CMax has recently come through product development and is now in full production at Ford's Saarlouis Plant in Germany. The CMax was selected as a demonstrator vehicle as opportunities for proving ground testing were still available and more easily accessible as the vehicle has completed its initial product launch development. During product launch it is unlikely that new types of components would be trailed on a vehicle and it is only after launch that new types of products that may provide cost and weight reductions are tried out on vehicles during proving ground tests.

Hoods are the simplest closures as they have a small number of parts, no welds or mechanical fastenings between the inner and the outer and reduced structural requirements (when compared with side doors). These attributes make a hood most suitable for manufacturing a low cost aluminium closure as there will be no electrical contact between the steel inner panel and the aluminium outer panel from either weld or mechanical fasteners that would put the component at risk of galvanic corrosion. The large outer panel makes best use of a premium material as there will be little material wasted as scrap during stamping and the weight of a hood out panel made of steel contributes a significant proportion of total weight of all closures on a vehicle. It has also been already proven by Mason (2003) that aluminium closures have been used on other vehicles they can also be designed to meet other crash and pedestrian safety requirement.

The CMax hood is currently an all steel construction, table 2.2 summarises the materials used and figure 2.2 shows the dimensions of the production part. The plan view is the surface area of the hood outer panel including subtraction of the cowl cut outs, headlamp cut outs and the addition of the

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part curvature. The dimensions shown in figure 2.2 will be used to calculate the cost of the closure in this business case.



Figure 2.2 Ford Focus CMax Hood

2.4. Manufacturing Considerations for Low Cost Aluminium Closures

The ability of aluminium to meet the functional demands of closures has been discussed and aluminium is suitable for use as a body closure material. Low cost aluminium closure concept selectively uses pre-coated aluminium as the outer panel for a CMax hood demonstrator and it is the production issues associated with manufacturing a low cost aluminium hood for a Focus CMax that will be discussed here.

2.4.1 Stamping Pre-coated Aluminium

Aluminium can be stamped with the same capital equipment as steel but some modifications to existing plant would be needed to process aluminium alongside steel. Currently steel is handled magnetically from blanking to the final press and assembly operations and magnetic sensors activate some presses and robotic stations. Aluminium would need to be handled by a vacuum system and alternative sensor technology would be required. Jaguar has used this method of handling successfully in manufacturing the XJ. All other body in white assembly processes for simple closures (such as hoods) are compatible with aluminium.

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Pre-coated aluminium has a number of advantages over bare aluminium. Alcan started work on pre-coated aluminium in 1995 and their initial investigations are summarised by Carr et al. (1997). Alcan originally intended pre-coated aluminium to be a replacement for electrocoat paint (e coat) in an all aluminium vehicle. However, as previously discussed all aluminium vehicle bodies are currently only produced by premium manufacturers and it is not economically feasible to produce a vehicle like a Focus CMax entirely from aluminium. As a result an alternative use for precoated aluminium was found by combining it with steel to create a cost effective closure. The low cost aluminium closure concept utilises the unique properties of pre-coated aluminium to successfully produce a mixed material closure.

Pre-coated aluminium has improved formability compared to bare aluminium. Carr et al. (1997) carried out press forming trials and found under deep drawing conditions that the pre-coating allowed for a 35% increased depth to failure. In some cases this may allow pre-coated aluminium parts to be stamped in dies originally designed to stamp steel. Pre-coating the aluminium also improves the flanging (flat hemming) performance.

Aluminium is sensitive to strain rate and as a result must be formed more slowly then steel, Mason (2003) noted that a 35% increase in cycle time is needed to stamp aluminium. Pre-coating the aluminium improves its overall formability but cannot reduce the increased cycle time. The outer panel of a low cost aluminium closure is directly joined to the hot dip galvanised (HDG) steel inner panel with an adhesive bond. The adhesive bonding performance of pre-coated aluminium has been proved by Carr et al (1997) to be excellent both in initial bond strength and durability. The pre-coating is a poly-amide poly-urethane based polymer and it should be compatible with most automotive adhesive systems and application techniques.

Carr et al. (1997) described a number of other benefits of using pre-coated aluminium, including: Reduced tendency for pickup/galling, reduced die

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wear in volume production, reduced contamination of the automotive paint line and reduced emphasis on cleaning prior to painting.

2.4.2 Corrosion Resistance of Low Cost Aluminium Closures

In order to prevent galvanic corrosion occurring between the dissimilar metals it is necessary to have an electrically insulating layer between the two metallic parts and the organic pre-coating can provide an effective barrier against galvanic corrosion. If the metals were to come in direct contact with each other the zinc from the zinc-coated steel would corrode preferentially to the aluminium and then when the zinc had been consumed the aluminium would corrode preferentially to the steel.

Carr et al (1997) amongst others noted the increased cut edge corrosion resistance after painting of aluminium compared to hot dip galvanised steel. Current all zinc coated steel closures have a sealant applied to the exposed cut edge of the outer panel to prevent cut edge corrosion, figure 2.3. This is a difficult, time consuming and costly process but is necessary on steel closures due to the possibility of red rust bleed out from the cut edge onto visible parts of the closure. Red rust bleed out is unacceptable to customers even if it is only a cosmetic corrosion issue. The sealant also prevents fluid such as water from road splash from entering the hemmed area and accumulating in the gaps between the inner and outer panels.



Figure 2.3 Cross Section of a Hem Flange with Over Hem Sealer

The increased stability of aluminium cut edges removes the need for over hem sealer and consequently manufacturing cost and process complexity are reduced.

2.4.3 Painting Pre-coated Aluminium

Aluminium can be painted successfully on conventional automotive paint lines designed to process aluminium. However, only a small amount of aluminium on a predominantly steel vehicle can be tolerated on a steel paint line. A steel automotive paint line consists of many stages but generally includes (as shown by Courval and Shores (1999)): Alkali cleaning, rinse, phosphate, rinse, electrocoat, cure, primer/surfacer, cure, basecoat/clearcoat and a final cure. When processing aluminium through the paint line outlined above a number of problems are encountered:

- The alkali cleaner must have a pH lower than 11.5 to ensure the aluminium surface is not etched during cleaning resulting in dusty phosphate coatings and poor electrocoat adhesion, Osman (2002a). Cleaner concentration may have to increase to effectively remove pre-lubes and dry film lubricants Osman (2002b). Ford alkaline cleaners currently operate at pH 12.
- Aluminium must not be allowed to dry out during rinsing after alkaline cleaning in order to prevent inter-stage drying that leads to patterning in the subsequent painted body, Simpson and Sudour (2004).
- Osman (2002a) and Simpson and Sudour (2004) have reported the requirement for increased zinc phosphate solution flow and increased free fluoride content. This ensures complete phosphate coverage of the aluminium body panel and allows conventional automotive materials (zinc coated steel and cold rolled steel) to phosphate normally.

 Processing aluminium through a zinc phosphate bath generates an increased amount of sludge compared to processing conventional substrates through the same bath. This sludge must be effectively removed from the bath to ensure the sludge does not deposit on horizontal surfaces leading to poor electrocoat appearance and adhesion, Osman (2002a).

Pre-coating aluminium reduces the amount of bare aluminium exposed to cleaning and phosphating processes and this improves the compatibility of the aluminium part with a conventional paint line. Osman (2002a) found that with the modifications listed above up to 30% aluminium by surface area of the vehicle could be processed in a conventional paint line. This would still represent a significant capital investment but as pre-coated aluminium reduces the amount of bare aluminium it becomes more economically viable to manufacture mixed metal closures for vehicles. The concept demonstrator will be painted on a standard production paint line, so the surface area of the hood was calculated from the approximate size of the vehicle and the plan view area of the hood. The percentage area of exposed aluminium (based on a one side pre-coated outer panel) is 1.7%. In the small trial of 5 hoods, especially considering the exposed area was so small it was considered acceptable by the production paint engineers to process the hoods through the existing paint line.

One or two side coated aluminium could be used for a low cost aluminium CMax hood and the cost for one or two side coated material is the same per kilo. Some uncertainty surrounds the use of two side coated material because of its possible response to a production paint system. It has been suggested that any defect on the surface of a two side coated panel exposing bare metal and the exposed cut edges would accumulate excessive amounts of electrocoat paint leading to unacceptable paint appearance. This hypothesis has not been tested and as such a conservative approach would suggest the use of one side coated material to minimise the risk of paint appearance problems. However, in the course of this research a two side coated material will be examined to assess the

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effects of automotive paint processes on two side coated pre-coated aluminium.

2.5 Cost Model

The low cost aluminium closure concept is based on a pre-coated aluminium outer panel with the pre-coating on the inside of the outer panel, joined to the existing standard production HDG steel inner. All other hood components including hinges, strikers and reinforcements are carried over from the current production CMax hood. The manufacturing process for the hood demonstrator is outlined in section 6.5. The current outer panel material is 0.65 mm thick and in order to meet the same dent resistance requirements the aluminium outer panel must be a minimum of 0.81 mm thick AA6016 (calculation shown above), in order to maintain a margin of safety a 0.9 mm gauge sheet would be recommended to account for the variations in bake response in the paint ovens.

Materials and Processes	Low Cost Aluminium CMax
	Hood (€)
Outer Panel	9.61
(Cost reduction opportunity from	
replacing Laser Blanking with	
conventional shear blanking)	
Coating	1.61
Carry Over Steel Parts	21.79
Scrap Reclaim	(0.07)
Over-hem Sealer	(2.75)
Forming (35% Increase in Cycle Time at	1.95
€0.83/minute)	
Sub Total	32.14
Current Cost of All Steel Hood	30.42
Cost Difference	1.72
Cost of Low Cost Aluminium Hood	25.54
including 3.3 kg Weight Saving (€2/kg)	
Cost Difference	<u>(4.88)</u>

Table 2.3 Cost Model Summary for Focus CMax Demonstrator


Figure 2.4 Outer Panel Cost Summary

Construction	Weight (kg)	Weight save over an all steel hood (kg)	Cost (€	Differential	Cost adj weight s (€2/kg)	usted for aving Differential
All Steel	11.2	-	30.42	-	-	-
All Aluminium	5.9	5.3	46.54	+ 16.12	34.88	+ 4.46
Low Cost Aluminium	7.9	3.3	32.14	+ 1.72	25.54	- 4.88

Figure 2.4 Weight Reduction and Cost Summary for All steel, All Aluminium and Low Cost Aluminium Hoods

2.6 Business Case Conclusion

The business case detailed above has shown that it is feasible to produce a low cost aluminium CMax hood in a Ford production plant with minimal disruption to current processes. It is necessary to modify the material handling systems used in the press shop and subsequent assembly operations for processing a non-ferromagnetic material. The capital cost of installing new material handling systems and scrap reclaim systems to optimise the price received for scrap would only make low cost aluminium hoods a realistic proposition for a new vehicle line as the in plant modifications would be made when preparing a new vehicle line.

Low cost aluminium closures could be applied on an existing vehicle with an alternative manufacturing process. Jaguar has a press shop designed to stamp aluminium and capacity permitting the outer panel for a low cost aluminium closure could be stamped at Jaguar and then shipped to the appropriate plant for assembly. During assembly it may be possible to make only minor alterations to assembly systems as half the closure is made of steel and ferromagnetic handling systems may be able to cope with the aluminium outer panel.

The business implications of low cost aluminium closures have been investigated and it is possible to produce a low cost aluminium closure economically. The structural and corrosion performance of this closure must now be assessed to prove the closure can meet the performance of the existing all steel closure.

Low cost aluminium closures offer the potential to save €4.85 over the existing closure when taken into account the cost saving associated with weight reduction. The closure demonstrator will save 3.3 kg per vehicle offering the potential to improve fuel economy. As consumers increasingly demand vehicles with additional luxury items such as in car media systems and climate control weight saved from the vehicle body allows additional feature content to be added to the vehicle without reducing performance or

fuel economy. The weight reduction may also allow increased safety features to be added to the vehicle without increasing curb weight. The overall benefits of low cost aluminium closures, including improved corrosion resistance provide a good incentive to incorporate aluminium selectively on mass production vehicles.

3.0 Review of Literature

The main body of this research into low cost aluminium closures can be divided into two sections:

- Corrosion
- Structural Performance of Closures

The cost of corrosion to vehicle consumers in the United States of America is estimated by Johnson (2000) to be \$23.4 billion per year. This annual cost can be divided into three components:

- 1. Increased manufacturing cost due to corrosion resistant materials and engineering (\$2.5 billion)
- 2. Repairs and maintenance necessitated by corrosion (\$6.5 billion)
- 3. Corrosion related depreciation (\$14.4 billion)

Vehicle manufacturers are primarily concerned with issues one and two as these costs directly affect the manufacturer. Part of the cost associated with the repairs and maintenance resulting from corrosion will be paid for by the manufacturer under the terms of a corrosion warranty offered by most manufacturers with the sale of new vehicles. Corrosion related depreciation is also important to manufacturers as it can have a deleterious impact on the brand image of the vehicle maker.

Automotive engineers must have a good understanding of the causes and mechanisms of corrosion in order to minimise the costs incurred from manufacturing corrosion resistant vehicles and warranty payments, when the measures taken are not sufficient to prevent corrosion in service.

The mechanisms and factors affecting corrosion will be summarised and the operating environment for vehicles outlined. The corrosion properties of common automotive materials and component geometries will be described

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with special emphasis on galvanic and crevice corrosion. Finally, a review of current testing procedures will be conducted including the differences between real time and accelerated testing and the difficulties of extrapolating between the two types of tests. Typical car corrosion problems will be described with specific references to corrosion occurring in hem flanges.

The joining method used between the inner and outer panel of the hood to form the hem flange in the demonstrator component is adhesive bonding. The effects of static loading on joint properties will be described in addition to the importance of joint geometry. The durability of adhesive bonds between common automotive materials will be reviewed with emphasis placed on surface treatment and environmental exposure.

3.1 Corrosion

3.1.1 Mechanisms and Factors affecting Corrosion

A comprehensive review of the types of corrosion affecting steel automotive vehicles is given by the Auto/Steel Partnership Light Truck Frame Project Team (2000). The five main types of corrosion that affect automobiles are:

- Uniform or general corrosion is the uniform loss of metal across the whole surface of the component.
- Crevice corrosion occurs in confined spaces where an autocatalytic reaction takes place accelerating the corrosion rate in the crevice. Hospaduk (1981) defined a crevice as having a width of 0.1 mm or less.
- Pitting corrosion involves the breakdown of passive films on metals exposed to chloride ions in solutions. During pitting attack corrosion is highly localised to the pit leaving the rest of the metal surface unaffected.

- Galvanic corrosion takes place between two dissimilar metals, where the most electrochemically active metal becomes the anode and metal dissolves from this surface in preference to the more noble metal. The more widely separated the metals are in the galvanic series the higher the rate of metal dissolution will be on the more anodic metal.
- Cosmetic corrosion is an automotive concept as manufacturers are concerned with corrosion that the customer can see, in addition to corrosion that may affect the structure of the vehicle. Cosmetic corrosion under paint films my take the form of blistering or filiform corrosion (threadlike corrosion trails starting from a defect, such as a stone-chip in a paint film) and will not generally affect the performance of the vehicle, it is however unacceptable to most customers. Bautista (1996) gives a comprehensive review of filiform corrosion.

Fontana (1986a) summarised the factors affecting the corrosion resistance of a metal in a diagram reproduced in figure 3.1. Fontana (1986b) also discusses the importance of environmental effects on corrosion. Electrolyte chemistry affects corrosion due to the power of the oxidising species present, such as hydrogen ions and the presence of other aggressive ions such as chlorides. Aeration of the electrolyte also has an effect on corrosion as oxygen is required in most cathodic reactions, as such velocity of the electrolyte (in systems with flowing electrolytes) is also important if corrosion is under cathodic diffusion control. Any increase in temperature increases the power of the oxidiser and galvanic coupling can also have the effect of increasing the power of the oxidiser as the area for cathodic reactions is increased and in addition some metals will allow easier evolution of cathodic reaction products.





Although corrosion is conventionally viewed as occurring in bulk electrolyte, atmospheric corrosion occurs under thin films of electrolyte. Trethewey and Chamberlain (1995a) state that temperature can affect atmospheric corrosion in two ways. Firstly an increase in temperature increases the reaction rate and approximately a 10 °C rise in temperature doubles the rate of reaction. Secondly, changes in temperature affect relative humidity and can cause dew point condensation.

Condensation can form on all surfaces that are cool enough, both internally and externally causing water droplets to form and collect in water traps within components. This produces pools of free electrolyte where none might be expected and so relative humidity also has an effect on corrosion. The effect of road salt on the relative humidity level required for deliquescence to occur on a metal surface was recorded by Baboian (1981) and is shown in table 3.1. The importance of calcium chloride being present in road salt should not be underestimated as it has a significant effect of lowering both the temperature and relative humidity required for a film of electrolyte to form on a metal.

Temperature (°C)	Critical Relative Humidity for Deliquescence		
	NaCl	CaCl ₂ .H ₂ O	
25	76	30	
10	76	41	
0		45	

Table 3.1 Critical Relative Humidity Required for Deliquescence

Road salt has been used extensively since it replaced abrasives as the primary method of de-icing in the 1950's. Baboian (1981) reported that usually 20 to 25% calcium chloride is added to sodium chloride to increase melting action. Hydrated calcium chloride is more effective for de-icing due to its lower eutectic temperature (-55 °C at 29.8 weight percent), hydrated sodium chloride (NaCl.2H₂O) has a higher eutectic temperature of -21.2 °C at 23.2 weight %. Hydrated calcium chloride ($CaCl_2.6H_2O$) is stable up to 29.8 °C and NaCl.2H₂O is only stable up to 0.15 °C. The lower eutectic temperature is important as this is the point in the phase diagram that the system is liquid, hence why hydrated calcium chloride is a more effective de-icing salt then hydrated sodium chloride. Time of wetness (i.e. the time there is electrolyte present on the metal surface) was found to increase in significantly where calcium chloride is used, since solutions of calcium chloride are readily formed by deliquescence. Hospaduk (1981) observed that time of wetness can influence the adhesion and compactness of the corrosion product film and long time of wetness can lead to loose, porous deposits.

Van de Streek (1985) also noted that road salts are deliquescent and can hold moisture in contact with steel with as little as 30% relative humidity in the presence of calcium chloride. Baboian (1995) revised his initial composition estimate of road salt and stated that that US road salt was approximately 5% calcium chloride in the 1990's. Chlorides are important in corrosion as they increase electrolyte conductivity and act as oxide film disruptors.

In addition to humidity allowing moisture films to form, precipitation has an important role to play in corrosion. Modern vehicles are designed to help prevent water entrapment; however debris such as mud or vegetation can block drain holes and allow water to accumulate. This water arises mostly from precipitation, car washing and road surface spray. Wang et al (2001) found positive correlation between roof top time of wetness and time of wetness inside the door with the inside of the door generally experiencing a higher time of wetness than the roof top. They also observed strong positive correlation between ambient (measured on the roof top) relative humidity and the relative humidity within the door, inside door and ambient relative humidity were broadly the same. A very strong positive correlation was also noted between roof top temperature and temperature within the door, with inside door temperatures being very similar to ambient temperatures. The one year average microenvironment for inside the door was calculated by Wang et al (2000) as an air temperature of 17 °C, relative humidity of 59% and time of wetness of 0.28.

The demonstrator under consideration in this research is a hood, but in general more severe corrosion environments are encountered in other closures with a vertical orientation such as doors and tailgates. The same study by Wang et al (2000) also evaluated under hood microenvironments. Under hood time of wetness was not strongly correlated to roof top time of wetness and the relative humidity under the hood was positively correlated with roof top relative humidity with under hood relative humidity being significantly less than ambient. Under hood time of wetness was not correlated with roof top time of wetness, probably due to most under hood wetness arising from road splash as opposed to precipitation or humidity. The one-year average microenvironment for inside the door was calculated as an air temperature of 35 °C, relative humidity of 27% and time of wetness of 0.17.

As mentioned above the chemistry of the electrolyte is an important factor in the corrosion of metals. In addition to road salt and salt available from coastal environments the chemistry of rain must also be taken into consideration. Baboian (1995) reported that sulphurous and nitrous oxides

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present in the atmosphere (both from natural sources and made-made emissions) undergo hydrolysis and oxidation reactions yielding nitric and sulphuric acid. Acid rain can be distributed over large areas and the synergistic effect of acid deposition and road salt on the corrosion rate was summarised. The combined effect of film disrupting chlorides and the reducible hydrogen ions from acids is more severe than the added separate effects.

Humidity and precipitation are the main sources of electrolytes for automotive vehicles and another possible source comes from the paint process. An automotive paint line consists of many stages nearly all of which are water based in Europe. The vehicle is sprayed or dipped in aqueous solutions to clean, rinse and prepare the surface for paint. A general overview of the automotive paint line is given by Gehmecker (1997).

The first stage of the paint process is degreasing the vehicle body to remove stamping lubricants and handling marks. Ford of Europe uses an alkaline based cleaning solution for this degreasing step. It is approximately pH 12. Trethewey and Chamberlain (1995b) have produced the E/pH (Pourbaix) diagram for zinc in water and it shows that the zinc corrosion product produced in solutions with a pH greater than pH 10 is soluble. Unlike the corrosion product produced at solutions of between pH 8 and 10 that is insoluble and adherent and therefore acts as a passive layer, preventing any further corrosion from taking place. It is possible that some residues may be left in areas of the vehicle after painting has been completed leading to electrolytes with an unfavourable pH. It should be noted that Pourbaix diagrams should be used cautiously as they do not take into account the kinetics of the corrosion reactions.

Rowe (1977) describes the corrosion of metals as essentially an electrochemical phenomenon and corrosion occurs because of an electrical current passing between two metal sites. In order for this to happen there must be a metallic conduction path and a conductive liquid. He goes on to say that the two metal sites must be at different potentials to produce a

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driving force for current (electron) flow. The site at which metal dissolves (oxidation) is referred to as the anode and the site where the electrons are consumed (reduced) is the cathode. Both oxidation and reduction reactions must take place for corrosion to occur. This condition can be satisfied either between two sites on the same metal or between separate pieces of metal connected through external contacts. Figure 3.2 shows a basic wet corrosion cell adapted from Rowe (1977). The most common reaction occurring at the anode is metal dissolution as shown in reaction [3.1]:

 $M \rightarrow M^{z+} + ze^{-}$

Where z is the valence of the metal atom, z = 1, 2, 3.

The most common reaction occurring at the cathode in acidic solutions is the reduction of hydrogen ions to hydrogen as shown in reaction [3.2]:

$$2H^+ + 2e^- \rightarrow H_2$$
 [3.2]

In neutral and alkaline solutions dissolved oxygen is reduced to form hydroxide ions as in reaction [3.3]:

$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$	[3.3]
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An important point to draw from figure 3.2 is the current flow from the anode to the cathode. In this thesis the direction of current and electron flow will be considered to be the same.

[3.1]



Figure 3.2 Basic Wet Corrosion Cell (Rowe (1977))

Paint is one of the methods automotive manufactures protect vehicle bodies from corrosion. Mattssonn (1996) provides a good summary of other measure used to prevent and reduce corrosion on automobiles. Firstly manufacturers select zinc coated steel for the vehicle body panels as a metal coating which is less noble than the substrate (such as zinc) provides cathodic and barrier protection for the base metal. Cathodic protection is most effective in electrolytes of high conductivity. In atmospheric conditions zinc is seldom effective over distances greater than 1 mm. It should be noted that zinc provides cathodic protection for steel at temperatures below 50 °C because at temperatures exceeding 50 °C the standard electrode potentials of steel and zinc reverse i.e. steel becomes cathodic to zinc. Three types of zinc coated steels are commonly used by auto manufacturers:

- Electrolytic zinc coated steel (EZ) Thin zinc coating (less than 20 μm, typically 10 μm), 1 or 2 side coated with low porosity, good formability and weldability. Current distribution issues can mean plating complex parts and edges is difficult.
- 2. Hot dip galvanised steel (HDG) Thick zinc coating (20 25 µm per side). Only two side coating available as steel sheet is run continuously off the coil into a molten zinc bath and the coating is trimmed to the correct thickness with gas knives. HD generally has lower base steel formability than EZ and HD as the steel is submerged in molten zinc at 450 °C and on removal from the zinc bath the steel substrate can suffer from quench aging (Townsend and Allegra (1981))
- Glavannaelled zinc coated steel (GA) Heat treated EZ to form an intermediate Fe-Zn alloy between the zinc layer and the steel substrate. GA has improved formability and weldability over EZ due to heat treatment stage.

The next stage of corrosion protection is applied on the automotive paint line. After cleaning the vehicle body in an alkaline bath the metal is submerged in a zinc phosphate bath. Zinc phosphate crystals form on the metal surface and in addition to adding more zinc to the zinc coated steel the phosphate coating provides an excellent base for subsequent paints to adhere to.

After phosphate, cathodic electro paint is applied by submerging the vehicle body in a tank of electrocoat (e coat). E coat penetrates hollow sections and parts of the body that would be difficult to paint electrostatically. Following e coat, sealers and cavity waxes are applied to selected cut edges and hollow sections. Electrostatic primer and top coat are then applied to the vehicle as the final layer of corrosion protection.

3.1.2 Corrosion Properties of Common Automotive Materials

Zinc coated steel

Vehicle bodies are still primarily metallic. Tiburcio and Yergin (2003) reported that prior to 1977 cold rolled steel was mostly used for vehicle bodies. In the mid 1980's coated steel was introduced and by the mid 1990's nearly all vehicle bodies were made from coated steel. Automotive manufacturers have extensively used zinc coated steel to reduce the impact of corrosion on vehicles. In 1998 three hundred and eighty six vehicles were evaluated for corrosion defects (blistering, perforation and red rust) of those 204 were manufactured between 1991 and 1992. 64% of vehicles made 1991-92 had a corrosion imperfection, compared to the survey undertaken in 1993 of vehicles made between 1986 and 1987 where 91% of vehicles had an imperfection. Most significantly the percentage of vehicles observed with a perforation halved from 16% to 8% between the 1993 and 1998 study. The authors attribute this performance improvement to the extensive use of zinc coated steel.

Automotive manufacturers use many different types of zinc coatings on steel. European manufacturers use mostly hot dip galvanised zinc coated steel (HDG) in conjunction with smaller amounts of electroplated zinc coated steel (EZ) and galvannealed steel (GA) and American manufacturers tend to prefer EZ and GA as it has improved formability, weldability and historically EZ and GA products have been lower cost in the US than in Europe.

An extensive survey of corrosion rate data presented in the literature is given by Zhang (1999) for zinc, steel and zinc coated steel. The corrosion rate of steel in atmospheric conditions is approximately a factor of ten higher than the corrosion rate of zinc under the same conditions. The analysis also examined the corrosion rates of zinc in soils and seawater and the author concluded that it was most beneficial to use zinc coatings for the corrosion protection of steel in atmospheric environments. Mattsson (1996) reported the corrosion rates of zinc coatings in various environments,

reproduced in table 3.2. The values reported in table 3.2 concur with the conclusions drawn by Zhang (1999) as the corrosion rates seen in rural and marine environments are significantly lower than those seen in submerged conditions.

Environment	Approximate Corrosion Rate (µm/year)
Rural	0.5-1
Urban or Marine	1-10
Marine	0.5-2
Indoor	<0.15
Fresh Water	2-20
Sea Water	10-25
Soil	5
	(Sometimes higher depending on soil chemistry)

Table 3.2 Approximate Corrosion Rates of Zinc Coatings

The corrosion mechanism for zinc exposed to the atmosphere is described by Falk et al (1998) for open specimens of electrolytic grade zinc. The authors found that CO_2 slowed down the corrosion rate of zinc in the presence of NaCl by a factor of three to six. This was explained by the neutralisation of the surface electrolyte resulting in the precipitation of the chloride ions in solution in the form of simonkolleite ($Zn_5(OH)_8Cl_2.H_20$). Simonkolleite forms by the reaction of chloride with ZnO, releasing hydroxide ions:

$$5ZnO(s) + 2Cl^{-}(aq) + 6H_2O \leftrightarrow Zn_5(OH)_8Cl_2.H_2O(s) + 2OH^{-}(aq)$$
 [3.4]

As carbon dioxide dissolves the electrolyte pH will decrease and therefore reaction [3.4] will be forced to the right and simonkolleite will be formed consuming chloride ions. Simonkolleite was not found to be protective under atmospheric conditions containing sulphur dioxide. In a NaCl electrolyte but in the absence of CO_2 ZnO is formed along with some simonkolleite precipitating close to the anodic sites.

The mechanism noted by Falk et al (1998) was concurred by Zhu et al (2000) on open specimens. Zhu et al (2000) and Zhu et al (2001) also investigated the corrosion products formed on confined zinc and electrogalvanised steel substrates.

Zhu et al (2000) examined the effect of periodic wet dry conditions on the corrosion products formed on confined and open zinc surfaces. The specimens were dipped in 1 wt% NaCl solution for one hour followed by either 0, 5 or 23 hours of drying time at 25 °C and 50% RH. The authors discovered as drying time increased on open specimens more simonkolleite was formed on the substrate surface. This observation can be explained by the thinning of the electrolyte film with increasing drying time and the rate of dissolution of CO_2 increasing with the reduction in electrolyte film thickness. Also, as the film thins the chloride concentration will increase allowing equation [3.4] to progress to form simonkolleite. The effects of drying time on confined zinc surfaces with varying crevice width were also observed.

Crevice corrosion is a severe localised corrosion phenomenon and a general definition of crevice corrosion is given by Trethewey and Chamberlain (1995c): as the attack, which occurs because part of the metal surface is in a shielded or restricted environment, compared to the rest of the metal which is exposed to a large volume of electrolyte. Dissolved oxygen required for the cathodic reaction to take place [3.5] is in short supply in the crevice. Aggressive chloride ions are drawn from the bulk electrolyte (available from de-icing salts and coastal atmospheres) to balance positive metal ions from the anodic reaction [3.6]. Metal and chloride ions react with water as in [3.7] and the hydrogen ions generated then accelerate metal dissolution further. Hospaduk (1981) reported pH values a low as 3 in crevices and noted that low pH and high concentrations of chloride ions would destroy any passive film normally present on the metal surface.

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$$
 [3.5]

$$M \to M^{z+} + ze^{-}$$
[3.6]

 $M^{z_{+}} + H_2O \rightarrow MOH^{(z_{-1})} + H^+$ [3.7]

The confined surfaces examined by Zhu et al (2000) can be considered to be crevices. The authors proposed a three stage drying mechanism for a crevice:

- Stage 1: The first phase lasts for the first several hours of the drying stage, during which the zinc surface is completely covered by chloride containing electrolyte. The electrolyte film was thick leading to a situation similar to complete immersion.
- Stage 2: The electrolyte layer reduces in thickness and becomes saturated with CO₂. This together with the high chloride concentrations inside the crevice (as noted by Trethewey and Chamberlain (1995c) above) provided favourable conditions inside the crevice for high corrosion rates.
- Stage 3: With extended drying times it is likely that the thin electrolyte film allowed oxygen to diffuse into to the crevice and into the electrolyte. The high corrosion rate would mean a high rate of oxygen reduction at the cathodic sites, generating large amounts of hydroxide ions and in the presence of CO₂ the ZnO would form zinc hydroxycarbonate (hydrozincite) as in reaction [3.8]. Small amounts of simonkolleite were formed at the anodic (pits) sites but generally the pH was too high (at approximately pH 10) for simonkolleite to be stable.

 $5ZnO(s) + 2CO_3^{2-}(aq) + 5H_2O \leftrightarrow Zn_5(OH)_6(CO_3)_2 + 4OH^{-}(aq)$ [3.8]

A crevice width of 0.25 mm was found to have the highest corrosion rate of the confined zinc specimens, more hyrdozincite was formed on the 0.25 mm crevice specimens than simonkolleite compared to crevices larger than 0.25 mm where the result was reversed. This is due to the increased drying rate favouring simonkolleite formation on the wider crevice specimens. As the crevice width decreased from 0.25 mm to 0.05 mm the authors observed more simonkolleite forming on the zinc surface. In a narrow 0.05 mm crevice is high and the diffusion of oxygen into the crevice is

slow, limiting the cathodic reaction that releases OH^- ions. As a result reaction [3.4] favours the formation of simonkolleite.

The effect of increasing chloride concentration was investigated and the quantity of simonkolleite increased with increasing chloride content. More simonkolleite formed on the confined specimens than the equivalent open specimens.

Zhu et al (2001) extended their investigations to electrogalvanised steel for open and confined specimens. The corrosion products formed on electrogalvanised steel surfaces in confined specimens were different to those formed on pure zinc surfaces of confined specimens. In general more zinc oxide and less simonkolleite were formed on the electrogalvanised steel. This can be explained by the high corrosion rate present in the crevice completely dissolving some sites of the zinc layer exposing bare steel. The exposed bare steel sites then acted as cathodes and the oxygen reduction reaction given in equation [3.5] occurred at a high rate generating a high pH. The high pH favoured the formation of zinc oxide as simonkolleite is not stable at high pH levels.

Following on from the work by Falk et al (1998) and Zhu et al (2000 and 2001), the next step in the corrosion mechanism shown by zinc coated steel substrates once red rust has started to form was investigated by Jordan et al (1996). They examined the contributions of several cathodic reactions to the anodic dissolution of electrogalvanised steel. The authors showed that the dominant cathodic reaction occurring on electrogalvanised steel with some red rust was the reduction of γ -FeOOH to Fe₃O₄ by the Evans reaction shown in reaction [3.9].

$$Fe^{2+}(aq) + 8FeOOH + 2e^{-} \rightarrow 3Fe_{3}O_{4} + 4H_{2}O$$
 [3.9]

This reaction [3.9] does not require oxygen to progress, once the iron oxyhydroxide has formed. Therefore, corrosion can continue in limited oxygen electrolytes. Reaction [3.9] is reversible as shown in reaction

[3.10] and upon drying Fe_3O_4 converted to FeOOH which provides a fresh supply of FeOOH to act as a cathode during subsequent wet cycles.

 $4 \text{ Fe}_{3}\text{O}_{4} + \text{O}_{2} + 6\text{H}_{2}\text{O} \rightarrow 12\text{FeOOH}$ [3.10]

<u>Aluminium</u>

Aluminium is generally regarded to be a corrosion resistant material in automotive environments, as observed by Brown et al (1998) on an extensive field study of vehicles up to 42 years in age. They reported that the corrosion performance of steel was clearly superior to that of steel.

Automotive manufacturers are currently using 6xxx and 5xxx series alloys for closures. 6xxx series alloys are alloyed with magnesium and silicon and 5xxx series alloys are alloyed with magnesium. Both 6xxx and 5xxx series alloys contain small amounts of other alloying elements, such as copper and manganese (Davies (2003)). 6xxx series alloys are favoured for outer panels as they do not show signs of Lüders bands (as 5xxx series alloys do at low elongations) on the surface of the panels that would show through paint and give a cosmetic appearance issue. 5xxx series alloys are used for inner panels and non-visible parts where high formability is required. It is well known that copper alloying additions can cause corrosion issues on aluminium alloys, copper additions increase the susceptibility of an alloy to filiform corrosion.

Ramamurthy et al (2005) analysed the corrosion products of aluminium closure panels a number of laboratory salt spray tests. The aluminium closure panels were treated with zinc phosphate, e coat, primer, basecoat and topcoat and scribed through to base metal prior to testing. The authors observed that no zinc remained on the surface of the aluminium at the scribe marks, however phosphorous was detected. This indicated that the zinc had preferentially dissolved leaving the phosphate ions behind. Chlorine was also detected in the scribes showing the importance of chloride ions in the mechanism of filiform corrosion. It was also noted that filiform corrosion was intergranular in nature and when filament cracks coalesced

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the grain surrounded by the filaments lifted off embedding in the corrosion product.

Colvin et al (1997) examined the importance of surface preparation on the prevention of filiform corrosion. Dry sanding with 150 grit aluminium oxide sand paper was found to greatly increase the susceptibility of the substrate to filiform corrosion especially in alloys containing copper. The effect of climatic parameters on filiform corrosion were examined by LeBozec et al (2004). Filiform corrosion was found to be highest in the range 75% to 95% RH but was observed propagating at relative humidity's as low as 40-50% RH. Titanium-zirconium pre-treatments were found to have very poor filiform corrosion resistance compared to conventional chromate or phosphate based systems in cyclic tests. Filiform corrosion (FFC) has been found by Zhou et al (2003) to be controlled by the near surface microstructure. They found that heavy deformation, fine grains and dispersed particles promote FFC. Removal of these surface features provides significant resistance to FFC.

Leth-Olsen and Nisancioglu (1998) observed the effects of an annealed surface on FFC on a painted aluminium sheet. They found the annealed surface to be reactive and this increased susceptibility to FFC. Increasing the iron content in the alloy also increased susceptibility to FFC. Removal of 1 μ m of the surface resulted in improved resistance. They found that directionality of the filaments could be attributed to the rolling topography. FFC often initiates at free edges and then growth continues under the paint film or coating in characteristic pattern. Hunter and Barlow (2002) investigated cut edge effects on the Ti/Zr electrocoat replacement pretreatment; they observed no edge or filiform corrosion, showing the coating has excellent adhesion to the substrate.

3.1.3 Hem Flange Corrosion

The geometry of the hem flange is represented schematically in Figure 3.3. The gaps between the inner and outer panel can be very small and result in a crevice geometry. Many authors have observed that decreasing the crevice width increases the rate and severity of corrosion. Nakazawa et al (1993) investigated the corrosion performance of a hem taken from a 7.5 year old vehicle which had been in service in North America. The door was sectioned and the sections ranked in order of the severity of corrosion. The authors identified the path of corrosion in a conventional all zinc coated steel hem.

Typically outer panels and inner panels are between 0.6 and 1.5 mm thick depending on the material and application. Hem flange joints in all steel closures are termed flat hems as they are formed around 180 degrees so the gaps between the inner and out panel are typically small (less than 0.25 mm). The adhesive should fill the hem flange joint and can be either a one or two part adhesive, most adhesive formulations are suitable for use as hem flange adhesives.



Figure 3.3 Schematic of an All Steel Hem Showing Inner and Outer Gaps

Nakazawa et al (1993) found that corrosion initiated at the inner panel [1] of the inside gap (figure 3.4) and then jumped to the outer panel of the inside gap [2]. Then, passing through the bottom of the two gaps the corrosion propagated to the outer gap. In the case of the hem examined in this study no adhesive was applied in the inside gap, but adhesive was applied to the outside gap.



Figure 3.4 Corrosion Path in a Hem Flange

The corrosion process proposed was the zinc coating first becoming damaged and then transformed to oxide. Iron oxide was also detected and the corrosion products were partially chlorinated. These corrosion products correlate well with the corrosion products observed by Zhu et al (2000 and 2001) and Falk et al (1998). In the crevice of the hem it is likely that the pH was too high for simonkolleite to form during the many wet and dry cycles the hem would have experienced during its service life. When bare steel was exposed at the anodic sites red rust would have formed changing the cathodic reaction to the Evans reaction shown in reaction [3.9], this would account for the iron oxide found by the authors and finally the chlorinated oxides could have formed at a later stage when the pH had fallen during a wet cycle. The authors noted that the presence of chloride ions changed the corrosion path and that corrosion was heavier under a drain hole. They attributed the increase in corrosion by the drain hole to the water path that was formed to the drain. It is more likely that the drain

hole allowed for a faster drying time and as previously noted a faster corrosion rate due to electrolyte thinning.



Figure 3.5 Specimen Set Up for Lapped Panels used by Nakazawa et al (1993)

Lapped panels can be used to form simulated hem specimens and are very effective at forming crevices. Lapped panels of electrogalvanised steel were used by Nakazawa et al (1993) to determine the effects of drain hole and crevice width, specimen set up is shown in figure 3.5. It was observed that the corrosion products on specimens with a wider crevice and a drain were "spot-like", indicating more localized corrosion. On specimens with a narrower crevice and specimens with a wider crevice and no drain resulted in uniform corrosion.

Spot welded lap joint specimens were made from electrogalvanised steel and galvannealed steel and exposed to salt spray by Almeida and Morcillo (2000 a and b), specimen shown in figure 3.6. The authors found that initially corrosion products formed at the upper entrance of the lap joint, with a tendency to fill the entrance. Humidification of the entrance lead to the motion of chloride ions into the crevice, then the specimens behaves as a conventional crevice with the oxygen and air at the entrance allowing relatively protective zinc corrosion products such as hydroxycarbonates and oxyhydroxides to form. The acidification of the inner part of the lap joint as a result of anodic dissolution producing H⁺ ions draws chloride rich media into the crevice. The chloride ions react with the zinc coating to form

simonkolleite. At the center of the joint very severe corrosive attack was observed, shown on figure 3.6 by the area of high chloride concentration.

Galvannealed steel proved to be more resistant to crevice corrosion than electrogalvanised steel and this was thought to be due to the less amphoteric nature of the Fe-Zn coating providing buffering capacity in the alkaline regions adjacent to cathodic sites. Although the corrosion propagation step was slower for galvannealed steel the corrosion products formed were found to be the same as those on electrogalvanised steel.

The corrosion products formed in this study are slightly different to those previously reported on confined specimens because there was no drying time and therefore the pH did not significantly increase allowing simonkolleite to remain stable in the crevice. Townsend (1996) found that electrogalvanised steel had increased crevice corrosion performance compared to aluminium.



Figure 3.6. Spot Welded Lap Joint Specimen used by Almeida and Morcilo (2000 a and b) with Corrosion Mechanism.

The corrosion path noted by Almeida and Morcilo (2000 a and b) was partially concurred by Miki et al (1989). They found the peak corrosion depth was located at the top of the lapped panel. The samples were exposed to a salt spray solution of 5% NaCl once a week for two years. Compared to the continuous salt spray exposure experienced by the spot

welded lapped specimens the peak corrosion depth measured would really only correlate with the initiation stage on the spot welded lapped specimens.

3.1.4 Galvanic Corrosion

_ .. _

Bimetallic corrosion (also known as galvanic corrosion or dissimilar metal corrosion) occurs when two metals with different potentials, are in electrical contact while immersed in an electrically conducting corrosive liquid. When a metal is immersed in a conducting liquid it takes up an electrode potential (also know as the corrosion potential or the open circuit potential). This is determined by the equilibrium between the anodic and cathodic reactions and is usually measured with reference to a standard electrode such as the standard calomel electrode (SCE). As the two metals have different natural potentials in the liquid, a current will flow from the anode (more electronegative) to the cathode (more electropositive) and will increase the corrosion on the anode.

A galvanic series of metal can be drawn up when the potentials of the metals of interest are measured in the same known solution. Commonly sea water is used as an electrolyte for drawing up a galvanic series. Table 3.3 gives a summarized galvanic series for automotive metals from Trethewey and Chamberlain (1995d). The ranges given illustrate how different alloy compositions, heat treatments and processing characteristics can affect the free corrosion of a metal.

Metal	Free Corrosion Potential vs Standard
	Calomel Electrode (SCE) (V)
Magnesium	-1.6 to -1.64
Zinc	-1.0
Aluminium Alloys	-0.75 to -1.0
Low Alloy Steel	-0.575 to -0.625
Stainless Steel	-0.15 to -0.35

Table 3.3 Galvanic series for some automotive metals in sea water (summarized from Trethewey and Chamberlain (1995d))

Galvanic corrosion can be prevented as the system is essentially a basic wet corrosion cell. Except, in galvanic corrosion the anodic and cathodic reactions occur on different metals. National Physical Laboratory (2000) states methods of prevention as breaking the electrical path in the metallic or electrolyte parts of the system, by excluding oxygen from the electrolyte, adding corrosion inhibitors to the electrolyte or by sacrificial protection.

A bimetallic system in an automotive vehicle body could consist of a number of different material combinations: cold rolled steel coupled to zinc coated steel, cold rolled steel coupled to aluminium and zinc coated steel coupled to aluminium. Vincent and Coon (1986) gave the galvanic series of various metals and alloys exposed to sea water. From that series zinc is anodic to electrogalvanised steel and electrogalvanised steel is anodic to aluminium. Cold rolled steel is the least active of common automotive materials in a bimetallic couple.

Area ratios (total exposed area of anode : total exposed area of cathode) between the anodic and cathodic metals have an important effect on galvanic corrosion. Mansfeld (1971) examined the effect of area ratios on three theoretical cases. He concluded that in metals that are widely separated in the galvanic series the only significant process occurring on the active (more electronegative) metal is anodic dissolution and the only process occurring on the more noble metal is reduction of the oxidser. In this case the galvanic current density will give an exact value for the dissolution rate of the metal. The galvanic current or the galvanic current density depends upon the area of the anode, or the cathode or the area fraction given in equation [3.11].

$$A_{A} = A^{A} / A^{C} + A^{A}$$
[3.11]

Where A_A is the anodic area fraction, A^A is the anodic area and A^C is the cathodic area.

The second case examined concerns metals separated only by a small potential. Tafel behavior is not observed in these cases and the galvanic current density is always smaller than the dissolution current density of the anode. However, a correlation between both quantities does exist.

The third case assumes that the corrosion rate of the anodic metal is controlled by the diffusion rate of the oxidizer (normally oxygen) to the surface of the anodic metal. For this case the catchment principle is derived according to which the dissolution rate of the anode in the galvanic couple is directly proportional to the area of the cathode. The measurement of galvanic current density will also result in a value which is smaller than the dissolution current density of the anode.

Mansfeld and Kenkel (1975) went on to study the effect of solution composition on the galvanic corrosion of aluminium alloys. They reported that electrochemical studies of galvanic corrosion initiated in 3.5% NaCl solution could be extended to electrolytes of lower conductivity such as tap water or distilled water without experimental difficulties. Chloride ions can act on aluminium alloys to maintain the potential of the aluminium alloy at the pitting potential which is only slightly more noble than the corrosion potential. In the absence of chlorides or at low chloride levels the aluminium potential can move in the more noble direction. An experimental study of the area ratio effects on aluminium alloys was completed by Mansfeld and Kenkel (1975) and the experimental results confirmed the mixed potential theory results from Mansfeld (1971).

Gao et al (2002) measured the galvanic corrosion rates on two galvanic couples and found that zinc/cold rolled steel couples corroded three to four times faster than aluminium/cold rolled steel couples. It is well known electrochemical theory that galvanic corrosion rates between metals closer in the galvanic series would not be as great as those with greater differences in potentials. In a previous publication (Gao (1999)) examined the effect of sodium chloride concentration on the galvanic current between a steel and aluminium couple. Increasing the chloride concentration increased the galvanic corrosion current of the aluminium/cold rolled steel

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couple. Temperature increases also increased the galvanic corrosion current.

The galvanic corrosion resistance of aluminium alloys coupled to electrogalvanised steel was found to be superior to aluminium/cold rolled steel couples by Townsend (1996). The effect of increased chloride concentration on the galvanic current was also noted to increase. Jordan (1990) found that the galvanic corrosion rate of zinc was higher when coupled to iron corrosion products than when coupled to bare steel.

Isaac and John (1990) observed an additional feature of zinc coated steel/cold rolled steel couples. They noted that during paint pre-treatment with zinc phosphate solution the zinc phosphate deposited preferentially on the zinc coated steel leaving the cold rolled steel less protected by phosphate. As phosphate is used to improve paint adhesion the bimetallic couples induced premature failure of the paint systems on the cold rolled steel side of the couple. They proposed that pre-phosphating the zinc surface could reduce this problem.

The performance of aluminium in bimetallic assemblies was evaluated by King et al (1975). The authors noted the importance of area ratio effects and the type of environment, they were especially concerned with chloride containing road splash. They did propose a number of solutions to galvanic corrosion in automotive bodies and found that sealant tapes, gaskets, transition materials (good reviews of using transition materials to join dissimilar metals are given by Baboian and Haynes (1976 and 1993)) and zinc chromate primers (significant amounts of zinc chromate primers are no longer permitted in European vehicles due to the End of Life Vehicle Directive). Most of all the authors observed that proper design and selection of insulating materials could prevent galvanic corrosion from occurring in automotive bodies.

3.1.5 Accelerated Corrosion Testing

The purpose of accelerated corrosion testing is to subject materials, components and even whole vehicles to a corrosion environment that allows a life time of normal exposure to be experienced in a much shorter time. Manufacturers are caught between two conflicting demands: the need for reliable in service corrosion data and the program production requirement that means you cannot run a vehicle in the field for twelve years to see if it corrodes before you build it. As a result many accelerated corrosion tests have been developed to assess the corrosion resistance of automotive materials and vehicles in a relatively short space of time. Wang et al (2000) discussed the continuing search for a predictive computer program that could take into account vehicle materials, designs, operating environments and corrosion mechanisms and give an accurate estimate of corrosion initiation times and metal loss over the vehicle life time. Currently such a program is still the "Holy Grail" of vehicle corrosion engineering and so accelerated tests are still very much required to give an estimate of material, component and vehicle corrosion resistance.

It is not the purpose of this literature review to describe in detail the many accelerated tests available or to evaluate the effectiveness of each of the individual tests. General conclusions will be drawn on the benefits of accelerated testing and the issues accelerated testing can raise.

Many groups have worked on developing accelerated tests that correlate well with in service environments and a review of the development of accelerated test methods for pre-coated sheet materials is given by Boelen et al (2003) based on environments encountered in the building industry. Although not directly relevant to the environments encountered by automotive vehicles the authors note that it is imperative that the corrosion mechanisms of materials are understood in natural conditions so that similar corrosion mechanisms can be replicated in accelerated tests.

Townsend and McCune (1997) and Townsend et al (1999) have made significant contributions to the development of an improved accelerated test for cosmetic corrosion; this test became SAE J 2334. During the development of SAE J 2334 good correlation between on vehicle specimens in Canada and accelerated test specimens was observed. Townsend et al (1999) extended this work to US on vehicle tests and found the US corrosion environment in Pennsylvania, Michigan and Ohio were found to be half as severe as the Canadian corrosion environment. In conclusion SAE J 2334 correlates well with Canadian on vehicle environments but not North American Snow Belt environments. This highlights the difficulty of assessing the corrosion performance of materials from accelerated test results.

It should be noted that accelerated testing when performed correctly can give valuable information about the ranking of materials in terms of their corrosion performance. Davidson et al (2003) documented the effect of a number of accelerated tests on a confined specimen. The authors observed that SAE J 2334, GM9540P and Ford APGE (Arizona Proving Ground Equivalent) gave results that were reasonably consistent with on vehicle behavior of autobody steel sheet.

A similar body of work is under way in the aluminium industry with collaboration from many automotive manufacturers by Courval et al (2003) and Bovard et al (2005). Initial tests are showing some signs of correlation between on vehicle tests and the accelerated tests. Most of the accelerated tests being examined were originally designed to assess the corrosion resistance of coated steel products and as such their suitability to assessing aluminium is limited. This point was noted by Corval and Allin (2000) in a precursor paper to those mentioned above.

The main factors used to accelerate corrosion in accelerated laboratory corrosion tests are:

- Concentration of NaCl
- Temperature
- Humidity
- Surface preparation
- Other aggressive chemicals such as SO₂, HCl and NO₂
- Wet/dry cycling

From previous discussions above the importance of chloride concentration in corrosion mechanisms has been seen especially in the formation of simonkolleite in preference of the more protective zinc oxyhydroxides and hydroxycaronates. Temperature increases the rate of reaction by increasing the solubility of aggressive ions and their mobility in the electrolyte. Increased humidity allows a film of electrolyte to form on surfaces that would not necessarily be susceptible to corrosion in the field. Surface preparation of test specimens can accelerate corrosion, for example it has been reported above that sanding aluminium increases susceptibility to filiform corrosion. Introducing other aggressive chemicals into the accelerated corrosion environment such as inorganic acids may result in unrepresentative film disruption. In addition sulphur and nitrous oxides may not react in an accelerated test the way they would in the atmosphere.

In conclusion, great care should be taken when assessing accelerated test results. As discussed by many authors the factors accelerating the tests may exploit a different corrosion mechanism to those occurring in the field. However, in some situations accelerated testing can provide valuable information on corrosion rate in the field.

3.2 Structural Performance of Closures

3.2.1 Single Lap Shear Joints

Closures are made from inner and outer panels adhesively bonded together at the hem flange as shown in Figure 2.3. The inner and outer panel are made from sheet material which is usually less than 1 mm thick. Many automotive manufacturers choose to test the performance of their substrates, adhesives and surface preparations on single lap shear joints. The thin substrates and the shear and peel loading that may be seen in service make this joint geometry particularly suitable. In addition, single lap shear joints are quick, simple and cheap to assemble and test in large numbers, allowing many test variables to be assessed efficiently. Figure 3.7 shows the geometry of single lap shear and modified peel joints using dissimilar substrates. Peel tests are also performed in the automotive industry to discriminate between surface conditions and assess surface degradation after environmental exposure. It is thought that during crash the joints within closures are subjected to high peel loadings.

The initial work done by Volkerson (1938) and Goland and Reissner (1944) has been extended by many authors in recent years. With the advent of cheap and readily available computing power finite element methods (FE) have been used extensively to further the understanding of the stress distributions in adhesive joints. Goncalves et al. (2002) used interface elements in conjunction with brick elements to calculate the stresses at the interfaces between the adherend and adhesive. They considered the interface between the adherend and the interface to be a critical region in the structure. Their analysis showed the three-dimensional nature of the stresses within a single lap shear joint and that stresses at the interface were much higher than in the middle of the joint. By considering the plastic deformation of materials in the joint they demonstrated that the stress concentrations in the critical regions were reduced. Perhaps the most important contribution from this work is the need to consider the three-

dimensionality of the stresses in the joint and hence use strength predictions from bi-dimensional models with care.

A schematic representation of the peel and shear stresses within a single lap shear joint were presented by Ciba-Geigy (1989) and reproduced here in figure 3.8. As discussed above a single lap shear joint experiences a combination of shear and peel stresses and the peak stresses operate at the ends of the overlap. The peel stresses act at right angles to the joint and are at a maximum at the ends. The shear stress varies along the length of the joint and also reaches a peak at the ends of the overlap.



Figure 3.7 Single Lap Shear and Modified Peel Joints

When low modulus adherends are used in a single lap shear joint the adherends will bend as shown in figure 3.8 as a result of eccentricity of the load path i.e. the joint will align along the axis of loading. Eccentricity in single lap shear joints can be avoided during testing by using spaces (tabs)

of equal thickness to the adherend plus the adhesive bond gap. This is not always feasible as tabs can slip under high loads and tabbing specimens is very time consuming. If tabs are not used the peel stresses at the ends of the overlaps will be higher than in equivalent tabbed specimens due to load path eccentricity and this may give unrepresentative test data.



Figure 3.8 Shear and Peel Stress Components of the Stress Distribution in a Single Lap Shear Joint

Lees (1981) found that for a toughened epoxy/steel single lap shear joint the peel strength increased with increased bond line thickness and the shear strength decreased with increasing adhesive thickness. The joints tested had adhesive bond lines between 0.050 and 0.5 mm and a schematic graph of the results is shown in figure 3.9.

Chiu and Jones (1992) examined the effect of adherend thickness and adhesive layer thickness on the stress distribution in a thin adhesive layer. They confirmed the original findings that high normal stresses exist close to the ends of the overlap and that the stress concentrations at the end of the

overlap can be reduced by increasing the thickness of the adherend or increasing the thickness of the adhesive.





Lang and Mallick (1998) investigated the effects of spew geometry on the stresses in a single lap joint using linear two-dimensional plane strain FE analysis. Although a standard single lap shear specimen is far from being in plane strain the research did support observed results. Their study showed that the presence of the spew significantly reduces the stress concentrations and peel stresses at the ends of the overlap. They also found that the larger the spew and the smoother the transition in the joint geometry the greater the reduction in the peak stresses.

It is now a well accepted fact that some of the highest stresses in an adhesive joint exist at the ends of the overlap. A study by Pires et al (2003) investigated the effects of applying adhesives of different stiffnesses along the length of the overlap. They applied a stiff adhesive in the middle portion of the overlap, while a low modulus adhesive was applied at the ends of the overlap. The low modulus adhesive was applied to overcome the high peel stresses and resulting stress concentrations encountered at

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the ends of the overlap. Results showed an increase in strength of the biadhesive joint compared to joints with a single adhesive applied over the whole overlap length.

Fracture mechanics can be used as a complimentary approach to the more traditional stress analysis methods. Chow and Woo (1985) have used FE methods to gain an understanding of the localised stress distributions arising from internal flaws along the bonded layer. It was observed that a flaw in the central portion of the bonding length would not reduce the fracture strength significantly. However, a flaw located near the lap ends can cause a marked reduction in the fracture strength. As it is at the ends of the overlap that the stresses are highest this is an anticipated observation.

Kafkalidis and Thouless (2002) used a fracture mechanics approach to investigate the effects of geometry and material properties on the fracture of single lap shear joints. They found that plasticity of the adherends was important when the adherends were thin, the yield strength of the adherends was low or the toughness of the interface was high.

The maximum stability of any system is achieved when its free energy is at a minimum, in accordance with the second law of thermodynamics. Considering an adhesive bond as a thermodynamic system Gutowski (1987) proposed that the minimum interfacial energy corresponded to maximum strength and durability. He calculated an energy ratio from the surface energy of the substrate compared to that of the cured adhesive. If this ratio has a specific value the energy is minimised. However, he also found that systems with ratios greater than his specific value still had engineering applications.
3.2.2 Durability

The importance of durability in automotive environments should not be underestimated and Gledhill and Kinloch (1974) were some of the first workers to look at the issues of durability in adhesive systems. They concluded that immersion in water considerably reduces the strength of adhesive joints. The observed mechanism of failure was the displacement of adhesive on the metal oxide surface by water. They also noted that in addition to interfacial failure the adhesive may also degrade in the presence of water and at temperatures above the glass transition temperature of the adhesive the rate of migration through the adhesive will be greatly accelerated. They suggested that using accelerated hot-wet tests to deduce durability may be misleading as other mechanisms other than those operative at room temperature might occur.

Ong et al (1992) also noted the problems of testing for durability; they suggested that the commonly used Boeing Wedge Test was not suitable for assessing joint durability of different surface treatments for the same reasons mentioned above. They considered long term immersion tests more suitable for this role as the operative failure mechanisms would be similar to those encountered in service.

The search for a more realistic technique for comparing the durability of different adhesive and substrate systems led Briskham and Smith (2000) to investigate cyclic stress durability testing. They found that cyclic stress durability testing was very effective at discriminating between different surface treatments in a short time scale. In this type of testing PAA out performed titanium/zirconium (Ti/Zr) based pre-treatments and amino silane coupling agents (which perform well in unstressed testing) responded very poorly to cyclic stress testing.

Kinloch (1987b) used a fracture mechanics approach to predict service life. After environmental exposure a joint will often debond, Kinloch hypothesised that this debond length was equivalent to an environmental crack length. The environmental crack length could then be used to

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calculate a critical water concentration at which this debond or crack would occur and therefore the service life of the bond could be predicted.

The durability of adhesively bonded steel under salt spray and hydrothermal stress conditions was assessed by Fay and Madison (1990). The authors observed that bonds made directly to "oily" steel (which was representative of steel received in plant) performed poorly compared to steel prepared with a good pre-treatment after environmental exposure. It was also noted that simply removing the oil had little or no effect on the performance of the joint. Stress durability testing of joints was found to be very discriminating between different surface pre-treatments, but for joints that survived exposure there was little difference between as made and exposed joint strengths.

It is not only the environment that can affect bond durability. Alloy composition can also be detrimental to durability. Minford and Vader (1974) and Moulds (1984) noted that alloys with a significant magnesium content had the lowest initial bond strength and retained strength after exposure. Lunder et al (2002) also observed the effect of magnesium content on durability in their work on sulphuric acid anodising.

3.2.3 Surface Preparation and Pre-treatment

Surface preparation and pre-treatment are necessary to improve the durability of an adhesively bonded system. A clean, contaminant free surface and a stable oxide layer ensure excellent initial adhesion and long term joint durability.

There are very few cases where mechanical interlocking contributes significantly to adhesion. Uehara and Sakurai (2002) proposed that the bonding strength of adhesives is influenced by the surface roughness of the substrates. They found that an optimum value of surface roughness exists with respect to the tensile strength of adhesion; this optimum value was a surface roughness (R_A) of 3 μ m to 6 μ m. Similar relationships were not observed for the shear and peel strength of adhesion. As peel and shear

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stresses dominate in single lap joints the surface roughness of the substrate would not play an important role in the strength of adhesion in the joint.

Grit blasting is one of the most reliable and repeatable methods of mechanically roughening a surface. Harris and Beevers (1999) conducted a detailed study on the effects of grit blasting with different alumina grits on the surface characteristics of mild steel and aluminium substrates. They found that the roughness of the surface was directly linked to the surface energy, the rougher the surface the lower the surface energy. Grit blasting was found to introduce chemical changes onto the surface, with smaller grit sizes introducing more contamination (in the form of sodium ions) that would cause the surface energy to increase.

Bockenheimer et al (2002) confirmed the findings of Harris and Beevers (1999) demonstrating that mechanical pre-treatment by blasting with alumina grit or glass beads changes the topography and chemical state of an aluminium adherend. They found that non-stoichiometric compounds of aluminium i.e. other that Al_2O_3 occur on the blasted surface. In this state the aluminium atoms will be highly reactive as they do not possess their maximum degree of oxidation and hence have an electron density deficiency. The chemical state of the surface influences the curing of the adhesive and a network structure in the epoxy adhesive is formed because of the preferential adsorption of the hardener onto the aluminium surface.

Anodising is one of the only surface pre-treatments that results in mechanical interlocking on a micro scale and as such anodised surfaces tend to give good initial bond strengths and good durability. Brockmann et al (1982) recognised anodised surfaces allow for micro mechanical linking to take place with adhesives of low molecular weight and that anodising gives a reactive surface allowing chemical bonds to form with adhesives. These authors also recognised that adhesion between a metal and a polymer can only be explained by chemical interactions and micro mechanical linking and any investigation into adhesion must consider the whole system.

Phosphoric acid anodising (PAA) consistently out performs any other anodising process in durability testing. Critchlow and Brewis (1996) conducted an extensive review of 41 mechanical, chemical and electrochemical pre-treatments specifically designed to modify the surface of aluminium and enhance bond durability. They found that in comparative trials PAA produced the best durability. They were also able to define two factors that contribute to bond durability: stability of the oxide layer and topography (increased surface area allows for more beneficial interactions to take place). Ong et al (1992) evaluated non-tank surface pre-treatments for aluminium bonding repairs. Once again the non-tank phosphoric anodising process out performed the other techniques under investigation. Although PAA is a very effective procedure it is not very environmentally friendly. Lunder et al (2002) found alternating current anodising in hot sulphuric acid (more environmentally sympathetic) to be a very effective alternative process on AA6060.

As has been shown above anodising is a very effective way of improving durability. However, due to the economic and environmental implications of anodising many other types of surface pre-treatments and coatings are being researched. Conversion coatings are a potential alternative to anodising. Rivera et al (2003) are evaluating rare earth oxide based conversion coatings. They propose a cerium oxide based coating as a potential replacement for chromate based systems. A conversion layer built up in fifteen minutes can withstand 1000 hours of salt fog exposure. Conversion coatings are susceptible to alloy composition. Brown et al (1993) found that on the heterogeneous surface of an alloy the grain boundaries and intermetallics provide a preferential path for electronic conduction. This leads to the coating growing on grain boundaries and other flaws preferentially, as such the coating on the bulk of the grain will be thinner than at the surface heterogeneities.

Chromium free surface pre-treatments are also of great interest to industry because of limitations imposed by the End of Life Vehicle Directive, European Parliament (2000). Kresse and Nowak (1995) found that chromium free systems had only a slight corrosion inhibiting effect on bare

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aluminium-magnesium-silicon alloys in their unpainted form. When painted the chromium free conversion treatments provided adequate protection. As would be expected it was observed that anodising provided the most stable surface. Ti/Zr pre-treatment performed as well as the traditional yellow chromating pre-treatment (Alodine 4840). Organic corrosion inhibitors were found to be an effective surface pre-treatment by Schulte et al (1995) when used in conjunction with zinc phosphates.

Ti/Zr conversion coatings have been examined by Carr et al (1997), the conversion coating was shown to have good initial bond strength and good durability in double lap shear specimens. Hunter and Barlow (2002) conducted further research into Ti/Zr conversion coatings and their application as an electrocoat replacement in automotive painting process. They also found that the coating gave good bond strengths before and after exposure.

Hard coatings can crack in service when applied to a soft compliant material such as aluminium. This is an area of concern for most coated material as many coatings are brittle. Wanstrand et al (2002) evaluated the influence of coating stiffness, hardness and thickness on the load carrying capacity of coated aluminium. Wanstrand proposed that the presence of an intermediate layer could increase the load carrying capacity of the coated material. The load carrying capacity of the system increased with the thickness and elastic modulus of the intermediate layer.

<u>3.3 Implications of Reviewed Literature on Low Cost Aluminium</u> <u>Closures</u>

Corrosion costs consumers and manufacturers large amounts of money every year in terms of manufacture, repair and depreciation. Any new technology such as a low cost aluminium closure that can reduce susceptibility to corrosion will have a positive impact on consumers and manufacturers. Vehicles are complex corrosion systems and operate in aggressive corrosion environments due to marine or de-icing salts and moisture from rainfall or humidity. Although the mechanisms of corrosion

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on metals are generally well understood applying these mechanisms to the complex geometries and multi-material systems of automotive components is challenging.

Many researchers have investigated the corrosion characteristics of automotive materials and the bulk of the work has concentrated on zinc coated steel in all its forms (HD, EZ and GA). There is no doubt that the extensive use of zinc coated steel on modern vehicles has reduced the incidences and extent corrosion. Aluminium sheet has been found to be more resistant to corrosion than zinc coated steel in automotive operating environments, but is at risk of a specific type of cosmetic corrosion called filiform corrosion.

The specific geometry of interest in this research is the hem flange and a small number of studies have been produced on this type of joint configuration. The path of corrosion in hem flanges has been identified and some possible corrosion mechanisms have been proposed. The importance of drying time within the hem flange as a result of periodic rain fall or an accelerated test environment was noted by some authors and this is of special interest as Ford of Europe uses cyclic wet/dry accelerated testing of vehicles and components to assess corrosion performance. Accelerated corrosion testing can be problematic as accelerating factors do not always allow similar in field failure modes to be repeated under accelerated conditions in the laboratory. Great care should be taken when interpreting accelerated corrosion test data to ensure that representative failures are being seen.

A low cost aluminium closure is made from steel and aluminium and in the absence of the pre-coating would be at risk of galvanic corrosion. The are ratio effects in galvanic corrosion are well understood and need to be carefully considered in relation to the corrosion system of a low cost aluminium closure. Published data on galvanic currents measured in-situ in a hem flange was not available at the time of writing this review. This area of research will help further understanding of the corrosion mechanisms

operating in a hem flange and is of even greater performance in mixed material systems like low cost aluminium closures.

The structural performance of the joints present in closures is generally assessed using single lap shear and T peel joints. The stress distributions within these joint geometries are well understood, although it is still a matter for debate which of these types of joints best represent the stress state seen in a hem flange. It is the opinion of the author that a single lap shear joint better represents a hem flange because of the length of overlap in a hem flange. Also, the constraint provided by the hem flange geometry (effectively a double lap joint) is unlikely to allow a hem flange to peel, as a T peel specimen would during test. It would not however, be appropriate to use double lap joints for routine automotive testing as they are more difficult and time consuming to make in the quantities required to optimise automotive adhesive bonding systems.

Surface treatment has an important effect on the durability of an adhesive joint but unfortunately the treatments that give the best durability performance are either no longer available (due to legislative changes) or too costly and time consuming to apply in a mass production environment. As such, automotive manufacturers must look for intermediate solutions. Roll applied pre-treatments/coatings like that used for pre-coated aluminium allow robust surface pre-treatments to be carried out quickly and cost efficiently at the supplier.

The review of literature here has shown that in the realm of published information the low cost aluminium closure is a new concept. The published data examined for this review has shown that the hem flange has not been extensively studied and knowledge of the corrosion mechanisms operating are still in the early stages of development. Studies on mixed material hem flanges have not been conducted and are needed to understand the corrosion performance of a low cost aluminium closure. The validity of using single lap shear joints as the primary method of assessing the structural performance of hem flange joints has been discussed and is deemed appropriate by the author as a suitable joint geometry for

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assessing the adhesive joint properties of low cost aluminium closures. T peel joints should also be assessed as they can be more discriminating on differences in surface preparation. Accelerated corrosion and environmental testing are considered a valid approach to aging materials and joints but data should be interpreted carefully to ensure representative failure modes are experienced.

4.0 Materials and Methods

The experimental work carried out to test the hypothesis was the investigation of the corrosion properties, structural performance and durability of low cost aluminium closures. The corrosion properties of low cost aluminium closures were assessed using electrochemical techniques and accelerated testing of components. The structural durability performance of low cost aluminium closures were assessed using single lap shear joints and modified peels joints. The performance of the component was evaluated with an accelerated proving ground test at the Ford proving ground in Lommel, Germany.

4.1 Corrosion Properties of Low Cost Aluminium Closures

4.1.1 Substrates

- Hot dip galvanised steel sheet 0.65 mm thick (60G60GHD) with 60 g/m^2 zinc on each side.
- Aluminium alloy 6016 sheet 1.2 mm thick.
- Pre-coated aluminium alloy 6016 T4 0.7 mm thick, the pre-coating and conversion coating shown in Figure 4.1. The composition of AA6016 is shown in Table 4.1.

Alloy Addition (Weight %)	AA6016
Silicon	1.0 - 1.5
Iron	0.5 maximum
Copper	0.2 maximum
Manganese	0.2 maximum
Magnesium	0.25 - 0.60
Chromium	0.10 maximum
Zinc	0.2 maximum
Titanium	0.15 maximum
Aluminium	rest

Table 4.1 Compositions of AA6016



Figure 4.1 Pre-coated Aluminium

4.1.2 Specimen Preparation

The specimens were degreased using lint free cloths and acetone to ensure all lubricants and contaminants were removed from the surface. Degreasing also ensures good adhesion of the masking tape to the surface of the substrate. The specimens were laser cut from the sheet materials using a Bystar 3015 3 Kilowatt Turbo machine. Two specimen sizes were used:

- 120 mm x 200 mm
- 60 mm x 100 mm

The specimens were masked as shown in Figure 4.2. The 60 x 100 mm specimen shown with 100 mm² of exposed substrate and the 120 x 200 mm specimen is shown with 100 mm² of exposed substrate. The cut edge of the exposed area is left unmasked to simulate in service conditions. In order to expose 10000 mm² of substrate the 120 x 200 mm substrate was used and an area of 100 x 100 mm left exposed. The black pre-coating shown in Figure 4.1 was always used as the exposed surface.

Three 120×200 mm specimens of pre-coated AA6016 (PAI) were stone chipped in accordance with FLTM BI 157-06. Stone chipping was used to

initiate random damage to the coating. A small area of the pre-coating and epoxy primer from were removed from the pre-coated aluminium to ensure good electrical connection. 60×100 mm sheet specimens were tested in 600 ml Pyrex glass beakers and 120 x 200 mm specimens were tested in 5000 ml Pyrex glass beakers.



Figure 4.2 Masking Pattern for Specimens

Hem Section Specimens

Hem sections were cut from an assembled and painted all zinc coated steel closure and low cost aluminium closure. Hem sections were nominally 100 mm wide and 200 mm long and the exposed metal edges were masked with 3M 851 PCB electroplaters tape to prevent exposure to the electrolyte.

Low Cost Aluminium Hood

The low cost aluminium hood and benchmarked all zinc coated steel hoods were manufactured in plant in Saarlouis on a standard production line. They were assembled using a one-part heat curable hem flange epoxy (Henkel Terosen 5811) and painted on a standard steel paint production line. Manufacturing the demonstrator components (hoods) was a significant achievement as production lines must meet daily targets and production engineers are reluctant to conduct any trials on their lines that may jeopardize normal production.

4.1.3 Experimental Design for Small Specimens

Open circuit potential, also known as free corrosion is measured to allow metals to be ranked into a galvanic series. A galvanic series is specific to the conditions it is measured under and as such the conditions of measurement, such as, electrolyte composition, aeration and temperature must be quoted when stating a galvanic series.

Each test was completed in triplicate on 60 x 100 mm specimens with 100 mm² of substrate exposed. All electrolytes were aerated and the current and potential were measured for a minimum of 3 days at a sampling rate of 1/minute. The current and potential was measured using an ACM Instruments 6 channel Zero Resistance Ammeter (ZRA), Silver/Silver Chloride reference electrodes were used. The experimental set is shown in figure 4.3.

The open circuit potential of sheet specimens of hot dip galvanized steel, uncoated AA6016 and pre-coated AA6016 were measured in 4 different electrolytes:

- 1. Tap Water
- 2. 1% NaCl
- 3. 3% NaCl
- 4. 5% NaCl

Tap water used was from Southern Water and was specified to have 30 ppm chloride ions (minimum annual value recorded was 23 ppm, mean 30 ppm and maximum was 34 ppm (Southern Water [2004])). Sodium chloride solutions were prepared by weight and with deionised water. The electrolytes were aerated during the test period

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Figure 4.3 Experimental Set up for Open Circuit Potential Measurements of Sheet Specimens

Corrosion Resistance of Sheet Specimens

Linear polarisation resistance (LPR) is used to analyse the corrosion resistance and passivation behaviour of metals by applying an over or under potential (voltage) to the specimen from its measured open circuit potential. This allows the cathodic and anodic behaviour of the metal to be studied. The linear polarisation resistance was measured using a Gamry Instruments Potentiostat. A silver/silver chloride reference electrode and graphite counter electrode were used to complete the cell. Each cell was prepared with the specimen, reference electrode, counter electrode and electrolyte and left for at least 1 hour to stabilise before testing commenced, as shown in figure 4.4.

A Tafel and Potentiodynamic scan of the specimen was conducted. These tests apply a potential to the specimen and measure the current. A Tafel scan is done by applying potentials from -0.02 V from the open circuit potential to +0.02 V from the open circuit potential at a scan rate of 1 mV every 2 seconds. A Potentiodynamic scan is conducted immediately after a Tafel scan and potentials are applied from -0.2 V from the open circuit

potential to +0.2 V from the open circuit potential at a scan rate of 1 mV every 2 seconds.

The corrosion resistance of hot dip galvanised steel and pre-coated aluminium were investigated in 5% NaCl using Tafel and potentiodynamic scans and the electrolyte was aerated during the test period. Only the metals used directly in a low cost aluminium closure were investigated and 5% NaCl was selected as the electrolyte as this concentration of solution is most commonly used in accelerated automotive corrosion testing.



Figure 4.4 Experimental Set Up for Tafel and Potentiodynamic Scans for Sheet Specimens

Galvanic Coupling of Sheet Specimens and the Effects of Area Ratio

The galvanic current flowing between pre-coated aluminium and hot dip galvanized steel was measured in an aerated 5% NaCl solution, using the experimental set up shown in figure 4.5. The mixed potential of the system was also measured using the ZRA. Different exposed area ratios of precoated aluminium to hot dip galvanized steel were assessed to investigate the effects of current concentration on metal dissolution. Area ratios investigated were:

- 1. Pre-coated Aluminium 1:1 Hot Dip Galvanised Steel
- 2. Pre-coated Aluminium 1:10 Hot Dip Galvanised Steel
- 3. Pre-coated Aluminium 1:100 Hot Dip Galvanised Steel
- 4. Pre-coated Aluminium Stone chipped:10 Hot Dip Galvanised Steel

Pre-coated aluminium sheets (200 mm x 120 mm) were stone chipped in accordance with FLTM BI 157-06 to damage the pre-coating and simulate in plant handling damage.





Corrosion Resistance of Hem Sections

The corrosion resistance of hem sections was measured using the Tafel and potentiodynamic parameters described above for sheet specimens and the experimental set up is shown in figure 4.6.

Three types of hem section specimen were tested and some were exposed to 480 hours neutral salt spray as specified in WSS-M2P180-A, paragraph 3.6.4 was carried out in accordance with ASTM B117, whilst others were tested in an unexposed condition. A summary of the test schedule is shown

in table 4.2. A 5% NaCl electrolyte solution was used and the electrolyte was aerated during the test.



Figure 4.6 Experimental Set Up for Tafel and Potentiodynamic Scans of Hem Section Specimens

Galvanic Coupling of Hem Sections

The outer and inner panels of hem sections were galvanically coupled together as shown in figure 4.7. A 5% NaCl aerated electrolyte was used and the galvanic current and mixed potential was measured for a minimum period of three days. The same experimental design was used as for the determination of corrosion resistance, shown in table 4.2 and specimens were tested in triplicate.

Inner Panel	Outer Panel	Over Hem Sealer	Exposure
Hot dip galvanised steel	Hot dip galvanised steel	Yes	None
			480 Hours Neutral Salt Spray
		No	None (Insufficient specimens available to assess the effects of Salt Spray)
	Pre-coated aluminium	No	None
			480 Hours Neutral Salt Spray

Table 4.2 Test summary for Corrosion Resistance Testing and Galvanic Coupling of Hem Sections



Figure 4.7 Experimental Set Up for Hem Section Galvanic Couple

4.1.4 Experimental Design for Hood

Two low cost aluminium hoods were assessed for corrosion resistance using 30 APGE cycles (accelerated laboratory corrosion test) and PASCAR 1 + 2, summarised in the sections below. PASCAR 1 + 2 is a structural durability test which all Ford of Europe vehicles must pass before commencing full scale production. The test uses salt loading and structural inputs to initiate and propagate any structural defects in the vehicle. It is an arduous test and is used here as a way of assessing corrosion resistance of a low cost aluminium closure on a vehicle.

As the CMax (the demonstrator component vehicle) was already well into production all the vehicle corrosion testing was complete and a PASCAR 1 + 2 test was available because some post launch modifications were being made to the vehicle. Vehicle accelerated tests such as PASCAR 1 + 2 and the vehicle accelerated corrosion test (both carried out at Ford's Lommel Proving Ground) are very expensive to conduct and it was extremely fortunate that a test vehicle was available in the duration of this research project. Scribe lines were applied (one vertical and one horizontal, figure 4.8) to both hoods to allow scribe corrosion creep to be measured during and on completion of both accelerated tests.



Figure 4.8 Scribe Lines to Assess Corrosion Creep

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Accelerated Laboratory Test (APGE)

APGE (Arizona Proving Ground Equivalent) is an accelerated environmental cycle designed to be equivalent to conditions experienced at the Ford proving ground in Arizona. The cycle includes spraying specimens with a 5% neutral salt solution followed by a low humidity drying cycle and a high humidity conditioning cycle. The procedure for an automated cabinet is shown in Table 4.3.

An automated procedure was used to condition the adhesively bonded specimens. The cycle was run continuously seven days a week until 30 cycles had been completed i.e. 30 days required to complete 30 cycles. A C&W SF/1000/CCT cabinet was used for the automated APGE cycling.

Automatic Cabinet Procedure							
Interval Initial Test		Final Test	Time				
123.4	Conditions	Conditions					
1	23 °C and 50% RH	Initial salt spraying of samples	1 minute to wet parts				
2	23 °C and 50% RH	23 °C and 50% RH, no spraying	4 minutes, loop to interval 1 three times in total				
3	23 °C and 50% RH	55 °C and 10% RH	30 minutes				
4	23 °C and 50% RH	55 °C and 10% RH	2 hours 30 minutes				
5	55 °C and 10% RH	55 °C and 85% RH	30 minutes				
6	55 °C and 85% RH	55 °C and 85% RH	20 hours and 15 minutes				
Repeat this 24 hour cycle for 30 cycles							

Table 4.3 Automatic Cabinet APGE Cycling Procedure

Accelerated Proving Ground Structural Durability Test (PASCAR 1 + 2)

PASCAR 1+2 is a vehicle system durability test for passenger cars:

- 1. A basic cycle at speeds between 35 and 60 kph.
- 2. A cycle on a gravel road at speeds between 20 and 50 kph.
- 3. A higher speed cycle at speeds between 20 and 130 kph.
- 4. A cycle containing gradients and hills.

- 5. A drive through a dust tunnel.
- 6. A drive through a mud solution bath.
- 7. A drive through a salt solution bath.
- 8. The basic cycle repeated at speeds between 45 and 75 kph.
- A high speed cycle on a "comfort road" at speeds between 10 and 90 kph.
- 10. A high speed cycle at close to the vehicles maximum speed.

The vehicle completes 300 basic cycles (steps 1 to 8) and 100 high speed cycles (steps 9 to 10). The vehicle will complete 42667 km during the test, the test duration is approximately 6 months.

<u>4.2 Structural Performance and Durability of Low Cost Aluminium</u> <u>Closures</u>

A low cost aluminium closure requires that hot dip galvanized steel be bonded to pre-coated aluminium. A suitable adhesive for this purpose is 3M 7036 as it can be formulated to bond steel to steel (4:1) and aluminium to aluminium (2:1). It would be reasonable to assume that an intermediate mix ratio would provide the best bond properties for a steel to aluminium joint.

Initial screening work was conducted by 3M using 3M 7036 at a number of mix ratios and the mix ratios found to perform best under shear and peel conditions were 4:1, 4.5:1 and 5:1 (on uncoated AA6111 and hot dip galvanised steel joints). It was decided to limit further investigations to these mix ratios.

4.2.1 Substrates and Adhesives

Hot dip galvanised steel and pre-coated aluminium (AA6016) were used to assess the structural durability of low cost aluminium closures and are described in section 4.1.1. Henkel Terosen 5811 is the current PVC Epoxy production hem flange adhesive in Ford of Europe and it is used in this

study as a bench mark. 3M 7036 is a two part epoxy system that can be mixed to bond steel to steel or aluminium to aluminium. The mix ratios are modified to optimize the amine to epoxy ratio for the substrate system being bonded. High amine to epoxy ratios are preferable for aluminium as they enhance durability, where as high epoxy to amine ratios are preferable on steel substrates (Sikkel, [2005]).

4.2.2 Specimen Preparation

Single lap shear specimens were made in accordance with SAE J1523. Peel resistance (T Peel Test) specimens were prepared in accordance with ASTM D 1876-01. The coupons were laser cut from the sheet materials using a Bystar 3015 3 Kilowatt Turbo machine. They were nominally 25.4 mm wide by 101.6 mm long. Single lap shear and modified peel specimens are shown in figure 4.9.

The coupons were degreased n heptane solvent and then re-oiled according to a 3M Specification. Hot dip galvanised steel coupons were re-oiled with of 6g/m² Quaker stamping lubricant. Bond line thickness was controlled with glass bead spacers in the adhesive. The bond line thickness was 1 mm. No lubricant was applied to the pre-coated aluminium as it is expected that no lubricant will be required during stamping because of the pre-coating. A closure adhesive joint (hem flange) usually receives an induction cure to promote initial adhesion, aid lubricant dispersion and adsorption and give improved handling strength. No induction cure was given to either the single lap shear or the peel specimens. Assembled specimens were conditioned at room temperature and humidity (23 °C \pm 2 °C and 55% RH \pm 5%) prior to curing. Three curing cycles were used:

- 1. Control, 30 minutes at 180 °C.
- Minimum Bake, 10 minute ramp from room temperature to 170 °C with a dwell at 170 °C for 10 minutes.
- Maximum Bake, 10 minute ramp from room temperature to 205 °C with a dwell of 30 minutes at 205 °C.

North American minimum and maximum bake cycles were used, as they are a more severe test than equivalent European bake cycles. The cycles are described in WSB-M2G373-A and WSS-M2G373-A2/B paragraph 5.6.3.





4.2.3 Experimental Design

An automotive adhesive joint (hem flange) is affected by many variables (noises) both in plant and in service and two of these variable were assessed in this research:

- 1. The effect of heat input from the production paint bake ovens
- 2. The effect of environmental exposure

Production paint bake ovens do not have an even temperature distribution and as such all parts of the vehicle do not see the same heat inputs. The minimum and maximum bake cycles described in section 4.2.2 are designed to replicate the worst expected lower and upper bake cycles experienced in a production paint oven. The control bake cycle would be the ideal heat input seen by a hem flange joint. Three environmental exposure regimes are used in this study:

- Humidity aging, conducted at 60 °C and 95% RH for 7 days in a C&W SF/1000/CCT cabinet.
- 2. 30 APGE cycles, as summarised in section 4.1.4.
- 3. Custom environmental cycle based on Wang et al [2000]. The average environmental conditions seen by a door hem flange were 59% relative humidity (RH), 17 °C and 0.28 time of wetness. It was not possible to meet 17 °C and 59% RH in the environmental chamber available. It was therefore necessary to compromise on one of these requirements. A cycle of 6 hours immersion in tap water followed by 18 hours at room temperature and humidity was chosen. The ambient environment is controlled to 50% RH \pm 5 and temperature is controlled at 23 °C \pm 2. It was not anticipated that the increase in temperature would be a significant accelerating factor over temperatures seen in service.

30 cycles of the custom environmental cycle were completed. One cycle per weekday was completed with the specimens held at room temperature and humidity during the weekend.

Shear Strength and Peel Resistance						
Environmental Exposure						
<u>Bake Cycle</u>		Control	Humidity		30 APGE	Custom
	Control	3M 7036 4:1	Shears	Peels		
		3M 7036 4.5:1	3M 7036 4:1	/		
		3M /036 5:1	3M 7036 4.5:1	/		
	Henkel 5811	Henkel 5811				
	Minimun	3M 7036 4:1	3M 7036 4:1		3M 7036 4:1	3M 7036 4:1
		3M 7036 4.5:1	3M 7036 4.5:1		3M 7036 4.5:1	3M 7036 4.5:1
		Henkel 5811	Henkel 5811		Henkel 5811	Henkel 5811
	Maximur	3M 7036 4:1	3M 7036 4:1		3M 7036 4:1	3M 7036 4:1
		3M 7036 4.5:1	3M 7036 4.5:1		3M 7036 4.5:1	3M 7036 4.5:1
		Henkel 5811	Henkel 5811		Henkel 5811	Henkel 5811

Table 4.4 Test Summary for Single Lap Shear and Peel Specimens

The experimental design used to assess the structural durability of low cost aluminium joints is summarised in table 4.4. Each specimen was replicated at least three times.

4.2.4 Experimental Design for Hood

One low cost aluminium hood was fitted to a CMax undergoing PASCAR 1 + 2 and assessed for structural durability as in section 4.1.4.

5.0 Corrosion Properties of Low Cost Aluminium Closures

5.1 Introduction

A low cost aluminium closure is made of dissimilar metals and is therefore at risk of galvanic corrosion. The geometry of hem flanges allow a fluid trap to form that can accumulate electrolyte and the dimensions of the gap (between the inner and outer panels) leads to the possibility of crevice corrosion occurring. As closure panels are stamped from coils of sheet material, cut edges are always present in hem flanges and therefore corrosion of the cut edges can also occur. Automotive vehicles operate in aggressive environments, where high humidity, precipitation and chloride ions (from road salt and coastal atmospheres) provide the ingredients for highly corrosive electrolytes to form.

It is clear that hem flanges are complex corrosion environments requiring a number of different experimental techniques to assess the corrosion properties and performance of low cost aluminium closures and more specifically hem flanges. The metals that make up the closure were ranked in a galvanic series to establish their relative electrochemical activities and the corrosion resistance of the metals was measured using linear polarisation resistance (Tafel). Linear polarisation resistance (potentiodynamic scan) was also used to investigate any passive behaviour. The different metals found in a hem flange were coupled together and the galvanic current and mixed potential measured to investigate the effects of galvanic coupling. The galvanic current of galvanic couples with unfavourable area ratios was also measured to examine the effects of possible current concentration. Similar measurements were made on sections of low cost aluminium closure to test the corrosion resistance of hem flanges and the galvanic currents flowing between the inner and outer panels. In addition to the small specimen laboratory tests full size demonstrator components were tested for corrosion resistance using an

accelerated proving ground test and an accelerated laboratory test. Where possible sections were taken from non-corroded and corroded test specimens for metallographic examination and these observations were used in conjunction with the measured test results to understand the corrosion behaviour exhibited by low cost aluminium closures and hem flanges.

The electrochemical corrosion properties of automotive hem flanges have not been extensively studied and as such no data is available about the corrosion rates of hem flange metals in-situ. This information would be very valuable to automotive manufacturers as it would allow them to effectively predict the life of this complex geometry component. The current method for evaluating the performance of a hem flange is either testing a component in an environmental chamber using an accelerated corrosion test or testing a component on a vehicle in an accelerated proving ground test. Accelerated laboratory testing can take upwards of six weeks and the minimum time period for an accelerated proving ground test at present is also six weeks. Both of these tests rely upon having representative production parts in order to conduct the tests. They are also limited by the accelerating factors used in the tests and how they correlate with real life exposure experienced by vehicles in use by customers.

Electrochemical corrosion testing of hem flanges would allow manufacturers to establish the corrosion rates of new materials systems (such as a new type of zinc coating or a reduced weight zinc coating) without having to build a component or a whole vehicle. This would reduce the need for expensive proving ground tests and allow any changes needed to corrosion protection systems to be made well before a new vehicle goes into production. The later in the new vehicle design and production process changes are made the more expensive they become to implement. In the case of a proving ground corrosion failure this may mean the need for additional cavity wax in an area which is difficult to access using current facilities and require the wax to be applied by hand. Such changes observed earlier in the design process can allow production planners to get the correct facilities in place at a lower cost.

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Ultimately a full understanding of the electrochemical performance of automotive sheet materials in their natural environments would allow manufacturers to reduce costs associated with accelerated laboratory and proving ground testing. It would also allow them to better plan the production line as late changes to corrosion protection measures would not be needed. It would also permit the use of new types of corrosion resistance coatings to be tested in a low risk environment and be able to compare them with the existing materials in a fair and constructive manner. The electrochemical tests conducted in this research are an initial investigation into this field of testing.

The corrosion performance of low cost aluminium closures was benchmarked against the corrosion performance of all steel closures in the small specimen laboratory tests and the accelerated laboratory test on the full size demonstrator. However, due to the limitations of proving ground testing direct benchmarking against an all steel closure was not possible. For clarity it should be noted that an all steel closure has a zinc coated steel inner and outer panels (figure 5.1) and a low cost aluminium closure has a zinc coated steel inner panel and a pre-coated aluminium (with the precoating on the inside of the outer panel, not shown to scale on diagram) outer panel (figure 5.2).



Figure 5.1 All Steel Hem Flange



Figure 5.2 Low Cost Aluminium Hem Flange

5.2 Galvanic Series of Metals found in Hem Flanges

All steel hem flanges are made from two panels of zinc coated steel and low cost aluminium hem flanges have a zinc coated steel inner panel and a precoated aluminium outer panel. Therefore there are two metals in an all steel hem flange: steel and zinc and three metals in a low cost aluminium hem flange: aluminium (AA6016), steel and zinc. The open circuit potentials (free corrosion potential) of uncoated AA6016, pre-coated AA6016 and zinc coated steel were measured using a zero resistance ammeter (ZRA) as a potentiostat (just using the logged vales of potential) in order to establish the galvanic series of these metals in four electrolytes: tap water, 1% NaCl, 3% NaCl and 5% NaCl.

The open circuit potentials (OCP) of pure zinc or zinc-coated steel with the zinc removed were not measured. The corrosion properties of metals are highly influenced by processing routes, alloy composition and surface condition. If a zinc plate had been used to measure the open circuit potential of zinc, the results may not have been representative of the open circuit potential of hot dip galvanised zinc coating on zinc coated steel sheet. As an inner panel in a hem flange has a cut edge exposing a small strip of steel it was considered more representative to measure the potential of the whole zinc coated steel system. Similarly, the electrode potential of the steel substrate was not measured, although it is possible to remove a zinc coating by chemical (etching) and/or physical (abrasion) methods the resulting surface condition would not have been representative of a standard mill finished steel. Unfortunately it is very difficult to obtain small quantities of steel sheet used in mass production and even more difficult to obtain material that is not commonly used, for example uncoated steel grade that is usually sold as zinc coated steel. A comparison between the electrode potentials of uncoated and pre-coated aluminium was possible as currently AA6016 is the most favoured aluminium alloy in Europe for vehicle closure outer panels and as such is readily available.

The galvanic series found for the four electrolytes listed above is shown in figure 5.3. It is important to note that a galvanic series is only valid if all the measurements are taken under the same conditions i.e. the same temperature, humidity, electrolyte composition, electrolyte aeration etc. The potentials shown are averages of three replicate specimens and the potential of each specimen was obtained by averaging all the potentials over a minimum period of three days.



Figure 5.3 Galvanic series for hem flange metals in four electrolytes with the Molar chloride concentrations of the electrolytes shown

Tap water has a very low chloride concentration and as expected the open circuit potentials of all the metals are substantially lower in tap water than in electrolytes with higher chloride concentrations. Also, tap water has other dissolved ions such as carbonates that aid passive film formation reducing the rate of metal dissolution. Chlorides increase the rate of dissolution of metals (the anodic reaction) as they are film disruptors and in crevices they act to help lower pH. pH is a measure of hydrogen ion concentration in a solution and the increase in hydrogen ions further accelerates metal dissolution. This is because hydrogen ions are reduced at the cathode (consuming electrons) and therefore driving the anodic reaction to produce more electrons. The highest potentials are observed in the electrolytes with the highest chloride concentrations and importantly it should be noted that the order of the metals does not change in electrolytes with significant chloride concentrations.

Pre-coated AA6016 and uncoated AA6016 have different free corrosion potentials and as they have the same alloy composition there must be another explanation for the differences in their OCPs. The pre-coated aluminium specimens only have a small area of base metal exposed at the cut edge, where as the uncoated aluminium specimens have base metal and a cut edge exposed to the substrate. It is likely that the small exposed cut edge of the pre-coated aluminium specimen is in some way restricting the anodic reaction. The surface condition of a cut edge is likely to be different to the surface of the uncoated aluminium and this may also have an effect on the corrosion rate. Laser cutting was used to prepare the specimens and so the cut edge may also have a heat affected zone and tenacious oxides present that may limit metal dissolution.

The order of metals in the galvanic series is important because it governs which metal will sacrifice itself when the metals are electrically coupled together. In the electrolytes with 1%, 3% and 5% NaCl the hot dip galvanised steel will sacrifice itself in preference to the aluminium. So it is the zinc of the hot dip galvanised steel that would sacrifice itself in preference to the aluminium, once a significant amount of zinc has been consumed then the aluminium would be anodic to the steel. Mattssonn (1996) discussed that the effectiveness of zinc protecting steel in atmospheric conditions is limited to distances of approximately 1 mm. So, in an automotive hem flange the effectiveness of zinc in protecting

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aluminium in the galvanic series is limited by the distance of remaining zinc from the corroding aluminium.

It is interesting to note that the OCPs of the metals under consideration do not vary greatly with increasing NaCl concentration. This is an important consideration from an automotive viewpoint as much debate has taken place about the actual NaCl loadings seen in service by vehicles. Automotive accelerated corrosion tests usually use a 5% NaCl solution (by weight) but it is thought that a much lower concentration is seen in service, a value of between 0.5 and 1% is proposed by Townsend (1996). Although chloride concentration it not the only factor that affects the corrosion rates and mechanisms seen by automotive vehicles it is an interesting observation that chloride concentration in the range studied i.e. 1, 3 and 5% does not affect the galvanic series of metals found in low cost aluminium and all steel hem flanges.

Hot dip galvanised steel developed a gelatinous oxide on the surface of the zinc during exposure to NaCl solutions. This oxide appeared to protect the surface of the zinc from further dissolution in the areas it covered. The composition of the gelatinous material was not investigated but is very likely that it could be a form of insoluble zinc hydroxychloride termed simonkoellite, observed by authors such as Falk (1998) and Zhu (2000). This compound forms in the presence of hydroxide ions and chloride ions. Investigation of the stoichiometry of this oxide could be conducted using X ray diffraction against a simonkoellite benchmark specimen. Authors in this field have noted that it is very difficult to remove and isolate enough simonkoellite to get a definitive result from x ray diffraction techniques.

5.3 Corrosion Resistance of Hem Flange Metals

Polarisation of metals is one of the most common methods of examining corrosion behaviour. A potential is applied to a metal sample and the current response of the sample is measured. Two types of polarisation tests are normally conducted: Linear polarisation technique (leading to a Tafel

plot and the calculation of linear polarisation resistance (LPR)) and Potentiodynamic polarisation. LPR data can be taken from a potentiodynamic plot but is more usual to conduct a linear polarisation test first as the small polarisations from the free corrosion potential do not affect the condition of the metal surface. Once a potentiodynamic scan has been completed the metal has been forced through such a large potential range that it would give invalid results if a linear polarisation plot were taken from this data. Potentiodynamic scans are used to investigate cathodic and anodic reactions separately on the same metal and also to examine any passive behaviour that may occur at potentials away from the free corrosion potential of the metal. This can be of particular interest as knowledge of the passivation behaviour of a metal can be used to prevent corrosion in certain situations where an over potential can be applied to a system.

Two hem flange metals were investigated for their potentiodynamic polarisation behaviour: Hot dip galvanised steel and pre-coated aluminium. The linear polarisation plots for hot dip galvanised steel specimens are shown in chart 5.1. The free corrosion potential of the three hot dip galvanised steel specimens are not identical and this is due to variations in the cut edges and surfaces of the samples. Although the samples were cleaned and prepared in the same way differences in surface condition for the hot dip galvanising process and subsequent in plant handing would account for the 3 mV difference between the three replicate specimens. I_{corr} ranges between 1.96 x 10⁻⁸ A and 6.99 x 10⁻⁸ A for the three hot dip galvanised steel specimens. The curves show that the linear polarisation behaviour of the three specimens is very similar. In order to calculate the linear polarisation resistance of the samples it is necessary to re-plot the data on a linear scale as shown in Chart 5.2.



Chart 5.1 Linear polarisation behaviour of hot dip galvanised steel





The data is shown plotted over a range of \pm 30 mV and over this range the data should be linear for a calculation of linear polarisation resistance to be valid. There are many reasons why a metal may not show linear behaviour

on a Tafel plot. Trethewey and Chamberlain (1995e) give three possible explanations for non-linear Tafel behaviour:

- If there is more than one electrode reaction and any corrosion products that form on the surface of the specimens, reducing the conductivity of the anode. This results in lower current densities than would be predicted by the Tafel equation and a deviation upwards on the potential/current plot.
- If the scan rate is too fast and the specimens cannot react to each potential step before the next one is imposed then linearity cannot be expected.
- If corrosion is controlled by transport of charge through the electrolyte and not by the kinetics of the electrode reactions then the corrosion reactions are under diffusion polarisation and the Tafel relationship will not apply.

As the linearised polarisation data is not linear over the plotted range it is not possible to calculate the linear polarisation resistance for hot dip galvanised steel under these experimental conditions. The data plotted does not deviate upwards so it is unlikely that more than more than one electrode reaction was occurring on the metal surface. However, more than one electrode reaction is possible as there are two metals in the electrolyte, but as we have already seen zinc is anodic to steel in the electrolytes under examination in this study (5% NaCl). The scan rate used for the test was one potential step change every two seconds, so it is therefore unlikely that the scan rate was too fast to prevent the specimen from reacting to the imposed potential step before the next potential increment was applied. The non-linearity observed in chart 5.2 is due to the rate at which oxygen can diffuse to the cathode surface and the corrosion rate of zinc is known to be diffusion controlled.

The potentiodynamic scan for hot dip galvanised steel is shown in chart 5.3. E_{corr} for the three specimens varies by 10 mV and again this variation is due

to differences in the metal surfaces being exploited by the applied potentials. The decrease in corrosion current seen at -0.85 V passivation behaviour of the hot dip galvanised steel commences. At potentials greater than -0.85 V a passive film forms and the anodic current decreases. The passive film does not begin to break down in the range measured during this potentiodynamic scan.



Chart 5.3 Potentiodynamic scan of hot dip galvanised steel

Pre-coated aluminium showed very complex current response behaviour under applied potentials. Chart 5.4 shows the logarithmic scale Tafel plot for pre-coated aluminium. Only one specimen is plotted as obtaining meaningful data from pre-coated aluminium was very difficult. This was due to the small area of bare exposed metal possibly limiting electrochemical reactions occurring on the exposed metal. The Tafel plot shows E_{corr} for pre-coated aluminium is -0.701 V and I_{corr} is 4.65 x 10⁻¹⁰ A. The linear plot (chart 5.5) of the Tafel data shows non-linearity over the measured range and Tafel behaviour is not obeyed. It is likely that the corrosion rate of aluminium is also under oxygen diffusion control. However, as the plotted line is tending to the vertical it may also be

possible that more than one reaction is occurring on the electrode. No stable passive behaviour is shown by pre-coated aluminium but an unstable passive region forms at -0.5 V as seen in chart 5.6.



Chart 5.4 Linear polarisation behaviour of pre-coated aluminium



Chart 5.5 Logarithmic scale Tafel Plot for pre-coated aluminium


Chart 5.6 Potentiodynamic scan for pre-coated aluminium

5.4 Galvanic Coupling of Hem Flange Metals

Pre-coated aluminium and hot dip galvanised steel sheets were coupled together and immersed in 5% NaCl solution. The current flowing between metals and the coupled potential was measured using a ZRA. As the data was recorded over many days (at least three) an average of the coupled potential and current was taken when the specimens had reached a steady state and as the currents and potentials fluctuate over time the averages were taken from one hour after coupling to the end of the exposure period. The mean coupled potential and mean current are shown in table 5.1. The corrosion rate is also shown and this was using current density to give a corrosion rate:

Assuming:
$$Zn \rightarrow Zn^{2+} + 2e^{-}$$
 [5.1]

is the anodic reaction and using Faraday's Law:

$$w / M = q / z F$$
 [5.2]

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Where:

	_				
W	=	mass of material lost during anodic dissolution			
М	=	Molar mass of material lost			
q	=	Electrical charge			
z	=	Number of electrons used in reaction 5.1 ($z = 2$)			
F	=	Faraday's constant (96485 A s mol ⁻¹)			
Subst w / M	itute q = I t /	= A t equation [5.2]: z F	[5.3]		
Rearrange to get mass loss per unit time: w / t = I M / z F $[5.4]$					
Substitute density into equation 5.4 (ρ = w / V = w / A x, where V =					

PAx/t = IM/zF	[5.5]

Rearrange to get thickness lost per unit time:

$$x / t = I M / \rho A z F$$
[5.6]

I / A is current density = j, so substitute into equation [5.6]: x / t = j M / ρ z F [5.7]

Equation [5.7] was used to calculate the corrosion rate shown in table 5.1. The anodic reaction is occurring on the hot dip galvanised steel, so the area taken to calculate current density is the area of exposed hot dip galvanised steel. This is because of the ranking of the galvanic series discussed above in section 5.2, that zinc will sacrifice itself for aluminium in 5% NaCl. The stone chipped areas exposed approximately 6.5 mm² of bare aluminium on a 284 mm² sheet of pre-coated aluminium. A photograph showing the type of damage inflicted by stone chipping is given in figure 5.4.

The mean coupled potential for all the area ratios is between that of aluminium and zinc. The mixed potential does not vary greatly with area ratio, as the dominant reaction influencing the potential is the dissolution of

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volume, A = area and x = thickness lost):

zinc. Recall from figure 5.3 that the mean measured potentials for hot dip galvanised steel and pre-coated aluminium were -709 and -1022 mV respectively. The mixed potentials shown in table 5.1 range between - 1007 and -1066 mV and as the measured coupled potential is closer to the open circuit potential of hot dip galvanised steel then the predominant anodic reaction occurring in the couple is the dissolution of zinc.

Area Ratio (Pre-coated AA6016 : Hot dip galvanised steel)	Mean Potential (mV)	Mean Current (µA)	Corrosion Rate (µm/year)
1:1	-1022	-0.51	7.6
	-1007	-1.1	16.5
	-1012	-1.2	18.0
1:10	-1033	-48.3	72.4
	-1007	-44.2	66.2
	-1027	-1.1	1.7
1:100	-1029	-1.9	0.3
	-1019	-0.8	0.1
	-1024	-1.8	0.3
Stone-chip : 10	-1014	-2.1	3.1
	-1011	-54	80.1
	-1066	-0.9	1.3

Table 5.1 Mean coupled potentials of pre-coated aluminium and hot dip galvanised steel galvanic couples and the effect of area ratio on galvanic coupling currents



Figure 5.4 Stone chipped pre-coated aluminium showing areas of perforation through pre-coating to bare aluminium

The actual area ratios are much smaller than those recorded above as although the area masked off on the specimen exposed 1 cm^2 of the precoated aluminium, the area of exposed metal was only that of the cut edge (0.7 mm x 10 mm). As discussed previously zinc is anodic to aluminium in the test electrolyte of 5% NaCl and so in these tests the dominant anodic reaction is the dissolution of zinc. This can be seen by the negative polarity of the current in table 5.1; referring back to figure 4.5 a current flowing from WE2 (working electrode two) to WE1 (working electrode one) is recorded by the ZRA as a negative current.

Higher corrosion rates are observed on 1:10 couples than on 1:1 couples because more zinc is available to provide electrons for the cathodic reduction reaction on the aluminium. The corrosion rate decreases on the 1:100 couples because the zinc now has significant amounts of cathodic sites on its own surface as well as the reduction reaction occurring on the aluminium cathode (it is not possible to measure the corrosion rate of an uncoupled metal directly and so the current being measured between the two metals is reduced by the electron consuming reactions occurring on the zinc itself). The stone chip to 10 couple sees a slight increase in corrosion rate as the aluminium surface available may be more active due to the stone chipping procedure, giving a larger effective area to support the cathodic reaction.

The variation in the results illustrates a very important feature of electrochemical corrosion testing; results are very susceptible to local surface conditions and local variations in electrolyte aeration and composition. As such, definitive conclusions cannot be drawn on small data sets, as in table 5.1. It is still valid to highlight trends and use the data for comparative assessments of the corrosion performance of specimens tested under equivalent test regimes.

The corrosion rate shown in table 5.1 is calculated from a current measured over a short time period (only a few days), if the current was measured over a much longer time period i.e. years the current would be much lower and the corrosion rate would then much better represent the corrosion rate

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seen by in service materials. The results given in table 5.1 do allow for useful comparison between the different areas of exposure and how these areas of exposure might relate to conditions in a hem flange.

The purpose of this work on the effect of area ratios was to determine what would happen if a small amount of aluminium was exposed in a hem flange. In a bare aluminium and steel couple this would result in the aluminium being consumed rapidly leading to perforation of the aluminium sheet. In a zinc coated steel pre-coated aluminium couple this does not happen in the time period studied as zinc is sacrificed in preference to the aluminium. The most unfavourable area ratio tested here was 1:100 (1:1500 on actual exposed aluminium area) and this resulted in the lowest corrosion rates, because the zinc corrodes within itself and in preference to the aluminium. The coupled system studied using two open-faced specimens is not representative of the system seen in a hem flange and so the galvanic coupling of a hem flange will be discussed in section 5.6.

5.5 Corrosion Resistance of Hem Flange Sections

Sections of hem flange were taken from a low cost aluminium closure and a conventional all steel closure. The conventional all steel closure was partially over hem sealed on the leading edge of the hood and the headlamp cutouts, this allowed hot dip galvanised steel hems to be tested both with (HD#OH) and without (HD#NoOH) over hem sealer. The low cost aluminium hood (PAI#) did not have any over hem sealer applied to the hem flanges. The corrosion resistance of the hem flange sections was assessed using linear polarisation (Tafel). A potentiodynamic scan was not possible on the hem sections as the total exposed area of metal within the hem was too large for the potentiostat to polarise, as most laboratory potentiostats are limited to 1 amp and this therefore limits the amount of exposed metal that can be polarised. Hem sections were either tested in an as made condition or were exposed to 480 hours neutral salt spray to accelerate the corrosion process.

Chart 5.7 shows the linear scale Tafel plot for unexposed hem sections tested in 5% NaCl solution. Three of each type of specimen were tested and as can be seen from the data on chart 5.7 not all specimens gave a result for linear polarisation resistance. This was due to the complex geometry of the hem flange and despite allowing the system to settle for at least one hour in the electrolyte the specimens not shown here, did not respond as expected to the applied potential. As potential was applied the current response was random and inconsistent and was not representative of the other specimens tested.

The polarisation resistance of the hems tested is shown in table 5.2. A simple measure of polarisation resistance is used in this analysis, as the corrosion rates of hem sections will be calculated in section 5.6 from the galvanic current flowing between the inner and outer panels. A material with perfect corrosion resistance would have a Tafel plot showing no change in current response with applied voltage i.e. a vertical line on chart 5.7. So, the closer to vertical the plotted lines are the better the corrosion resistance of the hem system. Corrosion resistance (LPR) is measured in Ohms, as the gradient of the line (Tafel slope) is simply applied voltage (V) divided by current response (A). Differences between specimens are assessed using changes in orders of magnitude of resistance. So, HD1NoOH has superior corrosion resistance compared to the rest of the specimens, with the remaining hot dip galvanised he sections showing similar corrosion resistance and the low cost aluminium hem sections have the least resistance to corrosion in an unexposed condition.

The free corrosion potential of the hem system is slightly lower than the equivalent measurements made on the galvanic couples in section 5.4 and shown in table 5.1. This is probably due to the effects of the hem flange geometry on the corrosion system. Recall from figure 5.1 that hem flange adhesive is present in a hem and this will limit the penetration of electrolyte into the hem and may shield the zinc coating from the electrolyte. As the OCP is closer to that of steel it is probable that the cut edge is the predominant metal present in the electrolyte as hem flange adhesive fill around the cut edge of the inner panel is difficult to achieve. The OCP

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measured for the low cost aluminium hems is not significantly different to the hot dip galvanized steel hems, so the aluminium is not having an participating in the corrosion process after short periods of immersion in the electrolyte.



Chart 5.7 Linear Polarisation Plot for Unexposed Hem Sections

Specimen	Linear Polarisation Resistance (Ω)	E _{corr} (V)
HD10H	1880.5	-0.9467
HD3OH	514.92	-0.8888
HD1NoOH	19955	-0.9824
HD2NoOH	2284.8	-0.9998
HD3NoOH	1957.3	-0.9964
PAI2	741.96	-0.9939
PAI3	463.42	-1.0124

Table 5.2 Corrosion Resistance of Unexposed Hem Sections

The Tafel data from hem sections exposed to 480 hours neutral salt spray is shown in Chart 5.8 and the corrosion resistance of these specimens is given in table 5.3. In general the corrosion resistance of the hem specimens after salt spray exposure was equivalent to the performance of the unexposed hem specimens. Zhu (2000) examined the effect of wet/dry cycling on open and confined zinc surfaces and concluded that environments with extended drying times were more aggressive corrosion environments than those with extended periods of wetness. This was thought to be because as the drying time increases the electrolyte film thins concentrating corrosion aggressive ions (such as chlorides) and altering the composition of corrosion products formed. The specimens exposed to 480 hours of neutral salt spray would have effectively seen the equivalent of 480 hours immersion in 5% NaCl, as they were oriented vertically in the salt spray chamber and prepared with masked edges to allow electrolyte to accumulate in the hem.

The effect of the salt spray exposure is more easily seen in the slight reduction of the free corrosion potential to bring it slightly closer to bare steel. With increasing exposure times it would be reasonable to assume that the zinc present on the steel is consumed reducing the amount of zinc present and therefore adjusting the ratio of exposed zinc to steel cut edge and this consequently would account for the slight shift in OCP. There is no evidence to suggest that aluminium is participating in the corrosion system from the data shown in table 5.3 and the corrosion resistance of the low cost aluminium hem is equivalent to the hot dip galvanized steel hems with increasing exposure time. It is noted that the number of specimens available for analysis here is small and as such only cautious conclusions will be drawn in chapter 7.

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Chart 5.8 Linear Polarisation Plot for Hem Sections Exposed to 480 Hours Neutral Salt Spray

Specimen	Linear Polarisation Resistance (Ω)	E _{corr} (V)
HD10HSS	4933.9	-0.8376
HD30HSS	367.89	-0.9239
HD1NoOHSS	1703.9	-0.9815
HD2NoOHSS	1623.8	-0.9714
HD3NoOHSS	1207.8	-0.9807
PAI1SS	1709.6	-0.9816

Table 5.3 Corrosion Resistance of Hem Sections Exposed to 480 Hours Neutral Salt Spray

5.6 Galvanic Coupling of Hem Flange Sections

The galvanic current measured between the outer and inner panel as shown in figure 4.7 was used to calculate the corrosion rate for the hem slice specimens. The area inside the hem flange joint was measured to allow a current density to be calculated and the exposed area inside the joint was estimated by subtracting the area of adhesive coverage in the opened joint from the total measured area. The corrosion rate measured from the exposed area current density (mean current divided by exposed area) gives a better representation of corrosion rate as it takes into account the actual area of metal available in the hem joint for corrosion reactions to take place. Corrosion rates for the total hem area and actual exposed area are shown in table 5.4.

Inner Panel	Outer Panel	Over Hem Sealer	Exposure	Mean Coupled Potential (mV)	Mean Current (µA)	Corrosion Rate (µm/year)		
						Total Hem Area	Exposed Area	
	_	Yes	None	-975	677	663	1326	
	beg	Not UIP Galvanised Steel o		-933	422	395	439	
	nic.			-942	1118	1047	1309	
e	Hot Dip Galva Steel		480 Hours Neutral Salt Spray	-909	371	412	549	
sed St				-872	18.9	16.7	23.9	
				-907	-217	199	332	
ü			None	-977	276	262	524	
2				-986	-760	616	1121	
ы С				-989	1189	1178	2357	
Hot Dip			No	None	-999	11.3	10.3	20.5
	nm	uiu uiu		-972	-13.8	14.8	29.5	
	oat			-947	-0.64	0.63	1.26	
-	0 E		480 Hours	-959	0.32	0.38	0.69	
	Pre		Neutral Salt	-939	-1514	1668	3336	
			Spray	-971	0.44	0.49	0.83	

Table 5.4 Corrosion Rates and Mean Coupled Potentials of Galvanic Coupled Hem Sections

The large variation in the corrosion rates of the specimens shown in table 5.4 is due to local differences in the specimens affecting the corrosion rates. The corrosion rates are calculated from a mean current taken over a short

period of time (minimum of three days) and so are not representative of the corrosion rates calculated from a galvanic current taken over the whole life of the vehicle. As such, they cannot be used as absolute values and are only suitable for comparing specimens with similar exposure periods.

The data shows that there is not much differences in corrosion rates for the all zinc coated steel hem slices, either after exposure or with or without over hem sealer. An important point to note on the all zinc coated steel hem slice samples is the changing polarity of the mean current. This is normal in a system when both WE1 and WE2 are made of the same metal, as the current is able to flow in either direction as the anodic reaction can take place on WE1 or WE2. For example the zinc could be dissolving from outer panel and the current would be positive or zinc dissolving from the inner panel would give a negative current.

The effect of the initial exposure on the outer panels has not affected the corrosion rate of the hem slices. As 480 hours of salt spray is a continuously wet environment with no drying cycle the effect of the exposure is limited in the area of the hem flange. This is because the hem flange will fill with electrolyte from the salt fog and be constantly replenished during the 480 hours (3 weeks) of exposure. The inner and outer panel were not electrically connected externally (i.e. with a wire) during the salt spray test and therefore unless an internal connection was present within the hem galvanic corrosion would not have been able to take place. Only on immersion in the laboratory and connection through the ZRA was galvanic corrosion being assessed. So, the only real effect 480 hours of salt spray could have had on the hem specimens was to create a crevice and allow accelerated corrosion of the zinc coating during the period of exposure. This suggestion is supported by the reduction in the mean potential in the salt spray exposed hems towards a value closer to the free corrosion potential of steel. No differences could be seen between the micrographs of exposed and unexposed hem sections.

The low cost aluminium hems had (with one exception) considerably lower corrosion rates than the all zinc coated steel hems. The one exception had

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pitting on the inner panel, showing that the zinc coating and then the steel had been dissolved and this observation is supported by the measured high negative current (which means current is flowing from the inner panel to the outer panel). This again shows the importance of local variations in surfaces in giving high corrosion rates. In the case of this sample the high corrosion rate was directed towards the inner panel and therefore no perforation would have resulted for the high corrosion rate. Figure 5.5 shows one of the areas of pitting observed on the zinc coated steel inner panel of the low cost aluminium hem with high corrosion rate.



Figure 5.5 Area of Pitting and Zinc Consumption on Low Cost Aluminium Hem Section

Some of the low cost aluminium hems have a positive current flowing from the outer panel to the inner panel and the reasons for this may be poor paint coverage over the aluminium cut edge allowing current to flow from the aluminium to the zinc coated steel. As the currents were small and no significant metal loss was observed from the aluminium outer panel cut edge.

Adhesive fill is an important consideration in the prevention of corrosion in the hem flange. One hundred percent adhesive fill and good adhesion to the hot dip galvanised steel would make mean that no exposed area was seen and therefore a very low corrosion rate would be measured. If a large area of the joint is not covered by adhesive then a large area of zinc coating can protect the steel. Conversely if there is near perfect adhesive fill the corrosion situation could be worse as there is less zinc available to protect the underlying steel and the cut edge corrosion mechanism comes into effect as described previously (the same effect is seen at paint defects). Figure 5.6 shows a void in adhesive fill on an all hot dip galvanised steel hem. The type of void shown in figure 5.6 was typical of the type of defect observed in most of the hem specimens analysed.



Figure 5.6 Void in Adhesive Fill of All Hot Dip Galvanised Steel Hem

The void defect shown above is of particular concern as the zinc coating on the inside radius of the outer panel appears to loose adhesion and come away for the steel substrate when the adhesive void forms. Figure 5.7 shows the zinc coating delaminating from the steel; the contrast and brightness of this micrograph have been modified to highlight the removal of the zinc layer. This removal of zinc from the substrate leaves the underlying steel unprotected and with the presence of a void this may allow corrosion of the steel to initiate. No corrosion on the steel was observed in the areas with any remaining zinc coating, but as exposure times were

short in the test programme studied here, it would be difficult to predict the longer-term consequences of the absence of zinc on the inner hem radius of an outer panel.



Figure 5.7 Zinc Coating Pull Out by Hem Flange Adhesive

5.7 Cut Edge Corrosion Performance of Hem Flange Metals

The cut edge performance of the inner and outer panel materials was assessed after the 480 hours of salt spray exposure. The effects of salt spray on the cut edge corrosion of both a low cost aluminium and all zinc coated steel hem are shown in figure 5.8. The painted zinc coated steel was severely affected by the salt fog and large amounts of blistering and red rust were observed on the cut edge. The pre-coated aluminium experienced no cut edge corrosion at all and was very resistant to the effects of salt spray.



Figure 5.8 Cut Edge Corrosion on Hem Sections Exposed to 480 Hours Neutral Salt Spray

5.8 Corrosion Performance of Low Cost Aluminium Closure

5.8.1 Accelerated Proving Ground Corrosion Testing (PASCAR 1+ 2)



Figure 5.9 Assessment of Corrosion Creep on PASCAR 1 + 2 Low Cost Aluminium Hood

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The low cost aluminium hood that completed PASCAR 1+ 2 structural durability testing was assessed for corrosion performance. There is a significant amount of salt loading used in PASCAR 1 + 2 testing and although this test is not considered as severe as the whole vehicle accelerated corrosion test used by Ford of Europe, in the absence of an opportunity to put a low cost aluminium hood through the corrosion test PASCAR 1+ 2 was the next best alternative. It also allowed the component's structural durability to be tested and this is discussed in the chapter 6. The low cost aluminium closure suffered from no scribe corrosion creep (figure 5.9) and the small amounts of red rust bleed out seen in figure 5.10 are not in an area readily seem by an owner and therefore are not considered as a cosmetic corrosion concern. As with the 30 APGE hood described below Ford Corrosion Engineering considered this level of corrosion to be acceptable.



Figure 5.10 PASCAR 1+ 2 Low Cost Aluminium Hood Cowl Edge Red Rust Bleed Out

5.8.2 Accelerated Laboratory Corrosion Assessment (30 APGE)

The low cost aluminium and all zinc coated steel hood exposed to 30 APGE cycles were assessed for scribe corrosion creep and visually inspected for cosmetic corrosion appearance. The all zinc coated steel hood showed zero millimetres of corrosion creep and no visible signs of corrosion on the hem flanges. The low cost aluminium hood also showed no scribe corrosion creep and small amounts of red rust bleed out (as shown in figure 5.11) were observed at the cowl edge hem; this is likely to be due to inadequate adhesive fill, as seen in figure 5.6. Both hoods were inspected by corrosion engineering and were classified as being acceptable for customer cosmetic corrosion appearance.

	Small Amounts of Red Rust Bleed Out
Cowl Edge Hem Flange PRE-COAT 05-00414	FII

Figure 5.11 30 APGE Low Cost Aluminium Hood

<u>6.0 Structural Performance and Durability of Low Cost</u> <u>Aluminium Closures</u>

6.1 Introduction

A closure has many parts and is subjected to a number of manufacturing processes and the combination of materials, processing and design give the closure strength and stiffness. Adhesives perform a number of important roles in the manufacture and in service performance of a vehicle. In plant adhesives are used to give handling strength to assembled parts and provide a first line of defence from corrosion, by filling voids inaccessible at later stages of manufacture. In service adhesives improve the static strength of joints by giving increased bond areas (compared to the discontinuous joints formed by spot welding) and give resistance to dynamic loads in a crash situation. Adhesives also improve the long-term ride and handling of a vehicle by giving good fatigue resistance.

The two important characteristics of an adhesive joint in an automotive application investigated in this research are:

- Static strength
- Dynamic load resistance

In order to evaluate the static strength of a joint found in a low cost aluminium closure single lap shear specimens were tested in tension to give a measure of shear strength. The dynamic load resistance of an adhesive joint was evaluated on a modified peel test specimen, it was not thought necessary to conduct high strain rate testing. Single lap shear specimens are simple to manufacture and provide a reasonable approximation of the joints seen in a vehicle. They are not being used in this study to give true measures of pure stress states, instead they are intended to give a measure of structural performance that would be seen in the complex stress states encountered in a vehicle adhesive joint.

As a low cost aluminium closure is made from a pre-coated aluminium outer panel and a hot dip galvanised inner panel the adhesive used to join the two panels together in the hem flange joint must be able to bond effectively to both surfaces and retain sufficient strength after environmental exposure. Two adhesives were evaluated in this study. The current one part PVC epoxy hem flange adhesive (Henkel 5811) and a two part epoxy adhesive (3M 7036) with adjustable mix ratio for bonding steel to steel of aluminium to aluminium. Prior to assembly the components of the closure must be stamped to form the inner and outer panels. The results of stamping the pre-coated aluminium outer panel will be discussed and the results of structural durability of a low cost aluminium closure evaluated in an onvehicle test assessed. The PASCAR 1 + 2 was described in section 4.1.4.

Error bars on all charts are absolute maximum and minimum recorded values for the specimens tested from the calculated mean of replicated specimens. At least three replicates were used for each test with four replicated tested for APGE exposure and five replicates tested for Custom exposure.

6.2 Structural Specification Requirements for Hem Flange Adhesives

The minimum structural performance expected from hem flange adhesives is specified by Ford Engineering Material Specifications: WSB-M2G373-A, A2 and B for two part epoxy adhesive for bonding aluminium (A and A2) and steel (B) and WSK-M2G330-A, A2 and A3 for one part epoxy (A), low viscosity epoxy/PVC blend (A2) and high viscosity epoxy/PVC blend (A3). The shear and peel strength minimum performance levels are shown in Table 6.1.

A low cost aluminium closure has a pre-coated aluminium outer panel and a hot dip galvanised steel inner panel. Adhesives are usually formulated to bond to a particular substrate so bonding steel to pre-coated aluminium presents an interesting challenge. The selected adhesive must be able to bond well to both the inner and the outer panel. Henkel 5811 and a two part 3M (3M 7036) adhesive were assessed for their structural durability

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performance on joints made from pre-coated aluminium and steel substrates.

Shear Strength						
Adhesive	Substrate	Oven Cured Adhesion Strength (MPa)	Aged Adhesion Strength, 30 APGE (MPa)			
Henkel 5811	Steel	7.5	No specification for strength retained after			
	Aluminium		30 APGE. 20-40% allowable loss for other environmental exposures (humidity, cataplasma and 500 hours salt spray)			
3M 7036	Steel	10	10			
	Aluminium	10	10			
		Peel Resistance				
Adhesive	Substrate	Oven Cured Peel Resistance	Aged Peel Resistance, 30 APGE			
and the set of the set of the		Initial peak load (N) divide	ed by specimen width (mm)			
Henkel 5811	Steel Aluminium	12 N/mm	No specification for retained peel resistance after environmental exposure.			
		Average peeling load over	127mm after initial peak (N)			
3M 7036	Steel	100	100			
	Aluminium	50	50			

Table 6.1 Shear Strength and Peel Resistance Specification Requirements

6.3 Initial Adhesive Selection Screening

3M 7036 was tested at a number of mix ratios as described in section 4.2.3. The optimal mix ratios for combined shear strength and peel resistance were 4:1, 4.5:1 and 5:1 and these ratios were assessed further as described in section 6.4.

6.4 Adhesive Mix Ratio Optimisation

6.4.1 Shear Strength

The shear strengths of single lap shear joints without environmental exposure (control) and after different bake cycles are shown in Chart 6.1. 3M 7036 meets specification requirements for strength, with the exception of 4.5:1 minimum bake at 9.52 MPa all mean strengths exceed 10 MPa. Henkel 5811 is a one part heat curable adhesive and is therefore sensitive to under bake, this can be clearly seen by the poor performance of the minimum bake specimens in Chart 6.1.

The effects of different environmental exposures on minimum and maximum bake cycle specimens are shown in charts 6.2 and 6.3. Minimum and maximum bake cycle conditions described in section 4.x. There is a general trend to reduction in strengths from control specimens with environmental exposures. The one exception to this trend is the performance of the specimens after exposure to 30 Custom environmental cycles. This exposure consisted of submersion of specimens in tap water for 6 hours a day with 18 hours drying at room temperature and humidity. This was repeated daily during weekdays and the specimens were held at room temperature and humidity over weekends and holidays. Tap water appears not to be an aggressive environment for the system under consideration here and the hydration of the adhesive in some cases (Max Bake 3M7036 4:1,4.5:1 and Min Bake 4.5:1) causes the mean specimen shear strength to increase slightly. This increase is not considered to be significant due to the variability in the specimens tested.



Chart 6.1 Effect of Bake Cycle on the Shear Strength of Control Specimens



Chart 6.2 Effect of Environmental Exposure on Shear Strength of Maximum Bake Specimens The low cost aluminium closure joints were most susceptible to joint strength degradation after 30 APGE cycles and this was most significant for Henkel 5811. 3M 7036 exceeds specification requirements after all environmental exposure regimes and Henkel 5811 meets the specification performance levels required of a one part epoxy. It should be noted that there is no specification performance level set for Henkel 5811 after 30 APGE cycles and this is entirely unsatisfactory as APGE accelerated testing is the most used environmental cycle within Ford of Europe for assessing the performance of adhesive joints.



Chart 6.3 Effect of Environmental Exposure on the Shear Strength of Minimum Bake Specimens

The percentage failure mode occurring on each of the specimens was estimated by eye and the mean predominate failure modes are shown in the colour coded table 6.2. The adhesive joint system under consideration is complex and figure 6.1 shows the types of failure modes and where they

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occur in the specimen. The joint geometry shown in figure 6.1 shows it is possible for many other failure modes could occur in this type of system, but in the experience of the author the failure modes shown are those most likely to occur. The most commonly observed failure mode was a cohesive failure of the pre-coating. This shows that the formed bond between the adhesive and the pre-coating is stronger than the internal (cohesive) strength of the pre-coating. The failure mode of some specimens shifts from cohesive in the pre-coating to cohesive in the adhesive (shown in pink in table 6.2). Now the cohesive strength of the adhesive is weaker than the cohesive strength of the pre-coating for a particular specimen and a change in predominant failure mode is observed. A cohesive failure mode is generally regarded to be a stable high energy failure mode and when comparing the mean shear strengths of cohesive and interfacial failure modes in table 6.1 there is a trend to lower shear strengths in specimens with a predominant interfacial failure mode.



Figure 6.1 Failure Mode Types and Locations in a Low Cost Aluminium Closure Adhesive Join

Environmental Exposure	Mean Shear Strength (MPa) Adhesiye				
	Bake	3M 7036			Henkel 581
	Cycle	4:1	4.5:1	5:1	
Control	Max	13.01	12.72		10.58
	Control	10.72	10.51	9.83	8.84
	Min	10.63	9.52		6.36
Humidity	Max	12.82	12.33		9.14
	Control	10.93	10.51		8.45
	Min	9.44	8.59		6.50
30 APGE	Max	10.04	10.41		5.59
	Min	7.76	8.15		5.18
Custom	Max	13.16	12.71		10.23
	Min	9.72	9.56		6.65
	Failure Mo	de		Colour	

	Code
Cohesive in Adhesive	
Cohesive in Aluminium Pre-coating	
Interfacial between Adhesive and Hot Dip Galvanised Steel	
50% Cohesive in Adhesive 50% Cohesive in Coating	
50% Cohesive in Adhesive 50% Interfacial between Adhesive and Hot Dip Galvanised Steel	

Table 6.2 Failure Modes and Mean Shear Strength of Low Cost Aluminium Adhesive Joints

Henkel 5811 did not generally adhere well to the hot dip galvanised steel substrate and this was probably due to the high coating weights of lubricant used on the steel substrate. A coating weight of 6g/m² of Quaker 6130 lubricant is high and would not be seen regularly in plant. However, when changes are made in the press shop often Stamping Engineers need to apply more lubricant to parts of a blank to ensure the part is stamped successfully. Also, during storage of pressed parts lubricant can pool along edges of component (stamped panels are stored vertically in racks until needed in assembly, sometimes for a period of a days) and these edges are where the hem flange will be formed. To overcome the high coating weights of lubricant, promote initial adhesion and give handling strength, Henkel 5811 (the current production hem flange adhesive) receives an induction cure at the closure assembly stage. The single lap shear specimens tested here were not induction cured and this may be one of the causes of the poor adhesion seen to the hot dip galvanised steel. Although

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the interfacial mode is undesirable because it can rapidly propagate and is consequently a lower energy process the Henkel 5811 specimens met their specification requirements. There is not a significant difference between mix rations of 4:1 and 4.5:1 with respect to shear strength.

6.4.2. Peel Strength

The peel resistance of control joints is shown in Chart 6.4 for mean plateau load and Chart 6.5 for initial peak load. The initial peak load is an indication of the resistance of the adhesive to shear and so the results given in Chart 6.5 are ranked in a similar way to the shear strength results in Chart 6.1.





The mean plateau load measured after the initial peak gives a better measure of the peel resistance and generally an adhesive that performs well in shear will not perform as well in peel. This is shown clearly by the softer lower modulus Henkel 5811 outperforming 3M 7036. Charts 6.4 and 6.5 are shown because of the discrepancy between the adhesive performance specifications given in Table 6.1. Henkel 5811 is a one-part heat curable adhesive and its performance is measured against the initial peak peel load

of 12N/mm and it does not meet the specification requirements. 3M 7036 is a two part adhesive and is measured against a mean plateau peel load of 100 N for steel substrates and 50 N for aluminium. 3M 7036 is on the borderline of meeting the specification requirements of aluminium under control conditions and after environmental conditioning the specification requirements are easily met due to the softening of the adhesive. Henkel 5811 generally performs better in peel that 3M 7036 and the failure mode is cohesive in the adhesive for all the Henkel 5811 joints (table 6.3). The 3M 7036 joints fail cohesively in the coating and there is not a significant difference between the two mix ratios in peel performance.

Environmental Exposure	Bake Cycle	Mean Peel Adhesive 3M 7036 4:1	Plateau (N) 4.5:1	5:1	Henkel 581
Control	Max	43	47		79
	Control	48	44	39	108
	Min	59	38		44
Humidity	Max	62	42	/	72
	Min	24	18		43
30 APGE	Max	90	148		88
	Min	71	75		88
Custom	Max	63	56		69
	Min	41	39		51

Table 6.3 Failure Modes and Mean Plateau Peel Strength of Low Cost Aluminium Adhesive Joints (For Colour Coding see Table 6.2)

The plateau peel performance of the adhesive joints after environmental exposure for minimum and maximum bake cycles are shown in charts 6.6 and 6.7. 3M 7036 had improved plateau peel strength with environmental exposure and this was probably due to the adhesive softening with moisture uptake during exposure to either high humidity, salt fog or tap water immersion. The exceptional result of 148 N mean plateau peel strength of maximum bake 3M 7036 4.5:1 specimens after 30 APGE should be noted. It is not known why this type of environmental exposure has produced such high peel resistance. The adhesive manufacturers are very interested in the chemistry of the mechanism operating in this special case and will be investigating the mechanism further.



Chart 6.5 Effect of Maximum and Minimum Bake Cycles on the Initial Peak Peel Performance of Control Specimens



Chart 6.6 Effect of Environmental Exposure on the Plateau Peel Strength of Maximum Bake Specimens

Henkel 5811 was less sensitive to environmental exposure and remained at approximately the same level of plateau peel strength. All minimum bake cycle joints responded well to 30 APGE cycles in comparison to the control joints and this is due to the significant heat input seen by the joints during the APGE cycling. Joints are exposed to 55 ° for extended periods of time as described in section 4.1.4 and this in conjunction with the moisture uptake helps to promote good peel resistance.



Chart 6.7 Effect of Environmental Exposure on the Plateau Peel Strength of Minimum Bake Specimens

6.4.3 Combined Shear and Peel Performance

The competing demands of shear strength and peel resistance can make adhesive selection difficult. Chart 6.8 shows peel resistance plotted against shear strength together with the appropriate specification limits. An adhesive with adequate shear and peel performance will lie in the upper right quadrant of the chart. Henkel 5811 exceeds the specification limit of 7.5 MPa in control and maximum bake conditions, it should be noted from

table 6.2, however that the mostly interfacial failure modes seen are not satisfactory. 3M 7036 exceeds both the peel and shear specification limits at 4:1 minimum bake cycle, all other 3M 7036 mix ratio and bake cycles are close to meeting their specification limits and the failure modes for the two part epoxy are of the more stable cohesive type.



Chart 6.8 Shear Strength and Peel Plateau Resistance for Control Specimens with Specification Requirements

Environmental aging using 30 APGE cycles is a useful way of discriminating between adhesive in a bonded system. The combination of salt spray, high temperature and humidity cycling is thought to replicate the conditions seen at the Arizona proving ground in the United States. Chart 6.9 shows the effect of minimum and maximum bake cycles on the shear and peel performance of Henkel 5811 and 3M 7036 at 4:1 and 4.5:1 after 30 APGE cycles. This chart shows two very interesting features, the peak in both peel and shear performance of 3M 7036 at a mix ratio of 4.5:1 (maximum bake) and the effect of adhesive type on the shear and peel performance. As previously discussed Henkel 5811 performs much better in peel than in

shear and 3M 7036 performs much better in shear then in peel, this effect is shown clearly on Chart 6.9.





6.5 PASCAR 1 + 2 Structural Durability

The low cost aluminium hood subjected to PASCAR 1 + 2 did not exhibit any structural durability issues. The usual failure mode encountered on hoods during PASCAR 1 + 2 is the failure of the striker and latch assembly. As the low cost aluminium closure weighs 3.3 kg less than the all zinc coated steel closure and the latch and striker assembly is a carry over part from the current closure system, failure of the latch and striker assembly should not have occurred. The test engineers did not report any issues with noise and vibration from the hood, with the exception of wind noise from the gaps around the closure due to dimensional problems caused by spring back. The low cost aluminium closure successfully completed PASCAR 1 + 2 structural durability assessment.

7.0 Low Cost Aluminium Closure Demonstrator Manufacture

Low cost aluminium closures are a new manufacturing concept and as such have never been produced in a mass production environment. As discussed in section 1.1.1 mass manufacture is very challenging and making changes in such a high volume production system can be risky as the implications of such changes may not be fully understood. In order to manufacture a production representative low cost aluminium closure it was necessary to use in plant equipment and this meant interrupting the normal production processes to do so. To make a closure the sheet metal must be stamped, assembled and clinched and finally painted. In plant these different manufacturing processes are controlled by different engineering functions and it was important to work effectively with all the engineering groups to make the closure.

7.1 Stamping Pre-coated Aluminium

The hood demonstrator components were manufactured at the Ford production plant in Saarlouis in Germany. The outer panels were stamped in existing production dies and the die set consisted of four dies. Production die sets represent a significant capital investment and a typical die set for a single stamped panel can cost in the region of one million dollars. So, as would be expected stamping engineers are reluctant to risk damaging a die set and potentially hold up production. Die sets are used in rotation every few days to ensure there is a constant supply of parts to the assembly line. If a die set needs repair then it can cause significant problems for the rest of the production line. In order to minimise the risk of damage to the die set advice was sought form the stamping engineers at Jaguar, as they have recent and extensive experience of the issues of stamping aluminium. The Jaguar stamping engineers recommended decreasing the flange depth to prevent cracking at the highly three dimensionally stressed cowl corners. The stamping engineers in Saarlouis took a number of attempts to produce five good outer panels that were used in this research. As only limited access to the die set was available due to normal production continuing it

took a three months to produce the required number of outer panels. It was necessary to visit plant to optimise the stamping parameters to get the most out of the die set and it was very helpful to be present when the parts were coming off the transfer press and be able to make changes to the stamping set up to improve the appearance of the parts.

The stamping was done on a transfer press, which uses magnetic sensors and electromagnets to move the outer panel from one die to the next. As aluminium is not ferromagnetic the panel had to be moved from one die to the next by hand. Aluminium alloys do not form in the same way as steel and as such a number of modifications had to be made:

- Step 1: The flat sheet (1300 x 2000 mm) was blanked.
- Step 2: The blanked panel was deep drawn in the draw die.
- Step 3: The panel was removed from the press and the cowl corners were trimmed to give a flange depth of 3 mm on the completed aluminium outer compared to a steel flange depth of 6 mm, as shown in Figure 7.1.
- Step 4: The panel was returned to the transfer press and trimmed.
- Step 5: The flanging steels were retracted by 1 mm and lubricant was applied to the cowl corners.
- Step6: The outer was flanged to 90°.

Five outer panels were manufactured in total. These hood outer panels were assembled as shown in Figure 1.4 using the existing steel inner panel, steel hinges and strikers. The current PVC epoxy hem flange adhesive, Henkel Terosen 5811 was used in the hemming operation to join the precoated aluminium outer panel to the steel inner. Production hem tooling was used to create a flat hem as shown in Figure 3.1. The assembled hoods were fixed to a sacrificial vehicle and painted in plant at Saarlouis.



Figure 7.1 Cowl Corner Flange Reduction

Despite the modifications made to the flanging steels and blanks some cracking (not full sheet thickness) still occurred during stamping. The shape of the assembled low cost aluminium hood and assembled all zinc coated steel hood were analysed using a laser digitiser coordinate measuring machine (CMM). The machine uses a combination of projected laser points and image processing software to capture the surface contours of the part. The software allowed the low cost aluminium hood to be compared to the all zinc coated steel hood.

Figure 7.2 shows the mesh representation of the low cost aluminium hood outer surface and figure 7.3 shows the differences in profile between the two different hood constructions. Figures 7.4 shows the on vehicle effect of spring back in the aluminium outer panel.



Figure 7.2 Mesh Drawing of Low Cost Aluminium Hood Outer Surface



Figure 7.3 Profile Differenced Between Low Cost Aluminium and All Zinc Coated Steel Hood Outer Surfaces

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Figure 7.4 The Effect of Spring back on the Fit of the Closure to a Vehicle

As the die set used in stamping was designed to stamp sheet steel it does not have the correct contours to allow the effects of spring back to minimised i.e. to "over strike" the aluminium panel and allow it to recover to a part of the correct geometry. The difference in contour along the red line shown in figure 6.3 is approximately 5.4 mm between the low cost aluminium and all zinc coated steel hoods and this equates to a large overall dimensional difference for the whole component assembly. This dimensional difference due to spring back is unacceptable when the closure is assembled onto the vehicle and figure 6.5 shows this problem very clearly. Modifications to the die profile could be made to allow aluminium outer panels to be stamped successfully to the correct contours and dimensions.

Modification of the existing die set would be an economically efficient method of producing aluminium outer panels to the correct geometry if the low cost aluminium closure was to be substitutes onto an existing vehicle. Jaguar have extensive experience of producing die sets for stamping aluminium and would be able to advise on the changes needed. The primary issue with the CMax Hood outer panel is the flatness or lack of profile on the part. To remedy this situation the curvature of the die would need to be increased.
Modifying a die set is not a trivial task as hardened steels are conventionally used and removing significant amounts of material from the die face together with subsequent finishing operation would require experienced operators and capital investment. However, the cost of producing a new die set would far exceed the cost of modifications.

The spring back of aluminium after stamping is not a well understood phenomenon and the complex nature of the three dimensional stresses experienced during stamping make it vary difficult to predict. Research programmes (under the guidance of Carl Johnson) are underway at Ford in the US to better understand spring back of aluminium and to model the responses of stamped panels. It is hoped that this research programme will result in a predictive tool that can be used to more efficiently produce die sets for aluminium.

7.2 Closure Assembly

The five pre-coated aluminium outer panels were assembled using standard production processes and parts to form low cost aluminium closures. The first stage of assembly involves the all zinc coated steel inner panel. During this initial stage the hinges, reinforcements and strikers are fixed to the inner panel using spot welds. The second stage of the closure assembly involves spray application of the PVC epoxy hem flange adhesive onto the periphery of the inside surface of the outer panel. Once the adhesive had been applied the reinforced inner panel is positioned above the inside surface of the outer panel. The panels are brought into contact in a fixture and the outer panel flanges are progressively formed to produce a flat hem. A flat hem is formed using a die which first folds the outer panel flange from 90 degrees (the 90 degree flange is formed during the stamping operations) to 45 degrees and then finally to flat, zero degrees. This type of hem is known as a flat hem or 180 degree hem. Curved regions of the component, for example the cowl edge present the greatest challenge to the material to form the hem without splitting or cracking.

During the hem flanging operation cracks formed splits at the cowl edge corners, because as previously discussed in the business case the preferred method of hemming for aluminium is either rope or compressed radius hemming as this is a less demanding forming operation. Even though precoated aluminium has improved formability it could not withstand production flat hemming without cracking in highly stressed areas. Compressed radius hemming could be performed using the same fixture arrangement as is currently used in production, with the only changes to the hemming tooling needed. Rope hemming requires a different hemming technique as the outer panel flange is rolled to meet the inner panel. This procedure could be done by an operator or by a robotic arm. In addition to compressed radius hemming being more compatible with current manufacturing processes, it also allows higher levels of craftsmanship to be achieved. A compressed radius hem appears much "sharper" than a rope hem and gives a similar appearance to a flat hem with less demands made of the material being formed.

Once the flat hem was formed the hem area of the assembled closure is induction cured whilst still in its fixture. The induction cure promotes adhesion by increasing the amount of stamping lubricant the adhesive can tolerate. It also gels the adhesive to give it handling strength until it receives the final cure during the e coat paint bake cycle. The assembled closure then joins the vehicle body in white before it is painted.

7.3 Painting

The issues associated with painting low cost aluminium closures have been discussed in the business case in section 2.4.3. The Saarlouis plant paint engineers were very reluctant to paint the low cost aluminium hood on the production paint line as they were concerned the aluminium would contaminate the phosphate bath. The section from the business case was presented to them to reassure them that a small amount of aluminium going through the paint line would not cause contamination. The approximate surface area of the vehicle was calculated and the area of

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exposed aluminium on a one side coated pre-coated aluminium outer panel was less than 3% of the total vehicle body surface area. This exposed area was well within the guidelines set out by Paul Osman (a Ford Paint Engineering Manager) in 2002. On further examination of the material supplied to Ford by Novelis for the trial a green epoxy primer was present on the outside surface of the one side coated pre-coated aluminium. This primer was non conductive and so in reality although the black PE134 coating was present only on one side the material used to make the demonstrator components was in fact two side coated with respect to painting.

A two side coated material is preferable from a paint line contamination perspective but previously it had been thought that the two side coating would lead to paint defects. As a two side coated sheet is stamped, hemmed and handled in plant the "A" class surface i.e. the outside of the outer panel can be scratched and scuffed. If these scratches and scuffs penetrate to the base metal it was thought that this could cause excessive e coat build up at the defects. Electrocoat is a conductive paint and deposits via an electric field in the e coat paint bath, so any defects in an other wise insulting coating would be susceptible to preferential e coat deposition.

This phenomenon has been observed by Novelis when painting parts in isolation of the vehicle body in white at another vehicle manufacturer. Although defects were present in the green epoxy primer no excessive e coat build up or subsequent paint defects were observed on the finished demonstrator components. It is thought that this is due to the very small area of these defects in relation to the rest of the highly conducting steel vehicle body. This implies that a number of low cost aluminium closures (using two side coated pre-coated aluminium) could be incorporated onto a steel vehicle body without excessive e coat build up occurring leading to potential "A" class surface failures that would require rework. As has been previously discussed reworking aluminium body panels increases the risk of filiform corrosion and would be entirely impractical is large numbers of closures required rework.

8.0 Discussion and Conclusions

The low cost aluminium closure concept was designed to produce a reduced weight and corrosion resistant closure for mass produced vehicles. Precoated aluminium allows aluminium and steel to be used together in a closure assembly. The organic pre-coating reduces the risk of galvanic corrosion occurring and gives a stable surface for adhesive bonding. The aim of this research was to prove that: a low cost aluminium closure could at least meet the performance of the existing all zinc coated steel closure in terms of corrosion resistance, structural durability, economic and manufacturing feasibility, so that the opportunity for weight reduction and decreased manufacturing complexity can be realised.

8.1 Business Case

The business case showed that it is practically possible to produce a low cost aluminium closure in a Ford of Europe production plant with minimal changes to the current production processes. It would be necessary to draw on experience within other parts of the organisation, specifically Jaguar to ensure that stamping and handling aluminium in plant is done efficiently. Changes to the hemming process from flat hemming to compressed radius hemming would be required to prevent splitting of the hem. The current steel production paint lines can effectively (without contamination) paint low cost aluminium closures and the paint appearance of a low cost aluminium closures can meet 'A' Class paint appearance requirements.

The economics of producing a low cost aluminium closure were assessed and when the cost implications of weight saving are taken into account, a low cost aluminium closure offers the potential to save \leq 4.85 over the existing closure. This cost save does not take into account the capital investment required to modify die sets to stamp aluminium outer panels or the sheet handling equipment needed to handle a non-ferromagnetic

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material. Low cost aluminium closures give a weight reduction of 3.3 kg per vehicle when used on a hood only. This allows vehicle designers to use the weight saved to increase the feature content of the vehicle, improve safety measures or reduce fuel consumption.

8.2 Corrosion Properties of Low Cost Aluminium Closures

The corrosion properties of low cost aluminium closures were benchmarked against the current all zinc coated steel closure. Hem flanges are complex corrosion environments and production hem flanges have not been previously studied using electrochemical techniques. The materials that make up a low cost aluminium and all zinc coated steel hem flanges were studied using electrochemical techniques to determine their galvanic series and corrosion resistance. Hem sections taken from production hoods were also studied using electrochemical techniques to assess the effects of geometry on corrosion properties. Full size components were tested using accelerated laboratory and proving ground tests to ensure the component could meet corrosion resistance levels required by Ford of Europe Corrosion Engineers.

The galvanic series established that in the environments commonly seen by hem flanges (electrolytes containing significant levels of chloride ions); hot dip galvanised steel was the most anodic material and therefore would sacrifice itself in preference to aluminium. The effect of anode to cathode area ratio was found not to cause rapid dissolution of the pre-coated aluminium outer panel, even in the presence of defects. This finding was very significant as within Ford of Europe, galvanic current concentration leading to perforation is an issue of great concern. The data generated in this research shows that under the conditions tested pre-coated aluminium is not likely to perforate as zinc will sacrifice itself in order to protect the aluminium. Significant amounts of zinc would need to be consumed before the aluminium would start to dissolve and this dissolution would only take place if there was a flaw in the pre-coating.

The corrosion resistance of hem metals was not determined as Tafel behaviour was not obeyed due to the corrosion of zinc being oxygen diffusion controlled. The corrosion resistance of hem sections was determined using linear polarisation resistance and the resistance of low cost aluminium closures was found to be equivalent to all zinc coated steel closures. The corrosion rates calculated from the galvanic current flowing between the hem sections was similar for all specimens and overall low cost aluminium hems had reduced corrosion rates. The demonstrator hoods exposed to accelerated laboratory and proving ground tests were assessed by Corrosion Engineering and were deemed to have acceptable corrosion resistance properties. The proving ground test and accelerated laboratory test gave very similar results and this is important to note as an accelerated laboratory test takes less time to conduct and is far less costly than a vehicle test.

Limited numbers of specimens were available for corrosion testing in this research and all testing was conducted over short time periods or under accelerated conditions; as such, conclusions must be drawn with caution. The corrosion rate and resistance data are not representative of the life time performance of a low cost aluminium closure, however the data does allow comparisons to be made between specimens tested under the same conditions. Conventional all zinc coated steel closures have been in production for many years and corrosion failures on modern vehicles are not frequent occurrences. By benchmarking the performance of low cost aluminium closures and materials against the current closure technology some extrapolation is possible. As the corrosion resistance and corrosion rates (calculated from galvanic coupling current) showed that despite experimental variation the performance of low cost aluminium closures was at least equivalent and in some cases superior to the current closure. It is therefore reasonable to conclude that a low cost aluminium closure will have equivalent lifetime corrosion performance to an all zinc coated steel closure.

Low cost aluminium closures were shown to have improved cut edge corrosion resistance compared to all zinc coated steel closures after 480 hours salt spray. Excellent scribe corrosion creep resistance was seen on

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the low cost aluminium closures and this is especially important as often filiform corrosion can be an issue on aluminium body panels.

The low cost aluminium closure and hem sections tested did not have over hem sealer and still reached an equivalent performance level to all zinc coated steel closures and hem sections with over hem sealer. This is important as it allows for the deletion of over hem sealer, which as previously discussed is difficult, time consuming and expensive to apply. This meets one of the hypothesis requirements that manufacturing complexity can be reduced.

8.3 Structural Performance and Durability of Low Cost Aluminium Closures

The structural performance of low cost aluminium closures was investigated using an on vehicle structural durability test. The static strength and dynamic load resistance of single lap shear and peel specimens were evaluated to determine the structural properties of a hem flange joint in a low cost aluminium closure. An optimised adhesive system (3M 7036) was benchmarked against the current hem flange adhesive (Henkel Terosen 5811) in unexposed and environmentally degraded adhesive joints.

Required performance level discrepancies were found between the Ford Engineering Material Specification for one part epoxy based systems (Henkel 5811) and two part epoxy systems (3M 7036). This made assessing the performance of each of the adhesive systems difficult as they cannot be directly compared to each other.

In general 3M 7036 at 4:1 and 4.5:1 was found to have superior shear strength and Henkel 5811 was found to have superior peel resistance. 3M 7036 met the performance levels required by its specification and despite having superior peel resistance Henkel 5811 did not meet its own specification. Single lap shear strength is considered by the author to be a better representation of hem flange geometry and is therefore shear strength is used as primary assessment factor for adhesive joint performance.

3M 7036 had excellent peel resistance at 4.5:1 mix ratio after 30 APGE cycles and as 30 APGE cycles are generally regarded to be representative of vehicle proving ground tests conducted in the US this result is of particular significance. The excellent peel performance at 4.5:1 3M 7036 (after 30 APGE cycles) would mean this mix ratio would be preferred over 4:1 for use in a low cost aluminium closure.

Both adhesives evaluated would be suitable for use in a low cost aluminium closure and the suitability of both adhesive allows production engineers to select the most appropriate adhesive for the closure being assembled. One part adhesives are generally less costly and easier to apply as they do not require mixing at prescribed mix ratios. However, for larger parts such as a Mondeo hood it may be necessary to use a two part adhesive to give increase handling strength. There is a cost implication of using two part epoxies, but in the case of large components this would be offset by the reduction in additional fixtures needed to support the component as it moves down the assembly line.

Stamping pre-coated aluminium in plant designed to stamp steel is possible but would require optimisation and modification to meet component geometry successfully. Dies can be modified to allow aluminium to spring back to the correct contour and hemming techniques can be altered to prevent spitting at highly stressed areas.

The low cost aluminium closure successfully completed PASCAR 1 + 2 without any structural concerns or reports of noise and vibration issues. PASCAR 1 + 2 is a harsh test and is designed to exploit any structural weakness in a vehicle or component. The reduced weight of the low cost aluminium closure reduced the possibility of striker and latch failure, which are the most common fault seen in the hood area during PASCAR 1 + 2 testing.

8.4 Conclusions

The business implications, corrosion performance and structural performance and durability of low cost aluminium closures have been investigated. Within the scope of this study and the limitations of the number of specimens tested, low cost aluminium closures are considered to be a viable alternative to the current closure architecture.

Low cost aluminium closures at least equal the corrosion performance of all zinc coated steel closures and allow manufacturing complexity to be reduced. The structural durability of low cost aluminium closures has validated by the successful completion of PASCAR 1 + 2. Low cost aluminium closures can be successfully produced with two hem flange adhesives, a one part PVC epoxy (Henkel 5811) or a two part epoxy (3M 7036, 4.5:1 mix ratio). Joints made with either adhesive meet shear strength level specifications and perform to acceptable levels after environmental degradation.

Low cost aluminium closures can be manufactured in Ford of Europe production plants with minimal changes. The part cost and performance advantages of replacing current closure architecture with low cost aluminium closures have been demonstrated in this research.

8.5 Further Work

Low cost aluminium closures have been shown to be viable replacements for current closures in Ford of Europe mass production vehicles within the scope of this research. However, due to the limitations of specimen numbers it is necessary for further work to be done before this new closure architecture is implemented on a production vehicle.

A larger sample of low cost aluminium closures should be tested under accelerated laboratory conditions with full tear down of the hem flange areas to assess the extent of any corrosion present. Long term assessments of electrochemical corrosion performance should be made to ensure no changes in corrosion mechanism occur as exposure times increase. A vehicle corrosion test of the low cost aluminium closure would validate the accelerated laboratory tests and should be conducted.

The structural durability of low cost aluminium closures has been investigated using the current one part PVC epoxy. If production is to go ahead using the two part epoxy in plant trials would be required to investigate the structural performance of this adhesive and assembly and to ensure the manufacturing feasibility.

Finally, only part costs have been considered in the business case presented here. It would be necessary to make a full assessment of the capital costs of die modification and try out; non-ferromagnetic handling systems and designated scrap reclaim systems.

References

ALMEIDA, E. and MORCILLO, M. (2000a) Lap-Joint Corrosion of Automotive Coated Materials in Chloride Media. Part 1 – Electrogalvanised Steel. <u>Surface Coatings and Technology</u>, 124 (2000), 169-179.

ALMEIDA, E. and MORCILLO, M. (2000b) Lap-Joint Corrosion of Automotive Coated Materials in Chloride Media. Part 2 –Galvannealed Steel. <u>Surface Coatings and Technology</u>, 124 (2000), 180-189.

AUTO/STEEL PARTNERSHIP LIGHT TRUCK FRAME PROJECT TEAM (2000). <u>Auto Steel Partnership</u>, Michigan. Available from: <u>http://www.a-</u> <u>sp.org/database/custom/cprotection/CorrosionProtection.pdf</u> [Accessed on 30/06/2005]

BABOIAN, R. (1981) Introduction – The Automotive Environment. <u>Automotive Corrosion by Deicing Salts</u>ed BABOIAN, R. NACE, 1981, 7.

BABOIAN, R. (1995) Automotive Body Corrosion Tests and Standards. In: NASIM UDDIN, M, ed. *Proceedings of the International Body Engineering Conference IBEC '95*, Detroit October 31st – November 2nd 1995. IBEC, Ltd. Publications, 143-150.

BABOIAN, R. and HAYNES, G. (1975) Joining dissimilar metals with transition materials. <u>Society of Automotive Engineers Technical Paper</u> <u>Series</u>, 750714, 1-14.

BABOIAN, R. and HAYNES, G. (1993) Transition materials for automotive applications. <u>Society of Automotive Engineers Technical Paper Series</u>, 930707, 1-5.
BAUTISTA, A. (1996) Filiform corrosion in polymer-coated metals.
<u>Progress in Organic Coatings</u>, 28 (1996), 49-58.

BENATI, F. et al (2002) Correlation between surface topography and lubricant migration in steel sheets for the autobody manufacturing process. <u>Measurement Science and Technology</u>, 13 (2002), 785-791.

BOCKENHEIMER, C. et al. (2002) Network structure in epoxy aluminium bonds after mechanical treatment. <u>International Journal of Adhesion and Adhesives</u>, 22, 349-356.

BOELEN, B et al. (1993) A Literature Survey on the Development of an Accelerated Laboratory Test Method for Atmospheric Corrosion of Precoated Steel Products. <u>Corrosion Science</u>, 34 (11), 1923-1931.

BOVARD, F. (2005) Development of an Improved Cosmetic Corrosion Test for Finished Aluminium Autobody Panels. <u>Society of Automotive Engineers</u> <u>Technical Paper Series</u>, 2005-01-0542.

BRISKHAM, P. and SMITH, G. (2000) Cyclic stress durability testing of lap shear joints exposed to hot-wet conditions. <u>International Journal of</u> <u>Adhesion and Adhesives</u>, 20, 33-38.

BROCKMANN, W. et al. (1982) Surface proerties and adhesion in bonding aluminium alloys by adhesives. <u>International Journal of Adhesion and</u> <u>Adhesives</u>, January, 33-40.

BROWN, K.R. (1998) The Corrosion Performance of Aluminium Automotive Body Panels in Service. <u>Society of Automotive Engineers Technical Paper</u> <u>Series</u>, 980460.

CARR, A. et al. (1997) Pre-coated aluminium sheet development for automotive applications, particularly outer skin body panels. IN: KELKAR, S.G. ed. <u>International Body Engineering Conference IBEC '97</u>, Stuttgart 30 September – 2 October 1997. Michigan Automotive Technology Group Incorporated, 39-47. CHIU, W.K. and JONES, R. (1992) A numerical study of adhesively bonded lap joints. <u>International Journal of Adhesion and Adhesives</u>, 12 (4), 219-225.

CHOW, C.L. and WOO, C.W. (1985) On flaw size and distribution in lap joints. <u>Theoretical and Applied Fracture Mechanics</u>, 4, 75-82.

CIBA-GEIGY (1989) User's Guide to Adhesives. <u>CIBA-GEIGY Plastics</u> <u>Publication No.A17F</u>, September 1989.

COLVIN, E.L. (1997) Filiform corrosion of aluminium autobody sheet in accelerated and outdoor environments. <u>Society of Automotive Engineers</u> <u>Technical Paper Series</u>, 970735.

COURVAL, G.J. and ALLIN, J. (2000) Cosmetic Corrosion of Aluminium Closure Panels: Laboratory Testing versus Field Performance. <u>Society of</u> <u>Automotive Engineers Technical Paper Series</u>, 2000-01-0064, 1-9.

COURVAL, G.J. et al. (2003) Development of an Improved Cosmetic Corrosion Test by the Automotive and Aluminium Industries for Finished Aluminium Autobody Panels. <u>Society of Automotive Engineers Technical</u> <u>Paper Series</u>, 2003-01-1235, 17-20.

COURVEL, G. and SHORES, S. (1999) Elimination of Electrocoating on Aluminium Intensive Vehicles. <u>Society of Automotive Engineers Technical</u> <u>Paper Series</u>, 1999-01-0352. CRITCHLOW, G.W. and BREWIS, D.M. (1996) Review of surface pretreatments for aluminium alloys. <u>International Journal of Adhesion and</u>

Adhesives, 16 (4), 255-275.

DAVIDSON, D. et al (2003) Perforation Corrosion Performance of Autobody Steel Sheet in On Vehicle and Accelerated Tests. <u>Society of</u> <u>Automotive Engineers Technical Paper Series</u>, 2003-01-1238, 45-63. DAVIES, J.R. (2003) <u>Corrosion or Aluminium and Aluminium Alloys</u>, ed DAVIES, J.R. ASM International, 2003, 58.

DAVIS, T.P. (1997) Robustness Thinking and Robust Engineering Design. <u>IMechE</u>, April 1997.

EUROPEAN PARLIAMENT (2000) Directive 2000/53/EC of the European Parliament and the Council of 18 September 2000 on End of Life Vehicles, Annex 2.

FALK et al. (1998) The Influence of CO₂ and NaCl on the Atmospheric Corrosion of Zinc: A Laboratory Study. Journal of the Electrochemical Society, 145 (9), 2993-2999.

FAY, P.A. and MADISON, A. (1990) Durability of adhesively bonded steel under salt spray and hydrothermal stress conditions. <u>International Journal</u> <u>of Adhesion and Adhesives</u>, 10 (3), 179-186.

FONTANA, M.G. (1986a) Corrosion Engineering McGraw-Hill 1986, 13.

FONTANA, M.G. (1986b) Corrosion Engineering McGraw-Hill 1986, 23-28.

FONTANA, M.G. and GREENE, N.D. (1967) <u>Corrosion Engineering</u> 2nd ed. McGraw-Hill New York, 39-44. GAO, G. et al. (2002) Corrosion rates of steel, zinc and bi metal couples in field and laboratory environments. <u>Society of Automotive Engineers</u>

Technical Paper Series, 2002-01-0206.

GEHMECKER, H. (1997) Automotive Corrosion Protection and Practices in Europe. <u>Society of Automotive Engineers Technical Paper Series</u>, 970733, 45-52.

GERMAN, J. (2002) Statement John German, American Honda Motor Co., Inc Before the Committee on Commerce, Science and Transportation (United States Senate). Available from: www.commerce.senate.gov/hearings/012402/german2.pdf [Accessed
14/11/05]

GLEDHILL, R.A. and KINLOCH, A.J. (1974) Environmental failure of structural adhesive joints. Journal of Adhesion, 6, 315-330.

GOLAND, M. and REISSNER, E. (1944) The stresses in cemented joints. Journal of Applied Mechanics, 2 (March) (A), 17-27.

GONCLAVES, J.P.M. et al. (2002) A three-dimensional finite element method for stress analysis of adhesive joints. <u>International Journal of</u> <u>Adhesion and Adhesives</u>, 22, 357-365.

GUTOWSKI, W. (1987) The relationship between the strength of an adhesive bond and the thermodynamic properties of its components. <u>International Journal of Adhesion and Adhesives</u>, 7 (4) 189-198.

HARRIS, A.F. and BEEVERS, A. (1999) The effects of grit blasting on surface properties for adhesion. <u>International Journal of Adhesion and</u> <u>Adhesives</u>, 19, 445-452.

HOSPADUK, V. (1981) Corrosion Fundamentals and their Applications to Automobiles. <u>Automotive Corrosion by Deicing Salts</u>ed BABOIAN, R. NACE, 1981.

http://www.corrosioncost.com/pdf/transportation.pdf [Accessed 06/01/2005]

HUNTER, J. and BARLOW, E. (2002) Pre-primed aluminium autosheet: Electrocoat replacement (ECR) applications. IN: <u>Vorlackiete Werkstoffe im</u> <u>Automobilbau</u>, Bad Nauheim 24 – 24 October 2002.

ISAAC, J. and JOHN, V. (1990) Automobile Corrosion and Corrosion Control at Bimetallic Couples. <u>Society of Automotive Engineers Technical</u> <u>Paper Series</u>, 900191, 1-16. JOHNSON, J.T (2000) Corrosion Cost Appendix N Motor Vehicles. <u>Cost of</u> <u>Corrosion</u>. Available from:

http://www.corrosioncost.com/pdf/transportation.pdf [Accessed 06/01/2005]

JORDAN, D.L. (1990) Influence of Iron Corrosion Products on the Underfilm Corrosion of Painted Steel and Galvanised Steel. IN: KRAUSS, G. and MATLOCK, D.K. ed. *Zinc-Based Steel Coating Systems: Metallurgy and Performance*. The Minerals, Metals and Materials Society, 1990, 195-205.

JORDAN, D.L. et al (1996) Relative Contributions of Several Cathodic Reactions to the Anodic Dissolution of Electrogalvanised Steel. <u>Corrosion</u>, 52 (3), 187-193.

KAFKALIDIS, M.S. and THOULESS, M.D. (2002) The Effects of Geometry and Material Properties on the Fracture of Single Lap Shear Joints. <u>International Journal of Solids and Structures</u>, 39 (2002) 4367-4383.

KELKAR, A. et al (2001) Automobile Bodies: Can Aluminium be an economical alternative to steel? Journal of Materials, 53 (8), 28-32.
KING, W. et al. (1975) Performance of Aluminium Bimetallic Assemblies.
Society of Automotive Engineers Technical Paper Series, 750464.
KINLOCH, A.J. (1987b) Polymer Surfaces and Interfaces: Chapter 4
Environmental Attack at Metal Adhesive Interfaces. Chichester: John Wiley and Sons Limited.

KRESSE, J. and NOWAK, A. (1995) Alternatives to chromating of aluminium and its alloys. IN: <u>DFO/DGO – Tagung</u>, Düsseldorf 14-15
February 1995.
KUROKAWA et al. (1997) Evaluation of the Corrosion Rate of Zinc Coated
Steel Sheets for Automotive Body Use. <u>Society of Automotive Engineers</u> <u>Technical Paper Series</u>, 971003, 143-150. LAHAYE, C. et al (2000) Aluminium alloy selection for closures with respect to functional demands. <u>Society of Automotive Engineers Technical</u> <u>Paper Series</u>, 2000-01-2696.

LANG, T.P. and MALLICK, P.K. (1998) Effect of spew geometry on stresses in single lap adhesive joints. <u>International Journal of Adhesion and</u> <u>Adhesives</u>, 18, 167-177.

LeBOZEC, N. et al (2004) Effect of Climactic Parameters on Filiform Corrosion of Coated Aluminium Alloys. <u>Corrosion</u>, 60 (6), 584-593. LEES, W.A. (1981) Toughened Epoxy on Steel. <u>International Journal of</u> <u>Adhesion and Adhesives</u>, July 1981.

LETH-OLSEN, H. AND NISANCIOGLU, K. (1998) Filiform Corrosion aluminium sheet I. Corrosion behaviour of painted material. <u>Corrosion</u> <u>Science</u>, 40 (7), 1179-1194.

LUNDER, O. et al. (2002) Pre-treatment of AA6060 aluminium alloy for adhesive bonding. <u>International Journal of Adhesion and Adhesives</u>, 22, 143-150.

MANSFELD, F. and KENKEL, J.V. (1971) Area Relationships in Galvanic Corrosion. <u>Corrosion</u>, 27 (10), 436-442.

MANSFELD, F. and KENKEL, J.V. (1975) Galvanic Corrosion of Aluminium Alloys – II. Effect of Solution Composition. <u>Corrosion Science</u>, 15, 183-198.

MANSFELD, F. and KENKEL, J.V. (1975) Galvanic Corrosion of Aluminium Alloys – III. The Effect of Area Ratio. <u>Corrosion Science</u>, 15, 239-249.

MATTSSON, E. (1996) <u>Basic Corrosion Technology for Scientists</u>, 2nd ed. Institute of Materials, 1996, 107. MIKI et al. (1989) Weathering Test of Hem Model Set Inside Automotive Door. <u>Society of Automotive Engineers Technical Paper Series</u>, 892568, 127-131.

MINFORD, J.D. and VADER, E.M. (1974) Adhesive bonding of aluminium automotive body sheet. IN: <u>Automotive Engineering Congress</u>, Detroit 25 February to 1 March 1974. New York: Society of Automotive Engineering Incorporated.

MOULDS, R.J. (1984) Some effects of alloying elements on the performance of bonded aluminium joints. <u>International Journal of</u> <u>Adhesion and Adhesives</u>, 4 (1), 23-25.

NAKAZAWA et al. (1993) Perforation Corrosion of Automotbiles – Field Car and Laboratory Investigation. <u>Society of Automotive Engineers Technical</u> <u>Paper Series</u>, 932367, 415-425.

NATIONAL PHYSICAL LABORATORY (2000) Guides to Good Practice in Corrosion Control: Bimetallic Corrosion. <u>National Physical Laboratory</u> Available from: <u>www.npl.co.uk/ncs/docs/bimetallic.pdf</u> [Accessed ONG, C.L. et al. (1992) The evaluation of non-tank surface treatments for aluminium bonding repairs. <u>International Journal of Adhesion and</u> <u>Adhesives</u>, 12 (2), 79-84.

OSMAN, P. (2002a) Private Communication between Paul Osman and Henkel Surface Technologies.

OSMAN, P. (2002b) Ford of Europe Internal Report: Pro's and Con's for the use of Aluminium in European Ford Products.

PIRES, I. et al. (2003) Performance of bi-adhesive bonded aluminium lap joints. <u>International Journal of Adhesion and Adhesives</u>, 23, 215-223. RAMAMURTHY, S. et al (2005) Corrosion Product Analysis of Aluminium Closure Panels. <u>Society of Automotive Engineers Technical Paper Series</u>, 2005-01-0541. RIVERA, B.F. et al. (2003) Deposition and characterisation of cerium oxide conversion coatings on aluminium alloy 7075-T6. <u>Surface Coatings</u> <u>Technology</u>, 176 (3), 349-356.

ROWE, L.C. (1977) The Application of Corrosion Principles to Automotive Engineering Design. <u>Society of Automotive Engineers Technical Paper</u> <u>Series</u>, 770292.

SCHULTE, G. et al. (1995) Corrosion control with organic corrosion inhibitors (abridged version of article). <u>Welt der Farben</u>, 17 (2/95)

SIKKEL, B. (2005) Private Communication between Lisa Young and Bernard Sikkel (3M Co).

SIMPSON, M. and SURDOUR, M. (2004) Advances in Aluminium Pretreatment. <u>Society of Automotive Engineers Technical Paper Series</u>, 2004-01-1669.

TIBURCIO, A.C. and YERGIN, M.J. (2003) U.S. Automotive Corrosion Trends: 1998 SAE (ACAP) Automotive Body Survey Results. <u>Society of</u> <u>Automotive Engineers Technical Paper Series</u>, 2003-01-1244.

TOWNSEND, H.E. (1996) Behaviour of Painted Steel and Aluminium Sheet in Laboratory Automotive Corrosion Tests. <u>Corrosion</u>, 52 (1), 66-71.

TOWNSEND, H.E. (1999) Licence Plate Cosmetic Corrosion Test of Automotive Coated Steel Sheet. <u>Corrosion</u>, 55 (4), 406-411.

TOWNSEND, H.E. and ALLEGRA, L. (1981) Pre-coated Steel Sheet for Automotive Applications. <u>Automotive Corrosion by Deicing Salts</u>ed BABOIAN, R. NACE, 1981, 337-351. TOWNSEND, H.E. and McCUNE, D.C. (1997) Round Robin Evaluation of a New Standard Laboratory Test for Cosmetic Corrosion. <u>Society of</u> Automotive Engineers Technical Paper Series, 970734, 53-68.

TRETHEWEY, K.R. and CHAMBERLAIN, J. (1995a) <u>Corrosion for Science</u> <u>and Engineering</u> 2nd ed. Longman Scientific and Technical, 75-77.

TRETHEWEY, K.R. and CHAMBERLAIN, J. (1995b) <u>Corrosion for Science</u> and Engineering 2nd ed. Longman Scientific and Technical, 108.

TRETHEWEY, K.R. and CHAMBERLAIN, J. (1995c) <u>Corrosion for Science</u> <u>and Engineering</u> 2nd ed. Longman Scientific and Technical, 165-168.

TRETHEWEY, K.R. and CHAMBERLAIN, J. (1995c) <u>Corrosion for Science</u> and Engineering 2nd ed. Longman Scientific and Technical, 137.

TRETHEWEY, K.R. and CHAMBERLAIN, J. (1995d) <u>Corrosion for Science</u> and Engineering 2nd ed. Longman Scientific and Technical, 137.

TRETHEWEY, K.R. and CHAMBERLAIN, J. (1995e) <u>Corrosion for Science</u> and Engineering 2nd ed. Longman Scientific and Technical, 120.

UEHARA, K. and SAKURAI, M. (2002) Bonding strength of adhesives and the roughness of joined parts. <u>Journal of Materials Processing Technology</u>, 127, 178-181.

VAN DE STREEK, G. (1985) Hem Flange Evaluation of Corrosion Performance. <u>Society of Automotive Engineers Technical Paper Series</u>, 85-05-65.

VINCENT, J.J. and COON, C.L. (1986) The relative effect of paint film thickness on bimetallic and crevice corrosion. <u>Society of Automotive</u> <u>Engineers Technical Paper Series</u>, 860109, 7-21. VOLKERSON, O (1938) Die Neitkraftveteilung in zugeanspruchten Nietverbindingen mit konstanten Laschenquerschnitten. <u>Luftfahrtforsch</u>, 15, 41-47.

WANG, T. et al (2000) A Vehicle Micro Corrosion Environment Study. Society of Automotive Engineers Technical Paper Series, 2000-01-1194.

WANG, T. et al (2001) A Vehicle Micro Corrosion Environment Study of Field and Proving Ground Tests. <u>Society of Automotive Engineers</u> <u>Technical Paper Series</u>, 2001-01-0646.

WÄNSTRAND, O. et al. (2000) An experimental method for the evaluation of the load carrying capacity of coated aluminium: the influence of coating stiffness, hardness and thickness. <u>Surface Coatings and Technology</u>, 127, 107-113.

ZHANG, X.G. (1999) Corrosion Ratios of Steel to Zinc in Natural Corrosion Environments. <u>Corrosion</u>, 55 (8), 787-794.

ZHOU, X. et al. (2003) The influence of surface treatment on filiform corrosion resistance of painted aluminium alloy sheet. <u>Corrosion Science</u>, 45, 1767-1777.

ZHU et al. (2000) Formation of Corrosion Products on Open and Confined Zinc Surfaces Exposed to Wet/Dry Conditions. <u>Corrosion</u>, 56 (12), 1256-1265.

ZHU et al. (2001) Formation of Corrosion Products on Open and Confined Metal Surfaces Exposed to Periodic Wet/Dry Conditions – A Comparison between Zinc and Electrogalvanised Steel. <u>Corrosion</u>, 57 (7), 582-590.