Product development of a nickel-plated fire fighting helmet

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ABSTRACT

This thesis describes the development of a fire fighting helmet for the French market for manufacture by Pacific Helmets (NZ) Ltd, including the major technical development of a process for electroplating unsaturated polyester resin (UP resin).

The need for this study arose from an opportunity identified by PHNZ to enter into the French fire fighting market. The major technical problem was that the helmet shell must be manufactured from nickel-plated UP resin. However, no current technology existed for plating UP resin with a suitably high quality or durability that would withstand the user conditions of a fire fighting helmet.

Literature from existing technologies for plating of similar materials, and attempts at plating UP resin for decorative purposes were reviewed, along with advice from Industry experts in order to understand plastics plating technology and to develop potential methods for plating UP resin for this application.

An iterative hypothesis generation and trial process was used to test potential plating methods in a laboratory on samples of UP resin. A successful methodology was identified. Following this an electroplating pilot plant was constructed and the successful plating methods were used to plate full UP resin helmet shells. Works-like prototypes were constructed using helmet shells that had been successfully applied with a quality and durable electroplated coating suitable for fire fighting helmets. The prototypes were successfully tested against the required product safety standards.

The project concluded with the successful development of a works-like prototype of a Nickel-plated fire-fighting helmet for the French market that met all consumer and technical requirements identified.

Going forward, Pacific Helmets (NZ) Ltd plan to showcase the product at the next annual International Fire-fighting trade show. Plans are currently underway to expand the production facility in Wanganui in order to accommodate the additional helmet production.

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1 INTRODUCTION

This section introduces the study topic, need for research, and the aims, objectives and approach of the study.

1.1 PRODUCT DEVELOPMENT

"The economic success of manufacturing firms depends on their ability to identify the needs of customers and to quickly create products that meet these needs and can be produced at low cost."(Eppinger and Ulrich 2000) A product development process is a set of activities used to achieve this goal by taking a market opportunity and developing it through to production, sale and delivery of the product.

Product Development is an interdisciplinary activity requiring contributions from nearly all functions of a firm; however, three functions are almost always central to a product development project: marketing, design and manufacturing. The marketing function mediates the interactions between the firm and its customers. The design function plays the lead role in defining the physical form of the product to best meet customer's needs; and the manufacturing function is primarily responsible for designing and operating the production system in order to produce the product.

The generic Product Development process includes six phases; planning, concept development, system-level design, detail design, testing and refinement and product ramp up. The process is adapted dependant on the unique context of any one product. Common variants of the product development process include; market pull, technology push, platform products, process intensive and customised product development. A market pull process arises when the firm begins with a market opportunity, then finds appropriate technologies to meet customer needs. A technology push situation is when the firm begins with a new technology, and then finds an appropriate market. A platform product is one in which the firm assumes that the new product will be built around an established technological sub-system. A process intensive product development is when characteristics of the product are highly constrained by the production process. A customised product is developed when new products are slight variations of existing configurations.

This study is an interdisciplinary product development process with emphasis on the manufacturing function. The product development opportunity was initialised when the company, Pacific Helmets NZ Ltd (PHNZ) identified an opportunity, a market pull in the French and greater European fire fighting helmet market. The marketing team identified

that the customers were unsatisfied with the existing products on the market and were interested in using PHNZ's helmets as an alternative. In order to meet customer needs it was necessary to customise; develop a product that was a variant of an existing helmet configuration. The company identified one major problem in meeting the needs of the French market; the helmet shells were required to be nickel-plated. At this point the product development project changed from what PHNZ initially thought to be a common customisation of an existing product into a complex process-intensive project with emphasis on the technical development of the process. The development of a process to nickel-plate the helmet material (unsaturated polyester resin) was therefore central to the development of the Nickel-plated F7A fire-fighting helmet.

1.2 THE OPPORTUNITY

Over the past three years, correspondence with PHNZ's existing European distributors identified an opportunity to enter the French fire fighting helmet market. A substantial number of fire brigade members were unsatisfied with the existing product commonly in use, the F1 helmet produced by MSA Gallet (France). Users complained that the design of the Gallet helmet created potential, yet unnecessary risk of injury and fatality through lack of impact and heat resistance. In addition, due to MSA Gallet's monopoly over the market, prices were not competitive and customer service disappointing.

In light of this market opportunity PHNZ conducted initial research on product requirements for the primary market. A comparison of the French product requirements and the specifications of helmets in PHNZ's existing portfolio identified that the PHNZ F7A helmet was consistent with the requirements of the French, bar one characteristic. The N.I.T.No.311 technical information sheet, rules for personal equipment for fire service and rescue personnel in France stated in the general description that the required helmet *"shall be "nickel" in colour, to enhance the thermal reflection properties"*. Further investigation into the needs of the customers identified that the helmet shells must not only be nickel in colour, but nickel-plated in order to compete with the existing product. This alteration to the product formed the major problem-solving challenge of this project.

A financial analysis of the project was made on the assumption that a conservative 25% of the 220,000 fire fighters market share would be gained within 5 years of product launch. The Nickel F7A sale price was estimated at NZ$330. The total cost of production was estimated at NZ$230 - NZ$258, which would result in a total profit of between $4.0 and $5.5 million over 5 years, after which PHNZ aim to continue to increase its market share. See Section 2.13 for further detail.

In addition, there is potential for profits from applications of the process to alternative industries and the intellectual property royalties that may arise from the technology development. Therefore, this project is not only financially viable, but had the potential to be highly profitable for the company.

At this stage a decision was made to progress in the development of a customized Nickel-plated F7A helmet for the French market.

1.3 THE PROBLEM

Gallet's F1 helmet is manufactured from an injection-moulded thermoplastic; acrylonitrile-butadiene-styrene (ABS), which can be electroplated readily due to the chemical make-up of the material. PHNZ helmets are manufactured from resin-transfer-moulded (RTM) unsaturated polyester (UP) resin, which is known to be very difficult, even thought to be impossible, to electroplate. The costs of PHNZ changing from UP resin to a thermoset material such as ABS are considered too high as they outweigh the increased profit that would result from the project. UP resin also offers advantageous mechanical properties over thermoset materials. Thermoset materials have lower melting points than thermoplastic materials. Given that the helmets are required to withstand extremely high temperatures for use in bush fires, the advantage of using UP resin will be central to PHNZ's 'increased safety' marketing strategy. Therefore the project's technical problem lies in developing a method to produce a quality nickel-plated coating on UP resin.

In addition, a constraint in the development of this process is the cost involved. The conservative (exaggerated) additional cost of plating the helmet shells was initially estimated at a maximum of $50NZD is based on existing electroplating costs for similar plastics. If this estimation is accurate, the Nickel-plated F7A will be competitive with Gallet's helmet price.

1.4 PLATING POLYESTER RESIN

"Electroplating is the coating of an object with a thin layer of metal by use of electricity. The industry was developed to plate metals such as copper, zinc, or silver on other less expensive metals, and more recently, plastics." (Hill 1992)

The plating of plastics with metal is an established technology most commonly used for applications in the printed circuit boards, automobile accessory and decorative industries. The process is of particular importance due to its ability to improve the mechanical and aesthetic properties of plastic.

The ability to plate on plastics has been dramatically improved with the development of the electroless plating process, discovered in 1946 by Brenner and Riddel. The reaction/action is purely chemical and runs by itself once started. Plastics most commonly plated in this way are thermoset materials such as ABS, polycarbonate-ABS blends and polycarbonate blends. ABS is the preferred plastic for plating because it has many butadiene rubber particles (seeding points) uniformly distributed throughout the plastic, that can be chemically etched from the surface to produce chemically active, minute holes in the plastic that provide sites for absorption of a catalyst for the chemical plating process (A.E.S.F. 2004).

Among methods of electroplating non-conductive plastics a widely employed method comprises, in succession; degreasing, etching, optionally neutralising and pre-dipping, then applying a catalyst for electroless plating using a colloidal solution containing a tin compound and a palladium compound, and optionally activating (accelerator treatment), followed by electroless plating and electroplating.

Despite advances in the plating of plastics such as ABS, a process achieving a quality surface plating of nickel on UP resin is yet to be found. It is possible to apply a coating of nickel on UP resin. However the low-quality coating is not durable enough for applications to products such as the helmet shells. This is because UP resin cannot be chemically etched to produce chemically active minute holes as readily as ABS.

Recent studies aimed at achieving a quality plated finish on UP resin include techniques of pre-treatment or conditioning of polyesters by exposing them to a solution to provide them with a hydrophilic surface. This permits electroless and electroplating to provide metal surfaces, which possess superior adhesive properties, as opposed to metal surfaces plated onto untreated surfaces (Sopchak and Skovrinski, 1989). However, to date there is no known method of plating UP resin with a nickel coating of high enough quality required for the application to the fire fighting helmets.

Therefore the development of the 'nickel-plating of UP resin' process is not only central to the development of the Nickel-plated F7A fire fighting helmet, but is the technical constraint and technical focus of this study.

1.5 AIM AND OBJECTIVES

The overall aim of this project is to develop a fire-fighting helmet to meet the requirements of the French fire fighting markets. A central focus of this research will be to develop a process to produce a quality nickel-plating finish on UP resin.

The specific objectives of the research were to:

- Identify initial product specifications.
- Develop a process for Nickel-plating UP resin for application to the F7A fire fighting helmet shell.
- Construct a pilot plant in order to produce sample plated helmet shells.
- Produce sample helmets for testing and validation purposes.
- Test the product to ensure all specifications are met.
- Plan production and commercialisation of the product.
- Evaluate the financial and technical feasibility of the project.

1.6 DELIVERABLES

- Process for quality nickel-plated UP resin.
- Nickel-plated F7A fire fighting helmet prototype.
- Recommendations for production plan.

1.7 CONCLUSION

In conclusion, the following thesis documents the development of the Nickel-plated F7A fire-fighting helmet for the French fire fighting markets. The product development began with the identification of an opportunity and was executed through to small-scale production and prototyping. The major technical challenge within the product development project was to develop a process for electroplating UP resin suitable for fire fighting helmets.

1.8 ORGANISATION OF THESES

The project can be divided into three major phases:

A) Product development of the Nickel-plated F7A fire fighting helmet targeted at the French market.
B) Technical development of a process for producing a quality nickel-plated coating on the surface of UP resin for application to the helmet shells.
C) Process development in which the technical process development (B) is scaled-up to accommodate the production of the product.

Figure 1.8-1 illustrates the organisation of the research in which the completion of the product development process (A) is dependant upon the success of the technical development (B) and the process development (C) phases. The relevant chapters to each phase of the process are also indicated.

Figure 1-1: Flowchart illustrating the organisation of the research

2 PRODUCT DEVELOPMENT CONTEXT

2.1 INTRODUCTION

New Product Development (NPD) is important for an organisations growth, profitability and competitiveness. Identifying and developing the right product that is either new to the market or far superior to a competitor's product is both challenging and formidable, and is the 'number one' factor of the product's success in the market (Cooper, 1994). It has been reported that as many as 3000 raw product ideas are required for one product to be commercially successful (Stevens and Burley, 1997). Companies look to new-product processes, or Stage-Gate systems, to manage, direct, and accelerate their product innovation efforts (Cooper, 2000). Development processes differ in accordance with a firm's unique context (Eppinger and Ulrich, 2000).

This chapter will outline the specific product development context of this project. It will begin with the background information of the company, and will go on to explain how the opportunity for this project was identified. It will then go on to outline the preliminary market, technical and financial assessments carried out in order to define the initial products characteristics, which led to the identification of the major technical development that made up the majority of the research project - the development of a process to electroplate unsaturated polyester (UP) Resin. The chapter will conclude by outlining the product development strategy and plan employed for the specific context of this project in order to increase the chances of the new-product development being successful.

2.2 THE COMPANY

The product being developed depends on an organisation's unique context' (Sethuram, 2004). This section outlines the relevant information about Pacific Helmets Ltd that affects the product, the project and the new-product development process and strategy.

2.2.1 Company Background and History

Pacific Helmets (NZ) Ltd is a privately owned company in Wanganui, New Zealand. Founded in 1980 to manufacture motorcycle helmets for the Australian market, Pacific Helmets Ltd has since expanded their product portfolio to include fire and rescue helmets, sports helmets and specialist military helmets. Exporting to over 60 countries worldwide, its main distributors are in the USA, UK, Australia and Hong Kong.

PHNZ specialises in manufacturing and exporting safety helmet products to the exacting design and performance specification of each customer. With its ever-increasing size, the company continues to recruit and train a highly skilled team of management and employees. There is currently 75 staff working to meet and frequently set the highest possible international standards for technical safety performance. PHNZ states that they have 'an on-going commitment to the development of new and innovative helmet products'.

2.2.2 Company Capabilities

Pacific Helmets Ltd currently has the capabilities to produce a large range of helmet safety products and accessories to cater for its growing number of target markets throughout the world. Designs include:

- Rescue/Emergency Services (6 Designs)
- Bushfire/Wild-land (7 Designs)
- Industrial (hot water, forestry, state emergency service) (2 Designs)
- Fire (11 Designs)
- Police/Riot (3 Designs)
- Sports/Recreation (3 Designs)
- Accessories (5 Articles including bags and torches)

The basic manufacturing process for the helmets is:

1. Helmet Shell Production: UP resin shells are manufactured by Resin Transfer Moulding (RTM). Pigment can be added for base colours of red, blue, yellow or white.
2. Drilling of holes in the shell using an automated drilling machine to place holes to aid assembly
3. Spray-painting the shell with Polyurethane Paint in one of 13 colours, or photo-luminescent paint.
4. Rubber extrusion of the outer rim of the shell.
5. Helmet liners are manufactured from vacuum moulded ABS and Unsaturated Polyurethane.
6. Sub-Assembly: of the helmet liners and all sub-components of the helmets by hand ready
7. Final Assembly: Components assembled by hand to complete products.
8. Dispatch: outgoing orders are packed and shipped.

The current production output is approximately 1700 helmets per week. Management are in the process of expanding and restructuring the factory to better accommodate a more comfortable workspace and allow easier flow of subcomponents and product within the building. The ultimate aim of this extension is to increase efficiency and

productivity. If the development of the helmet for the French market is successful, the extension will allow PHNZ to better accommodate the additional forecast orders.

2.2.3 Company Strategy

One of PHNZ major mid-term goals is to penetrate the European fire helmet market, more specifically the French market, which is considered of high importance due to its large size.

2.3 THE FRONT END PRODUCT DEVELOPMENT PROCESS

The front end of the product development process, otherwise known as the concept development phase, begins with the identification of an opportunity. Initial market, consumer and product research are used to establish target specifications for the proposed product. These specifications are used to generate and select product concepts that are in turn tested to gauge their technical feasibility and acceptance into the market. Based on the results of these tests, a set of final specifications is established, and a development plan is generated to guide the further development of the product.

Figure 2.3-1 is based on the 'front end activities' described by Eppinger and Ulrich (2002) and has been modified to represent the front-end activities carried out in this project.

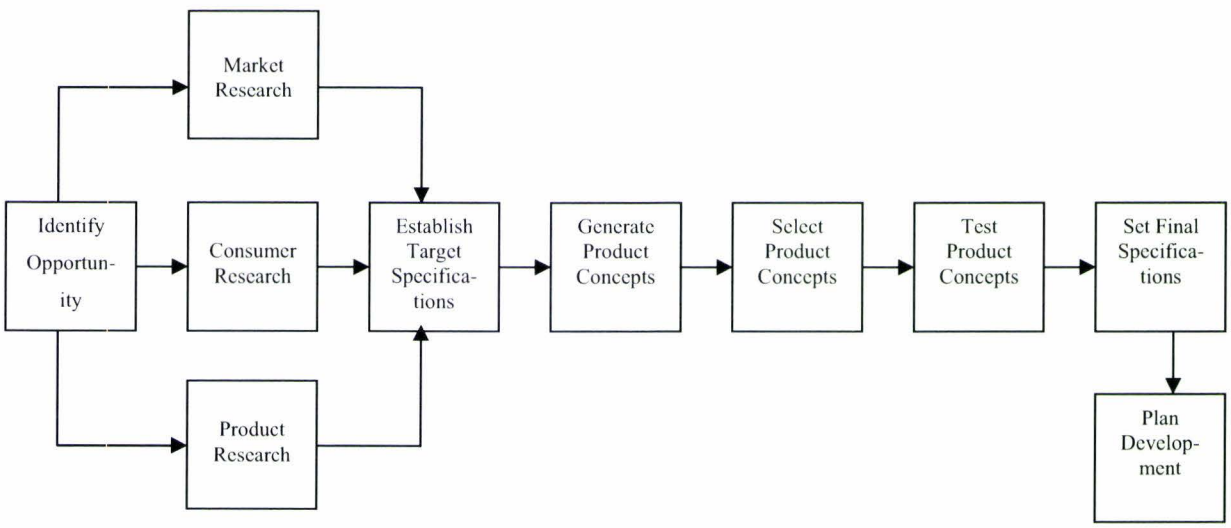


Figure 1-2: Front-end activities of product development process

2.4 THE OPPORTUNITY

Koen, Ajamian et al. (2002) defined an opportunity as "a business or technology gap that a company or individual realises that exists between the current situation and an envisioned future in order to capture competitive advantage, respond to a threat, solve a problem, or ameliorate a difficulty".

As outlined in the Introduction, Chapter 1, initial research identified that there was an opportunity for PHNZ to enter into the French fire fighting helmet market. Correspondence with PHNZ French distributors identified that consumer's were dissatisfied with the existing *Gallet F1* helmet product commonly in use throughout France. At this stage preliminary investigation into the market, technical and financial feasibility were carried out in order to assess the viability of the project.

2.5 MARKET RESEARCH

The market assessment was carried out 'to determine whether the proposed product has any commercial prospects' (Cooper, 2001).

2.5.1 The Market Attractiveness and Potential

The primary target market is French fire fighters of which there are approximately 220,000. This is one of the largest existing fire fighting helmet markets in the world and is therefore the prospect of entering into it is very attractive to PHNZ. Potential secondary markets may include Denmark and Greece of which there are approximately 20,000 fire fighters.

2.5.2 Existing Products in the Market - The Competition

Pacific Helmets Ltd has one direct competitor in the French fire fighting helmet markets, *MSA-GALLET.* Gallet produced their first plastic fire fighting helmet is 1975. In 1985 manufacture of the *F1 Nickel* fire-fighting helmet by Adrien Gallet began. Since then, the *F1 Nickel* (Figure 2.6-1) has been the common helmet in use for French fire-fighters. The F1 helmet system is used around the world by more than 400,000 fire fighters. Gallet states, "Its unique concept protects the fireman against penetration, flames, electricity and radiant heat". It is in compliance with both European and specific *French Fire Fighting Personal Equipment Standards*. In 2002, MSA a US company established in 1914 in Pittsburgh, and describes itself as the 'leader in the development, manufacture and supply of sophisticated products that protect people's health and safety' merged with *Gallet* to form *MSA-GALLET.*

2.5.3 PHNC Competitive edge

The enterprise's (PHNZ) product and process design approach must be linked to the business strategy. Hayes and Wheelwright define five dimensions to competition: cost, quality/performance, flexibility, dependability and innovativeness. A world-class manufacturer must be effective in all five dimensions, but can only excel in one or two dimensions. Pacific Helmets Ltd major dimensions for competition are quality/performance and flexibility. The quality of the F7A helmet is superior to the Gallet F1 helmet in comfort, safety and functionality. It is easy to use and is very similar in form, and is thereby similar in aesthetic appeal. Another major advantage Pacific Helmets Ltd offers all their customers is the flexibility to produce short runs of custom products.

2.6 PRODUCT RESEARCH

Research on the product was aimed at identifying any technical constraints. As the product being developed is primarily used to prevent injury, there are a number of strict standards the product must comply with. Standards include (see Appendix):

- BS EN443 (1997) – British/European Standard: Helmets for Fire fighters.
- N.I.T.No.311 (2002) – French Standard: Protection helmet for Firemen.
- Additional Standards such as the EN116 for eye-protection and face shields are also documented within the EN 443.

Figure 1-3: The MSA-Gallet Nickel F1 Helmet

Other technical constraints included:

- PHNZ are restricted to existing methods of manufacturing helmet parts. E.g. although the shape of a helmet shell can be re-designed, it was restricted to being formed by RTM of UP resin.
- PHNZ does not currently have the ability to produce a nickel-plated helmet as their direct competition MSA-Gallet does.

2.7 CONSUMER RESEARCH

2.7.1 Identifying Consumer Needs

Identifying customer needs is an integral part of the concept development phase of the product development process. The resulting customer needs are used to guide the team in establishing product specification, generating product concepts, and selecting a product concept for further development (Eppinger and Ulrich 2000).

In this project consumer needs were generated from consumer statements collected by PHNZ European (French) distributor, from both the users (fire-fighters) and buyers (brigades) of the helmet. The customer needs are listed below:

1. The helmet protects the user in a fire-fighting environment.
2. The helmet is comfortable to wear during fire fighting.
3. There shall have no sharp edges, roughness or projection on any part of the helmet which is in contact or potential contact with the head when it is worn, such as is likely to cause discomfort or injury to the wearer.
4. The helmet shall cause no irritation to the skin of the user.
5. The helmet can be worn without interference with the wearing of self-contained breathing apparatus or corrective or protective glasses.
6. The helmet is lightweight.
7. The helmet shall be adjustable in order to improve the wearing comfort and the helmet efficiency.
8. The helmet adjustment shall be easily adjustable by the wearer without the use of tools.
9. The helmet can be fitted, removed and adjusted quickly.
10. The helmet shall have the facility for the fitting of optional neck, ear and face protection.
11. The helmet is aesthetically pleasing.
12. The helmet shell is Nickel-plated.
13. The helmet is competitively priced.
14. The helmet product is supported by excellent customer service.
15. The helmet is durable.

16. The materials should be of durable quality. Their characteristics shall not undergo appreciable alteration under the influence of ageing or of circumstances of use to which the helmet is normally subjected (exposure to sun, rain, cold, contact with skin, effects of sweat).
17. The helmet can be customised to suit changing or individual user needs.
18. The helmet shall allow the wearer to hear under normal circumstances of use.

2.8 ESTABLISHING TARGET SPECIFICATIONS

Eppinger and Ulrich (2000) describe the term 'product specifications' to mean the precise description of what the product has to do. In this project, the metrics of the specification list were based on consumer needs and technical requirements resulting from International and French safety standards. Marginal and ideal target values for each metric were established using International Standards and consumer input. Competitive benchmarking information on the Gallet F1-S was gathered and tabulated against that of the PNHZ F7A to compare the products (Table 2.8-1).

Table 2.8-1: Product specification matrix - Comparison of the PHNZ F7A and MSA-Gallet F1-S

Product specification matrix							
Metric	Need No.	Imp.	Units	Marginal Value	Standard Value	Gallet F1-S	PHNZ nickel F7A
1. French Standards Tests							
a) Nickel in Colour	11,12	5	Binary	Pass	Pass	Pass	Fail
b) Total Mass	2,6	5	G	<1700	<1400	1200	1300
2. European Standards Tests							
a) Shock absorption	1	5	kN	<15	<14	<15	<15
b) Resistance to Sharp objects	1	5	Binary	Pass	Pass	Pass	Pass
c) Mechanical Rigidity	1	5	mm	<15	<14	<15	<15
d) Flame Resistance	1	5	Binary	Pass	Pass	Pass	Pass
e) Radiant Heat Resistance	1	5	°C	<47	<45	<45	<40
f) Electrical Properties	1	5	mA	<1.2	<1.1	<1.2	<1.2
g) Retention system strength	1	5	mm	<15	<14	<15	<15
h) Durability	15,16	4	Years	>3	>5	4	4
i) Sharp edges	3	4	Binary	Pass	Pass	Pass	Pass
j) Irritation to skin	4	3	Binary	Pass	Pass	Pass	Pass
k) Interference with breathing apparatus or eyeglasses.	5	4	Binary	Pass	Pass	Pass	Pass
3. Head Sizes	2	5	cm	54-62	54-64	53-64	54-64
4. Adjustable fit of helmet	7	4	Subj.	>3	>4	4	4
5. Time taken for user to fit helmet	9	3	s	<12	<9	9	9
6. Tools required for fitting adjustment	8	3	List	>2	0	0	0
7. Additional Feature availability	17						
a) Lamp		4	Binary	Pass	Pass	Pass	Pass
b) Neck Protector		4	Binary	Pass	Pass	Pass	Pass
c) Lights and Clips		4	Binary	Pass	Pass	Pass	Pass
d) Custom Badges/Decals etc		4	Binary	Pass	Pass	Pass	Pass
8. Traditional Helmet Form	11	4	Binary	Pass	Pass	Pass	Pass
9. Unit Manufacturing Cost	13	4	$NZD	<230	<200	7	208
10. Manufacturing Flexibility	14,17	4	Subj.	>3	>4	1	5
11. Helmet allows user to hear normally	18	4	Binary	Pass	Pass	Pass	Pass
12. Facilities for fitting optional:	10						
a) Neck protector		4	Binary	Pass	Pass	Pass	Pass
b) Ear protector		4	Binary	Pass	Pass	Pass	Pass
c) Face protection		4	Binary	Pass	Pass	Pass	Pass

2.9 PRODUCT CONCEPT GENERATION AND SELECTION

Eppinger and Ulrich (2000) state; "Once the targets have been set, the team can proceed to generate solution concepts. The target specifications then can be used to help the team select a concept and will help the team know when a concept is commercially viable."

In this project, the initial solution concept generated was the existing PHNZ F7A. PHNZ Management considered using this existing product as a method of saving significant development costs, time and effort.

2.10 THE SELECTED PRODUCT CONCEPT – THE F7A

The Pacific F7AK/2 Mk 3B Structural Fire Helmet EN443 Approved (a.k.a. The F7A) (Figure 2.10-1) is available in 3 popular configurations: standard, premiere, and premiere elite. PHNZ is currently supplying a small number of the 'premiere' model to the French market. As the model that best meets the French brigades specific needs, likes and dislikes, the product requirements for this project are based upon this product.

Figure 1-4: The Pacific F7AK/2 Mk 3B Structural Fire Helmet-Premiere Model

Premier Model Specification:

- Lightweight Kevlar® Shell
- Semi-gloss paint finish (Std Colours)
- PU impact liner c/w leather headband, ribbon cradle, BBN crown comfort cap
- Ratchet size adjustment 54-62cm
- 2 point polyester chinstrap c/w Pacific Snap-clip Buckle

- Internal Polycarbonate 2mm Face Shield, Certified to EN166
- SCBA Clip mounts
- Certified to EN443
- 2pt Nomex Chinstrap
- Leather Crown Comfort cap
- 3mm Face Shield, Certified to EN166
- Internal Eye Protector Certified to EN166

The following features and accessories are available in addition, and are sold separately to the F7A Premiere:

- Neck Protector – Various Designs/Materials
- UKE Lights & Easi-Glide Clip
- Customised Striping/Badge/Decals
- Face Shield 3mm "PACICARB" Anti scratch/Anti fog, Fire retardant

2.11 TESTING THE PRODUCT CONCEPT

The F7A was compared against the Gallet F1-S on how well they met the target specifications in order to gauge:

- Acceptance by the French market.
- Technical feasibility

The results show that the PHNZ F7A and Gallet F1-S met all specifications relatively evenly except for:

- The F7A was not Nickel Plated
- PHNZ offered a much better 'Manufacturing Flexibility'.

This led PHNZ to believe that the F7A would be able to penetrating the French market. Sample helmets were then sent to the French distributor in order to gauge consumer acceptance of the product.

2.11.1 Gauging Product Acceptance from Consumers

In order to gauge the acceptance of a competitive product the distributors showcased PHNZ's existing F7A product. The major outcomes of their correspondence with the consumers were as follows:

- Consumers were impressed with the PHNZ helmets functionality, which was rated higher than the existing product in use.
- The price was competitive.
- Consumers were enthusiastic about the variety of products available and PHNZ's willingness and flexibility in producing customised products.

- The aesthetic appeal of the product was high, with one exception; the existing product in use were Nickel-Plated, which was preferred.
- The only concern was that the consumers wondered why PHNZ could not produce Nickel-plated helmet shells. They questioned why PHNZ could not manufacture something that the French could, and therefore questioned PHNZ's integrity as a helmet manufacturer.

From this research PHNZ gauged the potential product acceptance as very good. If they could produce a Nickel-Plated helmet, then the product acceptance was gauged as excellent. It was evident that the consumers were unhappy with the monopoly the existing product manufacturer had over the market, in which a lack of competition within the market lead to uncompetitive pricing, unsatisfactory service and inflexibility in product improvements and customisation. Furthermore, informal consumer research identified that French fire fighters were happy to deviate from the existing product, the 'F1 Gallet', despite the helmet being produced by a USA owned and French based company *MSA-Gallet*. There was therefore little threat that loyalty created by a 'Made in France' product would affect PHNZ's competitive edge.

Overall, PHNZ believed there was huge potential in the French market. However, the helmet product would have to be nickel-plated in order to compete well, and prove PHNZ's integrity. Therefore the initial product design concept was based on the PHNZ F7A with a Nickel-plated shell.

2.11.2 Technical Feasibility

The proposed product is essentially the PHNZ F7A with a nickel-plated shell. Therefore every aspect of the helmet is technically feasible except for the nickel-plating of the helmet shell. Therefore the preliminary technical feasibility study focused on identifying whether or not it is possible to plate nickel onto unsaturated polyester (UP) resin - the helmet shell material currently used by PHNZ. If such a process were identified, it would be necessary to ensure that the plating process would not alter the mechanical properties of the helmet shell in such a way as to affect the products ability to meet international standards.

Initial research (including literature review and discussion with outside experts) into the ability to plate on UP resin was very negative. It was found that although some plastics, such as ABS can be plated with metal relatively easily; UP resin was very difficult to plate, and to the knowledge of NZ industry experts, a technology not currently in use. A review of the competitive literature identified that Gallet were using a thermo-set plastic called ABS, which is why they were able to plate their helmet shells readily.

Reviews of the literature and patent searches identified that the inability to plate UP resin was not due to lack of trying. A number of researchers had made efforts to unlock the secret of plating on UP resin but failed to achieve a quality plating finish, these included:

- Bauer, Johnson et al. (1971)
- Januschkowetz and Laub (1977)
- Sopchak and Skovrinski (1989)

Further searching found a website called *www.finishing.com* through which correspondence with a Mr Raafat Al Bendary began. Mr Bendary, an electroplating expert from Cairo, Egypt is the owner/operator of an electroplating plant at which he claimed he was using a process that he developed to electroplate UP resin with copper. PHNZ's Chief Operations Officer visited Mr Bendary's plant and viewed the plating of UP resin parts. Therefore it was confirmed that it is technically feasible to electroplate UP resin. However, Mr Bendary's plating was for a decorative application only, and it was unknown as to whether the process could be used for the application of fire fighting helmets. It became PHNZ goal to better understand Mr Bendary's plating technology and how it might be further developed to meet their specific requirements.

2.11.3 Technical risks

The biggest technical risk to this project was the possibility that the process for 'electroplating UP resin' would not be able to be developed to meet the requirements of PHNZ's specific application. It was acknowledged at this time, that although Mr Bendary's process was a trade secret. It was therefore at Mr Bendary's discretion to share his knowledge.

Additional technical risks include:

- The plating process may alter the mechanical properties of the UP resin. For example; if the process caused a decrease in the tensile strength of the material; the impact resistance of the helmet shell would be decreased and could affect the products ability to meet safety standards.
- The plating may not be durable enough to withstand the rough use of the product over its five-year average life expectancy.

2.12 ACQUISITION OF EXPERTISE

It was unlikely that PHNZ would be able to develop such a process with their existing expertise and technology capabilities. PHNZ established a relationship with Massey University for assistance with resources and expertise. The project quickly evolved into

this Masters in Technology (Product Development) project. An advantage of carrying out this project as an MTech was the availability of Massey expertise and facilities.

In addition a working relationship with Mr Bendary of Egypt was formed during the study in order to better understand plating technologies. Mr Bendary was happy to mentor the student on his understanding of the mechanisms of plating UP resin.

2.13 FINANCIAL ASSESSMENT

2.13.1 Expected Sales

There is an overall market potential of 220,000 Fire Fighters, and therefore potential fire fighting helmet sales in France. PHNZ management made a conservative estimate that 25% market share (55,000 helmets) would be gained within 5 years.

The F7A is currently selling for Euro 150 (NZ$275). The expected wholesale price of the Nickel-plated F7A is Euro 180 (NZ$330).

2.13.2 Expected Costs

The current costs of producing one F7A helmet (complete standard model) are broken down as follows:

Materials	$74
Consumables	$18
Direct Labour	$44
Overheads	$52
Total	**$208 (NZD)**

The only additional cost to the $208 for the Nickel-F7A would be in the electroplating of the helmet, which would depend upon the success of the project and if so then whether PHNZ decide to carry out the electroplating themselves or form a relationship with an existing electroplater who could carry out the plating for them.

A high level sensitivity analysis based on information collected from the NZ electroplating industry resulted in an expected cost of between $22 and $50 would be incurred for electroplating of the helmet shells. The most influential factors were economies of scale and whether the plating was carried out by PHNZ or an independent electroplater.

Therefore the total cost of producing the Nickel F7A is estimated to be between $230 and $258 (NZD). Therefore the profit made on each helmet is approximated between

$72 and $100. If the expected market share of 25% of the 220,000 French Fire Fighters is gained in 5 years then the profit over that time will be between NZ$4.0m and NZ$5.5m.

2.14 DEVELOPMENT PLAN

The market, technical and financial assessments reveal the project to have very good commercial prospects. The preliminary technical product and performance objectives were considered technically feasible, with the technical risks being outweighed by the potential for this project to be very profitable. Based on these outcomes, the decision was made to go forward with the development process.

The most significant outcome of the preliminary market and technical assessments was that the project relied on the successful development of a single technology. That is, the development of the process to 'electroplate UP resin' for the application of PHNZ's French fire fighting helmets. Figure 1.8-1 outlines how the technical development fits into the overall product development process.

It was also identified that no existing patent for the required technology had been identified. Following the development of the technology, the Intellectual Property would belong to PHNZ.

2.15 TECHNICAL AND PROCESS DEVELOPMENT PLANS

Technical Development Plan

The technical development of the 'Electroplating UP resin' process includes the following stages.

1. Identifying the problem – why it is difficult to electroplate UP resin?
2. Technical Research – secondary research to identify similar technology and research studies in this area and applying it to the problem in order to form hypothesis for solving the problem (see Chapter 3).
3. Establishing plating specifications – what technical specifications is the plated surface required to meet?
4. Plating process development – developing and testing hypothesis for each of the four stages of the electroplating process:
    - Etching (see Chapter 4)
    - Activation (see Chapter 5)
    - Electroless plating (see Chapter 6)
    - Electroplating (see Chapter 7)
5. The technical outcome is a process that meets the specifications.

Process Development Plan

Upon the successful technical development of a process for electroplating UP resin in the laboratory, the process will be scaled up to a pilot plant in order to produce full-scale looks-like and works-like product prototypes. The process development section of the project (see Chapter 8) will include:

1. Pilot plant design and development.
2. Construction of the pilot plant.
3. Define pilot plant plating parameters
4. Plating of the helmet using the pilot plant.
5. Product testing the prototype against the technical requirements including safety standards. Failures may result in technical re-development.
6. Consumer testing by PHNZ

3 LITERATURE REVIEW

3.1 INTRODUCTION

It was the technical aim of this project to develop a commercially viable process that would achieve a permanent, high-quality nickel-plated finish on PHNZ's fire fighting helmet shells, which are made from unsaturated polyester (UP) resin. To date, no literature has been found in support of such a process existing. Instead the relevant literature generally outlines the difficulties, shortcomings and disadvantages of attempted methods.

Initial research concentrated on existing electroplating practices, with specific attention to plating of plastics. It was found that plating non-conductors including a variety of plastic materials could be achieved through a method known as electroless plating (a.k.a. electroless deposition). The uses, properties and mechanisms of relevant electroless and electroplating processes are reviewed in this chapter in order to outline the difficulties in plating some plastic materials, in particular UP resin.

The literature also identifies attempts to plate onto UP resin including US Patent No. 3,567,594 in which Wells (1969) claims to have invented a method for electroplating plastics which Donovan, Maguire et al. (1981) quoted as being "futile for polyesters". This method was unsuccessful because although metal could initially be plated onto the UP resin surface, the adhesion was of poor quality, and the plating only temporary.

Sopchak and Skovrinski (1980) claim to have invented an improved process for plating polyesters in their patent 'Method for pre-treatment of polyesters for metal plating' in which they outline several disadvantages of prior art including that one "does not possess sufficiently high peel strength" (Januschkowetz and Laub 1977) and that they were: too expensive, required continual control of the process which considerably complicated its conduct, added difficulty in disposal of the used composition, required significant increases in process time, and required the use of dangerous chemicals.

In order to overcome these problems, research on plating technologies used on similar materials, such as ABS were analysed in order to understand how these processes might be adapted to plate UP resin and meet the aims of this project.

'Understanding the Material' was identified as the first step to developing a new plating process for the said material. Relevant literature on UP resin was subsequently reviewed.

In addition, it was important to identify if there were any methods of applying additional or intermediate material layers to the UP resin that might be more easily plated. In doing so, applying an acrylic-urethane coating to the helmet prior to plating was also visited.

Through gaining this understanding of the material, hypotheses as to how UP resin might be plated were established and tested. This section of the thesis follows the string of relevant literature that led to these hypotheses and the subsequent methodologies for plating UP resin in this project.

In summary, this chapter outlines the science and history of electroplating technologies, with specific focus on the plating of plastics. Prior attempts of plating on UP resin and similar thermosetting plastics are analysed in depth along with more successful methods of playing ABS and other thermoplastics in the hope that they may be modified or transposed into a process that might work to successfully plate UP resin for the application of this project.

3.2 ELECTROPLATING

Electroplating occurs by the process of electrodeposition. In the Electrochemistry Encyclopaedia Schlesinger (2002) states that "electrodepostion is the process of producing a coating, usually metallic, on a surface by the action of electric current. The deposition of a metallic coating onto an object is achieved by putting a negative charge on the object to be coated and immersing it into a solution, which contains a salt of the metal to be deposited (in other works, the object to be plated is made the cathode of an electrolytic cell). The metallic ions of the salt carry a positive charge and are thus attracted to the object. When they reach the negatively charged object (that is to be electroplated), it provides electrons to reduce the positively charged ions to metallic form." Figure 3.2-1 is a simple illustration of the mechanism of electrodeposition.

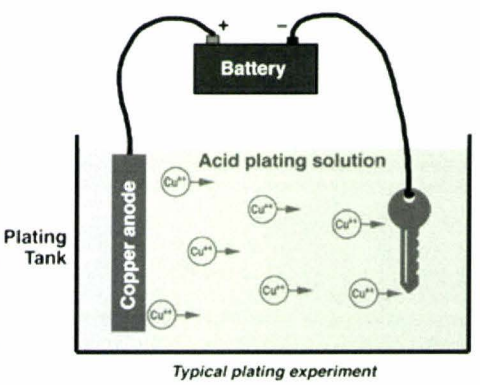


Figure 1-5: A typical electroplating experiment (A.E.S.F.2004)

While the plating of metal conductors is relatively easy, a challenge lies in plating non-conductive surfaces such as ceramics and plastics. The problem lies in developing a method of electro-deposition on a non-conductive surface. The following section will outline the development and mechanisms of plating on non-conductive, more specifically, plastic materials.

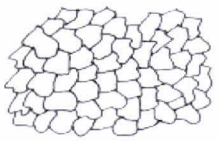
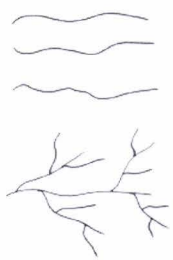
3.3 ELECTROPLATING PLASTICS

3.3.1 Plastics

Since the end of the Second World War the use of plastics has increased remarkably due to the systematic exploitation of their principle advantages, i.e. lightness, flexibility and toughness, ease of fabrication of complex components, and excellent surface quality as fabricated. This has led, in a very wide range of applications, to the replacement of metals with plastics as materials of construction (Hart 1996).

Plastics are produced by chemically modifying natural substances or are synthesized from inorganic and organic raw materials. On the basis of their physical characteristics, plastics are usually divided into thermosets, elastomers and thermoplastics. These groups differ primarily with regard to molecular structure, which is what determines their differing thermal behavior. The type of plastic greatly affects its ability to be plated. Table 3.3-1 lists the characteristics of the various types of plastics (GVD 2002-2005):

Table 3.3-1: Characteristics of plastics (GVD 2002-2005)

Molecular structure	Characteristics and applications
Thermosets 	Thermosets are hard and have a very tight-meshed, branched molecular structure. Curing proceeds during shaping, after which it is no longer possible to shape the material by heating. Further shaping may then only be performed by machining. Thermosets are used, for example, to make light switches.
Elastomers 	While elastomers also have a cross-linked structure, they have a looser mesh than thermosets, giving rise to a degree of elasticity. Once shaped, elastomers also cannot be reshaped by heating. Elastomers are used, for example, to produce automobile tires.
Thermoplastics 	Thermoplastics have a linear or branched molecular structure which determines their strength and thermal behavior; they are flexible at ordinary temperatures. At approx. 120 - 180°C, thermoplastics become a pasty/liquid mass. The service temperature range for thermoplastics is considerably lower than that for thermosets. The thermoplastics polyethylene (PE), polyvinyl chloride (PVC) and polystyrene (PS) are used, for example, in packaging applications.

3.3.2 The Plastics Plating Industry

The initial motivation for the development of processes for electroplating on to plastics came from the automotive industry and this market sector has consistently been by far the largest user of the product. After the automotive market, the next most important application for plated plastics is for domestic fittings where the hygienic qualities of the finish and ease with which it can be kept clean are important factors. Other significant uses included knobs and buttons in the electronics and white goods industry (Hart 1996).

The most common reasons various industries are interested in plated plastics include (Adcock 2004):

- Lower cost
- No secondary operations (i.e., no de-flashing or buffing)
- Design freedom (i.e., the ability to mould large and complex parts)
- Weight reduction

Plating on non-conductors (including plastics) has been achieved since the development of the electroless plating process. The process earned its name because it operates without using electricity. The action is purely chemical and runs by itself once started (A.E.S.F. 2004).

Electroless plating of metal is an important industrial technique for metallising insulators (e.g., plastics, glass) and objects with geometries that are difficult to coat by electroplating (Yosi, Valery et al. 1995). In contrast to electroplating, where an applied electric current supplied electrons to reduce a high-oxidation-state metal precursor, the basis of electroless plating is an autocatalytic redox reaction. The critical material prerequisite for initiating metal deposition is the presence of an appropriate catalytic surface.

The history of electroless plating began with the serendipitous discovery, by Brenner and Riddell, of electroless nickel phosphorus, during a series of nickel electroplating experiments in 1946.

Electroless copper chemistry was first reported in the following year by Narcus (1947) commercial application was reported by Cahill (1957) and Zeblisky, McCormack et al. (1963) using formaldehyde as a reducing agent in tartarate baths. Modified formulations have been more recently developed by Shipley (1984), Blurton and Nuzzi (1987) and Mallory and Hajdu (1990) that result in higher plating rate with extremely stable conditions under a wide range of operating conditions.

According to Mallory and Hajdu (1990), such plated non-conductive articles were mainly decorative, and adhesion of the plate to the substrate was minimal. In the early 1960's, due to technological advances in chemical processing techniques, plating on plastics began on a commercial level. Industries that utilise plated plastics include automotive, plumbing, appliance and electronics (Kuzmik 1990).

Hart (1996) describes how early plating on plastics processes, using conductive paint or chemically reduced silver on surfaces roughened either mechanically or by solvent attack, did not provide adequate adhesion. In the mid 1960's, etching solutions based on chromic acid were developed which could successfully be used with ABS. Use of these solutions resulted in selective removal of the butadiene phase from the resin to give a micro-etched surface providing bonding to the subsequent conductive layer.

This development came at a time when great improvements were also being made in the technology of electroless nickel and electroless copper deposition. These advances in electroless plating combined with the development of the etching technique gave rise to a system that provided a highly conductive coating exhibiting satisfactory adhesion to the plastics surface. Current plating-on-plastics processes still employ the basic technology developed at that time, although inevitably many refinements and improvements have been made (Hart 1996).

Practical experience has shown that not all plastics can be plated satisfactorily. The highest volume plate-able plastic is acrylonitrile-butadiene-styrene polymer, or ABS (Mandich and Krulik 1993). Others include epoxies, phenolics, polyphenylene oxide and smaller amounts of polypropylene, polysulfone, nylon, polyvinylidene chloride, polycarbonate and others (Krulik 1979).

Decorative deposits offer a pleasing, reflective appearance while also providing corrosion resistance, lubricity, and durability (Kirk and Othmer 2004). In this project, the aim was to achieve a primarily decorative coating, with similar importance lying on the durability of the coating being able to withstand the wear caused by use of the fire fighting helmet product.

3.3.3 Key properties of electroplating plastics

It is customary to apply standard test methods to determine the relevant parameters of electroplated materials. Documents on plating specifications for many phases of the plating process are published by organisations including the Federal government, the military, ASTM, ISO, SAE, etc.

The most tested properties of plated coatings include: Adhesion, deposit thickness, corrosion resistance and protection, electrical resistivity, hardness performance, melting point, deposit elongation, internal (intrinsic stress), magnetic tendency, solderability, ductility, porosity, hydrogen embrittlement, fatigue and appearance (Kirk and Othmer 2004).

It is also important to understand that many of the properties of the electroless deposits and the electroless coating processes used to deposit them are interrelated (Horner and Durkin 1997). For example, maximizing deposit hardness through a post plating heat treatment will reduce the corrosion resistance of the deposit.

A clear understanding of the inter-relationships concerning the properties for any of these coatings is important for the control of the overall performance characteristics for both the process and the resulting coating. Mechanical properties of electroless nickel–phosphorus alloys are dependent upon the amount of phosphorus in the deposit (Graham, Lindsay et al. 1963). Other electroless systems follow similar trends.

In this project, the most important properties of the decorative plating were that it had satisfactory adhesion, appearance and thermo-cycle resistance.

Adhesion

It has been the aim of many a research project to produce a plated plastic article having improved adhesion of the plate to the plastic surface (Wells 1969).

Adhesion is defined as the measure of the force required to separate the plated coating from the substrate. The bond between the two can be metallurgical/chemical, mechanical or both. When plating metal-on-metal, with good metallurgical bonding, the adhesive strength is greater than the strength of the weaker metal. Plating on surfaces is an atom-to-atom process. Even smooth-appearing surfaces can be relatively rough on a sub-microscopic basis, resulting in a physical keying/anchoring effect that adds to the adhesion. Plating on plastics and other non-conductors depends on this micro-etch for adhesion (Kirk and Othmer 2004).

Mandich and Krulik (1993) believe a low-key controversy exists in the literature about the adhesion mechanism itself. In doing so they explain "One school of thought claims that the plastic surface must be chemically modified so that the metal will be held by the polar or hydrophilic surface groups, such as carbonyls or carboxyls. Another group claims that a lock and key mechanism, the very rough etched surface itself, holds the metal to the plastic (Saubestre 1969; Saubestre and Khera 1971; Villamizar, Rojas et al. 1981; Wan and Cheh 1981).

It is very difficult to give a totally convincing picture for either argument because of the difficulty in separating these two effects in a practical system. The original plastics plating process used mechanical roughening – sanding – to get a good bond. However, this involves friction and local heating effects that can chemically modify the surface. On the other hand, some model polymers can be chemically treated to give a hydrophilic surface with minimal topographic changes, and these do show improved adhesion (Mandich and Krulik 1993).

Although either or both of these adhesion theories may be true, they neglect one important phenomenon: As long as there is *any* metal-plastic adhesion, the point of separation in a peel test is not at the metal-plastic interface. 'All peel test specimens that we have seen show that the failure takes place within the polymer itself'(Mandich and Krulik 1993). Moulding an ABS part introduces a highly stressed surface having properties much different from the bulk of the polymer. Significant adhesion improvements results when this strained layer is removed by etching, or the strain is partially relieved by a pre-etch (Bauer, Johnson et al. 1971; Maguire, Gardener et al. 1981; Saubestre, Durney et al. 1982).

Many of the qualitative tests vary with the plate thickness. Adhesion appears better for thin deposits. That has to do with the stress that is present in deposited films (Kirk and Othmer 2004). This must be taken into consideration when outlining the parameters of the plating in this project.

Appearance and Thermo-cycle Resistance

Plastics plating, whether for a decorative or a functional purpose, necessitates good appearance. The metal must also have good thermocycle resistance and, usually, good corrosion resistance. For the specific application of this project, it was important that the plating had all three. Mandich and Krulik (1993) state that 'the major difference is the etching step, essential for good adhesion and thermocycle resistance, and to increase corrosion resistance'.

In achieving a good appearance, the surface must be smooth and shiny. A number of factors affect how smooth the surface is including: etching, the moulding of the original part and foreign matter in the baths. The smoother the surface the shinier it will be. Another method of ensuring good appearance is to eliminate the risk of 'burning' the plated surface with a current that is too high and concentrated in a small area. It can be assumed that good adhesion is another factor that affects appearance. That is, if adhesion is insufficient, bubbling of the plated surface will occur rendering the surface aesthetically displeasing.

Thermocycle resistance is the ability to perform under extreme temperature change. That is, when moved from a specific high temperature to a specific low temperature, the plating quality is not affected adversely. For the application to a fire fighting helmet this is of particular importance. In this project it was necessary for the plated surface to resist intense increases in temperature.

Part 5.7 of the EN 443:1997 outlines a radiant heat resistance test in which it stated 'any damage or distortion exhibited by the helmet (due to radiant heat) shall not adversely affect the helmets operational capabilities or protection during impact. In a similar way, it is necessary that under similar conditions, the plating on the helmet maintain its integrity. Further details of radiant heat test procedures are outlines in the Appendix (EN 443:1997).

3.3.4 The Mechanisms of electroplating plastics

Overview of the Mechanisms of electroplating plastics

Quality plating on plastics involves the following three basic steps (Mallory and Hajdu 1990):

- Moulding – converting plastic into desired parts
- Pre-plate – processing the moulded part through an electroless bath in order to render it conductive.
- Electroplating – building additional metal thickness using current.

Moulding consists of transforming the plastic into the shape (part) to be plated. Moulding must be done properly to ensure a part with the high quality necessary for plating is achieved. If there are any imperfections in the moulded part they will be amplified by the shiny finish of the metal electroplated coating. The mould design and moulding parameters are extremely important to ensure good parts that are free of stress and other imperfections (Kuzmik 1990). A mould of the part must be built and in doing so, certain design features must be taken into account for the finished part (Borg-Warner 1967).

The first layer of plating is called pre-plating, otherwise known as electroless plating or electroless deposition. It is this step of the process that overcomes the major technical problem of making a non-conductive material electrically conductive so that it may be electroplated.

Once the electroless plating renders the material electrically conductive, any form of electroplating can be performed on the now 'metal' surface of the part. This step of the process is used to add thickness to the plating, or to change the exterior metal coating from the electroless metal to another metal.

Mechanisms of the Pre-Plate Step (Electroless Plating)

In this project, the research concentrated on the pre-plate step, as this is where the technical development was required. Existing moulding and electroplating techniques were generally used. It is however, possible that these techniques may be altered to better accommodate the development of the pre-plating.

The general pre-plate (electroless plating) methodology has been outlined many different ways. Mr Bendary described the process simply and accurately, as follows:

- Etch the Surface of the Material.
- Activate the Surface of the Material.
- Electroless Plate the Surface of the Material.

In all three steps, one factor is repeated - 'the surface of the material'. Mr Bendary believes "It is possible to plate any material, but first we must understand the surface of the material, so that we can etch it, in order to activate it, and apply an electroless coating that will adhere well". Section 3.4 goes on to research the material - UP resin - in order to understand how it may be plated.

Etching

Mandich and Krulik (1993) identify the major difference between plating plastics and plating other materials is the etching step. In order to manufacture plastics having firmly bonded metal coatings, the plastic must be subjected to a pre-treatment step, during which the surfaces of the plastic are treated to increase the peel strength and adhesion of metal surfaces coated thereon. This step of the process is known as etching.

Sopchak and Skovrinski (1989) state that various methods have been employed in such a pre-treatment step. In one such prior art method, the surfaces of the plastic are treated with a mixture of chromium trioxide, sulphuric acid and water, or a mixture of such ingredients and phosphoric acid. While relatively effective, the chromium-sulphuric method suffers from a number of disadvantages including confinement to use on a narrow class of plastics, the extremely corrosive nature of the composition itself, difficulty in maintaining optimum concentrations of the solution and difficulty disposing of the used composition. These are detailed further in US Patent No. 4,820,553.

Januschkowetz and Laub (1977) state that in contrast to most other plastics, the electroplating of thermosetting plastics is technically difficult. Mechanically roughening methods are usually complicated and often, no fast-adhering metallisation is obtained. It is known that thermosetting plastics can be chemically etched, particularly by an oxidising attack. Subsequent metallising as with thermoplastics is also possible

Etching the surface has advantages additional to promoting improved plating adhesion. An etched surface gives a long, more or less tortuous path, greatly slowing any diffusion-mediated corrosion (Kuzmik 1990; Mandich and Krulik 1993).

Kuzmik (1990) also identify the etchant as the most critical step in obtaining an acceptable finished part. An under-etched part can result in poor adhesion and possible skip plate. Over-etching a part can degrade the surface causing poor adhesion and cosmetics.

Etchants are usually strong oxidising solutions that eat away the plastic surface to varying degrees, accomplishing two purposes. First, the surface area is greatly increased, making the part turn from hydrophobic (water-hating) to a hydrophilic (water-loving) material. Second, the microscopic holes left in the surface of the plastic by the etchant provide the bonding sites for the deposited metal. These sites are needed for adhesion between the plastic and the metal (Kuzmik 1990).

Activation

The key step in electroless deposition process is the activation or seeding of the dielectric substrate prior to metal plating (Chen, Li et al. 2004). The electroless plating baths are based on the process of catalytic reduction of metal salts and are so formulated that the metal salt and the reducer will react only in the presence of a catalyst. For the reaction to start, the basis material has to be either catalytic or has to be activated by the application of a catalyst on the substrate. The commonly used activators are compounds of precious metals, such as gold, palladium or platinum (Julve 2001). Historically, the most widely used methods were the "two-step" process and "one-step" process. In the two-step method, the object was immersed successively in $SnCl_2$ and then in $PdCl_2$ solution (Ebneth 1993). The one step process, on the other hand used a mixed $SnCl_2$ / $PdCl_2$ solution (Meek 1975).

Electroless Plating

After activation, the parts are put into the final step in the pre-plate cycle. This is the electroless bath, which deposits a thin, adherent metallic film, usually copper or nickel, on the plastic surface by chemical reduction. This is accomplished by using a semi-stable solution containing a metal salt, a reducer, a complexor for the metal, a stabilizer and a buffer system. While idle, the baths are stable, but when the catalysed surface is introduced into the solution, a chemical reduction of metal occurs on the catalytic sites, and through autocatalysis, continues until the part is removed (Kuzmik 1990). The basic reactions for electroless copper plating is:

$$Cu^{2+} + 2\ HCHO + 4\ OH^- \rightarrow Cu^0 + 2\ HCOO^- + H_2 + 2\ H_20$$

The minimum necessary components of an electroless plating solution are a metal salt and an appropriate reducing agent. The source of copper is a simple cupric salt, such as copper sulphate, chloride or nitrate. Various common reducing agents have been suggested by Pearlstein (1974) for use in electroless copper baths, namely formaldehyde, dimethylamine borane, borohydride, hypophosphite, hydrazine sugars (sucrose, glucose, etc.) and dithioite. In practice, however, virtually all commercial electroless copper solutions have utilized formaldehyde as reducing agent. Once plated with the electroless coating, the surface is rendered conductive and can be electroplated using conventional methods to achieve the desired coating.

3.3.5 Difficulties in Electroplating Plastic

The metallisation of thermoplastics, particularly of copolymers of acrylonitrile, butadiene and styrene (ABS) is known. However, the electroplating of thermoplastics is technically difficult. Mechanical roughening methods are usually complicated and often, no fast-adhering metallisation is obtained. It is known that thermosetting plastics can be chemically etched, particularly by an oxidising attack. Subsequent metallising as with thermoplastics is also possible. Chromic-sulphuric acid solutions are particularly well suited for roughening thermosetting plastics, particularly phenolic resins and unsaturated polyester resins. This method, while permitting the metallising of thermosetting plastics, especially phenolic resin mouldings, does not produce coatings that adhere sufficiently strongly for many applications (Januschkowetz and Laub 1977).

In order to overcome these difficulties, the research looked more closely at how ABS is plated with comparative ease to UP resin. It was hypothesised that there could be a way of modifying UP resin so that it acts in a similar way to ABS and thus be plated in a similar way to ABS. The following section outlines how ABS is plated. This is followed by research into 'Understanding UP resin' (see section 3.4) in order to understand how it might be plated in a similar way.

3.3.6 Plating of ABS

ABS is by far the easiest plastic to plate, with the best adhesion and thermocycle resistance. This polymer is comprised of three different types of molecules - styrene, butadiene and acrylonitrile. They are not polymerised or attached to each other in random order (Mandich and Krulik 1993).

ABS is a two-phase system that exhibits some of the properties of metal systems, including grain boundary phenomena, surface layer disorder, and differential solubility. Its properties depend critically on such parameters as the amount of polybutadiene, the

ratio of acrylonitrile to styrene, and the sizes and dispersion of the polybutadiene spheres (Mandich and Krulik 1993).

ABS has an acrylonitrile-styrene matrix with butadiene rubber uniformly distributed in it. This makes it unique for plating, as the butadiene can be selectively etched out of the matrix, leaving microscopic holes that are used as bonding sites by the electroless plate.

The plastic part is first etched chemically by a suitable process, such as dipping in a hot chromic acid - sulphuric acid mixture. Key-holes are formed in the surface as illustrated in Figure 3.3-1 (A)

Next it is sensitised and activated by dipping in stannous chloride solution and then in palladium chloride solution. The holes are lined with the catalyst, represented by the red dots in Figure 3.3-1 (B)

It is then coated with electroless copper or nickel before further plating. A useful degree of adhesion is obtained (withstanding pressure of 1 to 6 kg per cm^2) but is in no way comparable to the adhesion of metals to metals (Mandich and Krulik 1993). This is represented as the grey surface in Figure 3.3-1 (C)

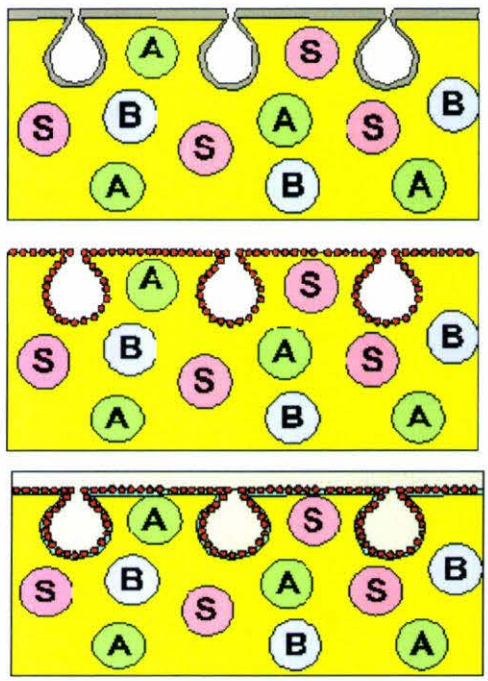


Figure 1-6: A) Etching, B) Activation, and C) Electroless plating of ABS (Astro Electroplating, 2004)

3.4 PLATING UP RESIN

The reviewed literature outlines that UP resin is difficult to electroplate and that prior researchers have failed to obtain a satisfactory adhesion. With a basic knowledge of electroplating, it was necessary to research UP resin, the material used in the production of PHNZ's fire fighting helmet shells. Understanding the chemical and mechanical properties of the material will bring us closer to successfully plating UP resin.

Introduction to UP Resin

"Unsaturated polyester resins are thermoset materials that first became available over 60 years ago. The principal advantage of polyester resins is the ease with which they may be fabricated, a consequence of polymerisation via a free radical reaction. Such reactions are rapid and easily controllable, thus production cost is relatively low. UP resins are very versatile materials. At room temperature, the liquid resins are stable for months even years but can be triggered to cure by a peroxide catalyst." (British-Plastics-Federation 2005)

UP resins are formed by polycondensation of unsaturated and saturated dicarboxylic acids with diols. UP resins are hardened (cured) or cross-linked by free-radical polymerisation with initiators (e.g., peroxides) and accelerators at normal temperatures (10-40°C), or with peroxides alone above 80°C. The unsaturated groups of the polyester chains react with the double bonds of the copolymerizable solvent monomer. Solid products are formed that are used as moulding materials or in paints. They are also reinforced with fibres or filled, and used as putties and mortars.(Kramer, Aktiengesellsaff et al. 2002)

Many types of UP resins are available. Selection depends on processing properties and end properties. Processing properties include reactivity, viscosity, and thickening behaviour with magnesium oxide. End properties include mechanical behaviour, thermal stability, flammability, resistance to chemicals, and colour (Kramer, Aktiengesellsaft et al. 2002).

Standard resins are formulated from inexpensive raw materials and have a wide variety of uses. They can be supplied with or without additives (light stabilizers, thixotropic agents, accelerators, or UV stabilizers) (Kramer, Aktiengesellsaft et al. 2002).

Flame-resistant resins generally contain chlorine or bromine in the polyester chain or in added compounds. Flammability can be adjusted to satisfy widely differing regulations

and standards by using other additives such as phosphorus compounds, antimony compounds, and aluminium hydroxide (Kramer, Aktiengesellsaft et al. 2002).

Mechanical Properties of UP Resin

Mechanical properties are often the critical factors in selecting a polyester resin for a specific application. Sangeeta (2005) describes how the mechanical properties are substantially influenced by the selection of monomeric diols or dibasic acids (the building blocks of polyester), their amounts and temperature of processing. While tensile strength and flexural strength characteristics are only slightly affected by different formulations, the following variations should be noted:

- Higher molecular weight Isophthalic resins have higher tensile and flexural strengths than lower molecular weight phthalic resins. This may because the Isophthalic usually form more linear, higher molecular weight polymers than orthophthalics.
- Glass and Kevlar fibre reinforcements improve both the tensile and flexural strength characteristics of the plastic composite laminate.

UP Resin Resistance to Chemicals

In addition, it is important to take the chemical resistance of the material into consideration, as the material will be treated with chemicals in the electroplating process. Of particular importance is the materials ability to be etched.

Table 3.4-1: Chemical resistance of UP Resin (British-Plastics-Federation 2005)

Dilute Acid	***
Dilute Alkalis	***
Oils and Greases	**
Aliphatic Hydrocarbons	*
Aromatic Hydrocarbons	*
Halogenated Hydrocarbons	*
Alcohols	***

Key:

*	Poor
**	Moderate
***	Good
****	Very Good

Methods of Modifying Polyester Resin

"UP resins display a wide range of applications depending on the proper choice of raw materials and cure conditions. However, some applications are limited to their low-impact resistance, which can be enhanced by the incorporation of modifiers that increase the flexibility of the network.

"Unsaturated polyester resins are widely used in the fibre-reinforced plastic industry. The fracture toughness and impact resistance of rigid unsaturated polyester can be improved by blending with elastomers bearing reactive functional group. An improvement in toughness, impact resistance, and tensile strength has been achieved without seriously affecting any other propery" (Cherian and Thachil 2003).

The addition of fillers to the resin can create problems when plating of the parts is involved. In some cases fillers are added to the resin to increase strength (i.e., glass fibres), to impart colour (i.e., carbon black or titanium dioxide), or for fire retardancy (organic phosphates, antimony oxide). In any case, problems can arise. Glass, for example can build up in the processing tans and cause a rough surface after plating. Some of the fire retardants and other fillers can leave a non-adherent film on the surface that results in no adhesion after plating. If the film can be removed prior to catalyst, good results are usually obtained (Society-of-Plastics-Engineers 2004).

Other fillers such as calcium carbonate are added to facilitate etching. These fillers are preferentially etched out of the surface to create bonding sites required for adequate adhesion. If these particles are large, a poor surface results. Generally, a happy medium is reached where adhesion is adequate and the surface is acceptable (Society-of-Plastics-Engineers 2004).

Manufacturing with UP Resin

Conventional moulding and thermoforming methods (e.g., injection moulding, press moulding, stamping) are used when processing thermoplastic matrix composites. However, the addition of fibres or filler particles to thermoplastics significantly alters their rheological properties and thermal conductivity, which can greatly affect moulding conditions (Mallick and Newmann 1990).

PHNZ use resin transfer moulding (RTM) to manufacture their fire fighting helmet shells.

UP Resin for fire fighting helmet

As described earlier in this section, UP resin selection depends on processing and end properties. For the application of fire fighting helmet shells the key material properties are those that affect the products ability to meet safety standards. The helmets for fire fighting European standards are summarised below (see Appendix for details).

Section 5.6 - Flame Resistance: When the helmet is tested in accordance with 6.6 the material shall not show:

- Any drip during the whole test
- Any visible flame or glow 5 s after removal of flame.

Section 5.7 - Radiant heat resistance: When the helmet is tested in accordance with 6.7 the temperature measure at the surface of the artificial head shall not rise more than 25°C above the standard laboratory temperature, (20±2)°C. No part of the helmet shall melt to such a degree as to cause dripping of material. Any damage or distortion exhibited by the helmet shall not adversely affect its operational compatibility or protection during impact test.

Section 5.3 Shock Absorption: When a helmet is tested by the method described in 6.3, the force transmitted to the head-form shall not exceed 15kN.

Section 5.5 - Mechanical Rigidity: When the helmet is tested in accordance with 6.5, the maximum transverse and longitudinal deformations of the helmet shall not exceed 40mm. The residual deformation shall not exceed 15mm.

Section 4.4 - General Characteristics: The material should be of durable quality. Their characteristics shall not undergo appreciable alteration under the influence of ageing or of circumstances of use to which the helmet is normally subjected (exposure to sun, cold, contact with the skill, effects of sweat).

The French fire fighting helmet standards are the same as the European standards for the above-mentioned sections. The most significant addition in the French Standards is in the *General Description of the Helmet* in which it states "The helmet for fire service and rescue staff shall be "nickel" in colour, to enhance its thermal reflection properties".

PHNZ's UP Resin selection – Polyplex 9486

PHNZ procure their resin products from Nuplex Industries (Aus) Pty Limited. As resin specialists, Nuplex were able to recommend 'Polyplex 9486' as the best UP resin product to meet the specifications for fire fighting helmets.

Polyplex 9486 is an un-promoted fire retardant UP resin, which exhibits excellent glass wet out and flow in closed mould situations such as the RTM process used by PHNZ. That is, the resin easily and quickly fills all the voids between the fibreglass strands within the mould. Its composition is 30 to 40 (%weight) Styrene and 60 to 70 (%weight) Trade-Secret Synthetic-Resin. The exact make-up of the Polyplex 9486 resin is a trade secret of Nuplex, and is therefore not available for review.

Manufacturing Process

PHNZ use resin transfer moulding (RTM) to manufacture their helmet shells. They have two RTM machines running up to 24 hours, 6 days a week. The F7A uses a three-piece mould, due to the unique shape of the F7 range. In resin transfer moulding (RTM) a

piston-type positive displacement pump injects a premixed resin–catalyst stream into a closed mould thoroughly impregnating a pre-placed reinforcement pack. Glass, graphite, or aramid fibres in the form of continuous strand mat, woven rovings, and their combinations are typical reinforcements. RTM differs from structural RIM in that it uses slower reacting formulations and injects under lower pressures components that are premixed or homogenized by passing through static mixers. Molds are made of lower cost materials and cycles are longer (10–60 min). RTM machines have been adapted for a variety of resins including polyesters, epoxies, polyurethane's, and isocyanurates. (Kirk-Othmer, 2004)

PHNZ Curing Process

The Polyplex 9486 Technical Data sheet recommends that Polyplex 9486 be cured with 0.4% of a 6% cobalt solution, and 0.04% dimethly aniline (DMA) with between 1% and 2% of a medium reactivity grade of MEKP, such as MEKP9 Norox, used by PHNZ. Levels of cobalt and DMA can be increased to reduce the gel time with maximum recommended levels being 0.5% of cobalt and 0.1% of DMA. The accelerator levels should not be reduced below the recommended level of 0.4% cobalt and 0.04% DMA. Table 3.4-2 shows typical gel times with varying catalyst content and temperatures, when using the recommended 0.4% of a 6% cobalt solution, and 0.04% DMA.

Table 3.4-2: Gel times for UP resin

	Gel Time (minutes)		
MEKP Catalyst	**1.0%**	**1.5%**	**2.0%**
Temperature 15°C	40	30	25
Temperature 20°C	30	22	20
Temperature 25°C	20	16	13

Additional Materials Used

Additional materials used in the manufacturing of the helmet shell include::

- Kevlar Sock – A Kevlar sock made specifically to cover the inside of the F7A shell mould is the first additional material placed on the 'male' half of the mould.
- Fibre Glass – An F7A specific patterned 225gm/m^2 mat is placed on top of the Kevlar sock and covers the entire inside of the mould. A thicker 600gm/m^2 Mat F7A Strip is placed along the ridge of the helmet shell for added strength across this area, which is most threatened by impact.
- Finishing cloth - to go on top of the Fibreglass to give smooth outer surface to shell.
- Pigment – to colour the helmet shells white, yellow, blue or red Polyplex 9019 and the desired pigment paste is added prior to RTM.
- Fire Retardant – Aluminium Trihydrate is added prior to curing.

Alternative Materials used for fire fighting helmets

Fire fighting helmet shell materials are not limited to UP resin. The competitor company uses 'Thermoplast' or 'Duroplast'. These materials are similar to ABS in that they are easily electroplated. However, as thermoplastics they have significantly lower radiant heat resistance. Unlike thermosetting plastics, thermoplastics can be melted down and re-shaped. Thus, they are more likely to disintegrate under high temperatures, rendering them less safe when used in fire fighting helmets.

PHNZ choose to use UP resin for their products because it is safer. Also, as the existing material in use at the factory, a huge expense would be incurred should PHNZ wish to change to a thermoplastic, which would require new tooling, machinery and manufacturing processes.

Understanding Acrythane Paint

Acrythane is the two-component acrylic-urethane enamel that PHNZ use to coat their fire fighting helmet shells. The Acrythane MSDS states it is suitable where a tough, durable, chemical resistant finish is required. It is made up primarily of Xylol, lead chromate pigments and methoxyl propyl acetate.

Acrythane is described by its manufacturer Resene (2004) as having hard excellent abrasion resistance, excellent exterior durability, highly resistant to yellowing and chalking, Good U.V. resistance, excellent chemical and solvent resistance and excellent polish-ability.

No literature has been identified relating to the plating of acrylic-urethane coatings. However, from a manufacturers point of view if research is being done into a potential intermediary coating on the UP resin for the purpose of plating, attempting to plate onto a coating that is already being used on the product is beneficial as it can be done on site without further capital investment. It is because of the availability of this coating that Acythane was investigated as a potential intermediary coating for plating on.

In addition, this coating has already been accepted by the greater fire-fighting industry as durable enough for application to helmets. If plating was successful it is likely the coating will maintain its durability and adhesive integrity. It is for these reasons that Acrythane coated UP resin was included in trials for plating on UP resin in order to increase the chances of achieving a metal plated coating on the helmet shells.

More detailed background information on specific steps of the plating on UP resin process are detailed in the dedicated step chapters 4 through 7.

3.5 INTRODUCTION TO TECHNICAL DEVELOPMENT

As outlined in section 3.4.4 the plastics plating process is made up of four core steps, which will be presented in the chapters of this document as follows:

- Chapter 4 - Etching
- Chapter 5 - Activation
- Chapter 6 - Electroless plating
- Chapter 7 - Electroplating

Although the four process steps are presented sequentially in this thesis, the development of the process steps was carried out more or less in parallel. There are two reasons for this:

- Firstly, the process itself must be carried out continuously; a delay between any of the steps may result in the part becoming chemically inactive leading to unsuccessful plating.
- Secondly, the best *true* test of the success of an individual process step hypothesis (methodology) is to test the quality of the resulting plating.

An exception is the etching process, including the material development and selection. The etching process was perhaps the most difficult step of the process because it involved trying to make UP resin act like more readily plated materials such as ABS. Therefore many trials were required to establish successful etch holes. It was possible to develop and test the etching process independently of the last three steps, but only to a certain degree. For the etch step, dispersive x-ray analysis (EDX) and scanning electron microscopy (SEM) technology could be used to analyse the surface of the material without being plated. SEM was used in the initial etching trails to identify etch-hole size and distribution. EDX was used during the etching, and in some cases the following activation and electroless plating stages in order to identify success of the etchant to remove particles, and the success of the activation and electroless processes to deposit particles on the surface of the material.

Therefore, with the exception of the earlier stages of the etching development process, the development of all steps of the plating process was carried out in parallel. Chapters 4 through 7 will outline individually the literature, hypothesis and testing carried out to iteratively develop and refine each step of the process in order to achieve the best quality resulting plating.

Given the breadth of the initial concepts and subsequent process sequences resulting from them, there were initially a very large number of potential processes. Early trails

quickly identified which concepts were likely to result in plating of UP resin. For this reason, only those concepts critical to the understanding of the development of the process have been presented.

For continuity and ease of understanding, table 3.5-1 outlines the ingoing concepts that will be detailed in chapters 4 through 7 in which the concept names / abbreviations will be explained.

Table 3.5-1: Process concept matrix

Process concept matrix																								
	Concepts																							
Material	X						Y						Z						PAINTED					
Etching solution	A		B		C		A		B		C		A		B		C		A		B		C	
Activation	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd
Electroless plating	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni
Electroloplating	Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu	

The table illustrates that there were four ingoing material concepts (detailed in the Chapter 4 with etching), three ingoing etching solution concepts, two activation concepts, two electroless plating concepts (which were only compatible with one of the activation processes each) and one electroplating concept.

An important note is that the electroplating concept is 'acidic copper plating', which Nickel plating can subsequently be plated to at any time. It was hypothesised that a process to initially apply acidic copper plating to UP resin was more likely to be successful than nickel plating. The process of nickel electroplating onto acidic copper plated surfaces is a known technology. Therefore achievement of said copper plating would lead to the successful plating with nickel.

It should be noted that going into the technical development, these were broad concepts. Going forward, these concepts were iteratively developed, tested and refined. As the steps of the process were refined, concepts were selected and others eliminated using a specification matrix, which led to the number of trials reducing throughout the technical development.

4 ETCHING METHODOLOGY

4.1 INTRODUCTION

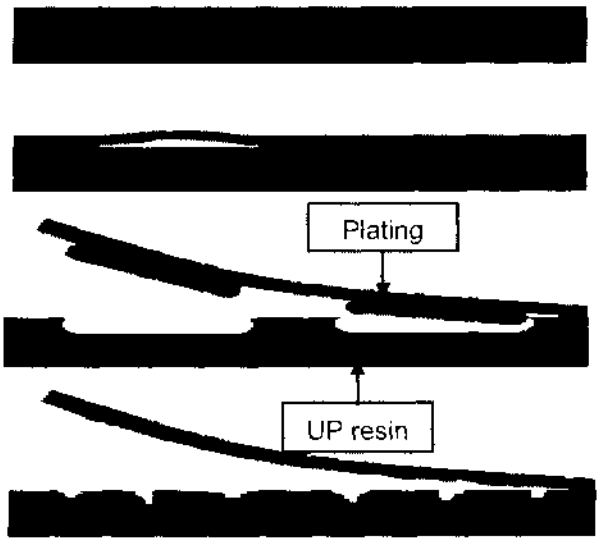
This section will provide a background to etching UP resin including prior arts and difficulties encountered. From this, the basic etching process established within the plating on plastics industry will be outlined. Taking this into consideration a strategy for overcoming the shortcomings of prior arts is then developed and the resulting hypothesis and process concepts are tried and tested.

Patent and journal article searches found several attempts at etching UP resin either as part of a complete plating process or as specific developments of the etching process. In general the research presented results in plating of a quality too poor for industrial applications. One case outlines the modification of UP resin to render it more readily etchable and thus more readily plateable. However no method of etching conventional, unmodified UP resin such as that used by PHNZ were found.

4.2 BACKGROUND - ETCHING U P RESIN

Donovan III, et al (1982) describes how etching aims at providing a surface uniformly receptive to metals, which catalyze electroless deposition of nickel and copper.

Mr Bendary described how in order for the plating to adhere optimally, the 'key-holes' must be an optimum size and even distribution in the surface. Figure 4.2-1 illustrates how 'hole' parameters affect the adhesion of the plating.



a) Optimum etch-hole size and even distributed results in copper coating locked to surface with good adhesion.
b) Under-etching results in bubbling of the metal coating due to lack of mechanical adhesion.
c) Over-etched surface results in holes being too large to hold the copper coating onto the surface.
d) Under-etching the surface results in holes that are too small to lock the metal coating onto the surface.

Figure 4-1: Affects of etch-hole parameters on plating adhesion quality

In contrast to most other plastics, etching thermosetting plastics (such as UP resin) is technically difficult. Mechanically roughening methods are usually complicated and often, no fast-adhering metallisation is obtained (Januschkowetz and Laub 1977).

It is the tightly cross-linked *thermoset* structure of UP resin that makes it difficult to etch. Not only does this structure give UP resin excellent chemical resistance to both acid and alkaline solutions, it also results in an inability to selectively etch molecules from the surface of the part as is done in the process of etching butadiene molecules from the surface of ABS plastic (British Plastics Federation, 2005).

It is known that some thermosetting plastics can be chemically etched, particularly by an oxidising attack. Chromic-sulphuric acid solutions are particularly well suited for roughening thermosetting plastics, particularly phenolic resins and unsaturated polyester resins. This method, while permitting the metallising of thermosetting plastics, especially phenolic resin mouldings, does not produce coatings that adhere sufficiently strongly for many applications (Januschkowetz and Laub 1977).

In some cases, the material itself may need to be modified, by for example, adding a filler to the resin prior to moulding, which is subsequently etched out of the material.

US Patent No. 3,567,594 (Wells, 1971) disclosed a process of electroless plating a plastic that comprises the steps of:

1. Incorporating a siliceous filler into a plastic;
2. Moulding the resulting plastic composition into the desired configuration;
3. Conditioning the resulting moulded plastic product by treating the plastic product, in series, with (a) an acid chromate etch and (b) an HF treatment;
4. Pre-plating the conditioned article with an electrolessly plateable metal;
5. Electroplating the pre-plated article.

The process was represented as futile for polyesters (Donovan III, et al 1982).

Despite the failure of the method described in US Patent No. 3,567,594, the incorporation of a filler into the UP resin as a method of modifying the material so it might be more easily plated was an key concept taken from the literature. It provoked the question of 'what appropriate filler material might be added to UP resin that could later be etched out of the material to create an etched surface such as that described in the process for plating ABS?'

In April 1982, US Pat. No. 4,325,991 illustrates how filled polyester substrates are conditioned for electroless plating by contact with an alkaline conditioner having a pH of

at least 8, followed by contact with an aqueous acid fluoride etch solution having a pH less than about 5 and a fluoride concentration of at least 1 mole per litre of solution.

In more detail; It was found that electroless plating of filled polyesters can be enhanced by first contacting the filled polyester substrate with an alkaline conditioner having a pH of at least about 8, preferably an aqueous solution of at least one alkali metal hydroxide in which the alkali metal hydroxide content is from about 2 percent by weight to solution saturation, more preferably from about 10 to 50 percent by weight, still more preferably from about 25 to about 35 percent by weight. The alkaline conditioner is maintained at a temperature of from about 135 °F to the lesser of the boiling point of the solution and the softening point of the polyester substrate, preferably from about 145°F to about 175°F. The alkaline conditioner serves as an initial etchant. Contact is for a time sufficient to enable etching in an aqueous acid fluoride etch solution and may range from 0.5 minute or less to 20 minutes or more, preferably from about 3 to about 8 minutes. In general, short contact time gives the best appearance and lowest adhesions, whereas long contact times increase adhesion to the detriment of appearance.

This Patent lead the reader to believe that if a filler is added to the UP resin that an alkaline conditioner prior to the acid etchant is necessary to expose the filler particles so that they can in fact be etched out of the material thereby producing the etched 'key-holes' necessary to hold the plated surface in place.

This is the most recent and relevant literature on etching UP resin and led to a number of key findings. The process is directed to electroless plating of filled polyesters only, which means polyesters containing at least 10 percent by weight filler, in the form of mineral, glass and silica fillers, and mixtures thereof. The process is noted as being particularly adaptive to electroless plating of articles molded of thermoplastic polyester resins, preferably thermoplastic polybutylene terephthalate resins. However, the patent does not outline such a methodology or prove quality plating can be achieved on conventional, unmodified UP resin such as that used by PHNZ.

From this literature it was hypothesised that fillers such as fine powdered Calcium Carbonate ($CaCO_3$, a.k.a. chalk) could be mixed into the liquid UP resin prior to moulding the part. Etching the surface layer of UP resin from the part with a strong alkaline etch (or pre-etch) would then expose these $CaCO_3$ particles. Once exposed the $CaCO_3$ particles, could be etched from the surface of the material due to ease of which they are dissolved by acids such as HCl, whilst the UP resin surface would not be etched due to its relative resistance to such acids as HCl. Therefore, the UP resin would be left with tiny key-holes in the surface resulting from the removal of the $CaCO_3$, and be more readily plated with electroless copper with a greater adhesion to the surface.

Contact with the aqueous acid fluoride etch solution is followed by seeding the surface with a metal electroless plating catalyst which is a solution of metal ions or a suspension of metal particles. This step of the process is investigated in Chapter 5 on Activation.

To enhance surface appearance and eliminate bright spots on the final coating, it is preferred to precede contact with the aqueous alkaline conditioning solution with a detergent rinse followed by pre-conditioning with a hydrolizer solution, which functions as described in U.S. Pat. No. 3,689,303, to render the surface hydrophilic (Donovan III, et al, 1982).

Mr Bendary states that it is possible to plate *any* object by first applying a coating of a readily plateable material to the surface of the object and gives examples of first coating such objects as flowers or leaves with wax and then e.g. ABS in order to plate the objects. This method of plating could therefore, in theory be applied to plating UP resin. The disadvantage being that the adhesion of the plating is only as good as that of the intermediate coating between the object and the plated coating.

4.3 THE ETCHING PROCESS SUMMARY

Within the etching process itself, there are five individual steps. These are identified throughout the existing literature, including Mallory and Kuzmik (1990), Mandich and Krulik (1993), Donovan III et al (1982). The steps are as follows:

1. Moulding of the material: In addition to conventional moulding, the material can be modified with the addition of fillers prior to moulding to aid the ability to be etched. Application of a coating to the surface of the material is another method of modifying the material to enhance plating.

2. Degreasing: It is necessary to degrease the material prior to any chemical treatment in order to remove any foreign matter and grease from the surface, to ensure that any such organic matter does not stop the chemicals from contacting the surface evenly. The degreaser also works as a conditioner that swells the surface for the subsequent uptake of the catalyst, following the etching step. Degreasers are usually mild alkaline cleaners. The following degreasing solution was suggested by Mr Bendary and was used throughout the project methodology:

- 1g.L Surfactant
- 20g/L Sodium Borate
- 30g/L Sodium Phosphate

The above solution is heated to between 80 and 90°C while stirring to dissolve the chemicals and the solution becomes clear. The parts were degreased in this solution at no less than 70°C for no less than 5 minutes. It is essential that all degreasers be heated so that the solution melts the grease. Grease has a melting point just lower than 70°C. To ensure that the part has been degreased properly, a simple test of running cold water over the part and seeing if any beads of water remain 'stuck' to any patches of grease remaining on the surface. If so, the part must be degreased again, and it is possible that there is something wrong with the degreasing solution, which may then need to be replaced. This degreasing method proved successful throughout the process development and was not developed any further.

3. Rinsing: It is necessary to rinse between chemical processes such as degreasing and etching in order to remove any excess solution from the material, which may contaminate the solutions. Once the part has been sufficiently degreased, it is rinsed to remove any excess degreasing solution and is then ready to be chemically etched. Regular tap water can be used for this rinsing step. The water should be filtered and renewed continually to avoid becoming contaminated with the degreasing solution itself.

4. Etching: The removal of some of the surface of the material using an etching solution in order to create etch-holes. Etching of modified materials such as filled substrates may require several etching sub-steps. This is the most important stage of the etching process and is where the majority of research has been carried out.

5. Final Rinsing: It is essential to rinse the strong alkaline etching solutions from the material before progressing into the next stage of the process – activation. This is because the activation solution is very expensive and is easily contaminated. Therefore the final rinse is carried out in two steps:

1. Tap water rinse – to remove excess etching solution.
2. Distilled water rinse – to neutralise the pH of the material so as not to contaminate or change the pH of the activation solution.

4.3.1 KEY FINDINGS

1. The aim of etching is to provide a surface uniformly receptive to metals which catalyse electroless deposition
2. UP resin is difficult to etch because of its tightly cross-linked thermoset molecular structure
3. The conventional etching process is comprised of 5 steps: moulding, degreasing, rinsing, etching and final rinsing.
4. Generally, developments are made in the etching and/or the moulding steps

5. In some cases modifying the material itself can enhance its ability to be etched. E.g. Adding a filler to the resin prior to moulding, which is subsequently etched out of the material
6. Strong alkaline etching solutions are the most effective at attacking the surface of UP resin
7. After alkaline etching, the surface may be contacted with an acid solution to increase the bond of the electroless deposition
8. Prior to etching an alkaline degreaser is necessary to remove grease from the surface to enhance surface appearance and reduce faults
9. Rinsing between solutions reduces contamination and preserves solutions

4.4 ETCHING PROCESS DEVELOPMENT STRATEGY

A process development strategy similar to that used in the overall plating process development was used to guide the development of the etching process. One distinct addition to the process is the need to understand the material in order to generate etch process concepts. This will lead to an understanding of how best to etch a material.

We can think of the development of the etching step of the process in the same way as a subcomponent in the development of a product. That is, a list of target specifications can be used to aid the development and selection of the etching method that best creates the etch 'holes' in the UP resin surface. The process below was used to develop the etch process for this project and therefore shapes the rest of this chapter.

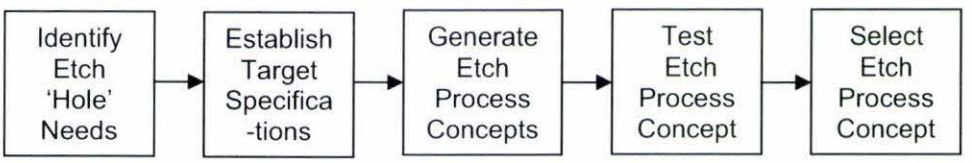


Figure 4-2: Flow diagram of the etching process development

4.5 IDENTIFACTION OF ETCHING 'KEY-HOLE' REQUIREMENTS

The primary purpose of the etching step of the plating process is to produce etch 'holes' in the surface of the material so as to improve the mechanical adhesion of the metal coating to the UP resin. However it is also necessary to take into consideration the following manufacturing constraints:

- Design for manufacture – the process is manufactured easily
- Time efficiency – the process is time efficient
- Cost – the process is cost effective

In addition, the major constraint is to ensure that the etching process does not affect the mechanical properties of the material in such a way that it causes the end helmet product to fail safety standards. The etching stage is the most invasive stage of the plating process. The etchant attacks the materials surface, stripping its top layer. This weakens the material, which may cause the helmet to fail the required European impact and sharp object resistance tests. However, the affect of the overall plating process on the material is of more importance, as it is likely that addition of the plated coating will counteract the weakening caused by the etching to a certain extent. For this reason the affect on the mechanical properties of the material will not be a specification for the etching process, but for the overall plating process, and will be tested on complete plated helmets in Chapter 8. It is important however, to take this constraint into consideration during the process development and to try and keep the negative affects to a minimum.

Testing Methods

A number of different methods were used to test the etching process effectiveness. Initially the etched surfaces were tested using scanning electron microscopy (SEM) and energy dispersive x-ray analysis (EDX). These methods were non-invasive and could be used to gain an idea as to whether etching was being achieved without having to go through the full plating process.

- Scanning electron microscopy (SEM) was used to look at, and photograph the etched surfaces very closely. This allowed the analysis of the relative hole sizes and distribution, and was used to identify optimum etch times and temperatures.
- Energy dispersive x-ray analysis (EDX) was used to carry out a non-destructive elemental analysis of the surfaces and was used to identify what elements were found on and just below the surface of the material.

These tests allowed the most promising etching process concepts to be selected and continue through to the following plating stages of activation, electroless plating and electroplating. Upon plating be achieved on the surface, etching concepts could be further refined and the resulting plating quality assessed using four common plating adhesion tests:

1. The bend test: bending the object until breaking point to identify if metal coating breaks or if de-lamination occurred, signalling under-etching.
2. Scratch resistance – involved impacting the plated object with a sharp object to see if the plating delaminated and test plating durability.
3. Texture test – touching of the plated surface to gauge if it is rough or smooth A rough surface indicates the object has been over-etched.
4. Visual test – the smoother the plated surface, the better. An over-etched surface will be rough and therefore not shiny.

4.6 ESTABLISHING TARGET SPECIFICATIONS

Table 4.6-1 outlines the initial (non-plating quality) etching target specifications set in order to aid the development of the etching process. In this table the specifications are weighted by importance and the marginal and target values for each metric are set. In many cases, the results were a subjective analysis of the SEM and EDX outputs. In other cases quantitative results were estimated, such as cost per helmet. With these specifications in mind, the generation of potential etching methods began.

Table 4.6-1: Target and marginal specifications for etching metrics.

Etching Target Specifications – non plating quality					
Metric No.	**Specification**	**Importance**	**Unit**	**Marginal Value**	**Target Value**
1	Holes Achieved	5	Binary	Pass	Pass
2	Holes size	4	Subj	3	4
3	Hole distribution	4	Subj	3	4
4	Cost per Helmet	4	NZ$	0.5	0.3
5	Time to Etch	4	Min	20	10
6	Ease of Manufacture	4	Subj	3	4

Table 4.6-2 outlines the plating quality specifications. These tests were only carried out on concepts that were able to produce a reasonable plating on the material surface.

Table 4.6-2: Etching target specifications – marginal and target value

Etching Target Specifications – plating quality					
Metric No.	**Metric**	**Importance**	**Unit**	**Marginal Value**	**Target Value**
5	Bend test	5	Subj	4	5
6	Sharp object resistance	4	Subj	4	5
7	Texture test	4	Subj	4	5
8	Shine test	5	Subj	4	5

4.7 HYPOTHESIS GENERATION

7.1 Etching Hypothesis 1 - Strong Alkaline Etching Solution

In the process of Donovan III et al (1982) invention, the alkaline conditioner serves as an etch function to a limited degree, but is described as insufficient for industrial application. The first hypothesis was built around challenging this idea. It was hypothesised that given the right solution and conditions, a strong alkaline solution could serve as an etchant for the purpose of plating UP resin for application to PHNZ fire fighting helmets.

Mr Bendary suggested three such etching solutions of increasing alkalinity have been used in the plating of similar resins. The three alkaline etching solutions are outlined below and were used to test hypothesis 1:

A. 200gm/L NaOH + 100ml/L methanol at 25°C.
B. 400gm/L NaOH + 200ml/L methanol at 70°C.
C. 250gm/L NaOH + 100ml/L Ethylene Glycol + 150ml/L Triethanolamine (TEA) at 70°C.

7.2 Etching Hypothesis 2- Modification of UP Resin

The second etching hypothesis was based on building on the work of Donovan III et al (1982) in which UP resin is modified by adding a filler prior to moulding of the material and then etching it with a strong alkaline solution followed by an acid solution.

This hypothesis was based around the high level concept that the main function of the alkaline solution is to remove a thin layer of the UP resin, thereby exposing the filler particles just below the surface of the material so that they may be etched out by the acid solution and thus form etched 'key-holes' similar to those formed in etched ABS.

The best filler materials are cheap and easily etched from the surface. Therefore the filler must be able to be dissolved out of the resin material using a chemical that the resin is comparatively resistant to. Calcium Carbonate (CaCO3) is such a material, and is dissolved easily with Hydrochloric acid.

Therefore it was further hypothesised that fillers such as fine powdered Calcium Carbonate (CaCO3, a.k.a. chalk) could be mixed into the liquid UP resin prior to moulding the part. Etching the surface layer of UP resin from the part with a strong alkaline etch (or pre-etch) would then expose these CaCO3 particles. Once exposed the CaCO3 particles are etched from the surface of the material due to the ease at which they are dissolved by such acids, whilst the UP resin surface would not be etched due to

its relative resistance to such acids as HCl. The UP resin would be left with tiny key-holes in the surface resulting from the removal of the CaCO3, and would therefore be more readily plated with electroless copper with a greater adhesion to the surface.

Two potential methods of modifying the UP resin to render it more etch-able were considered:

Y. Donovan III et al (1982) suggests a method in which not more than 10% (weight) CaCO3 is used as a filler, and is etched it out of the resins surface using an acid etch such as HCl, which dissolves CaCO3 particles, but does not dissolve UP resin, thereby leaving spherical 'holes' just below the surface of the resin, which act as keyholes, locking the metal coating in to place.

Z. In addition to this, Mr Bendary suggested adding CaCO3 and fumed silica as a filler to UP resin. The CaCO3 works in the same manner as in the first method. The addition of fumed silica is to counteract the weakening of the material caused by the addition of the CaCO3 and subsequent plating, by strengthening the UP resin.

It was important to explore both material modification methods as the invasive etching process has potential to weaken the material, which may result in the helmet shell failing to meet safety standards, in particular impact resistance standards.

In order to identify the best alkaline solution to etch the modified materials with, solutions A, B and C were tested on both modified UP resins Y and Z. As a result of this there were nine initial etching concepts (see Table 4.7-1).

Table 4.7-1: Etching concept matrix

Etching Concepts Matrix			
	ETCHING SOLUTION		
MATERIAL	**Solution A** · 200gm/L NaOH · 100ml/L Methanol · run at 25°C	**Solution B** · 400gm/L NaOH · 200ml/L Methanol · run at 70°C	**Solution C** · 250gm/L NaOH · 150ml/L T.E.A. · 100ml/L E.Glycol · run at 70°C
X: Unmodified UP Resin	Concept 1	Concept 2	Concept 3
Y: CaCO3 filler	Concept 4	Concept 5	Concept 6
Z: CaCO3, Fumed Silica Filler	Concept 7	Concept 8	Concept 9

4.8 HYPOTHESIS TESTING

4.8.1 Testing Hypothesis 1

Solutions A, B and C were tested on samples of unmodified UP resin cut from helmet shells manufactured at PHNZ. The methodology and results from these tests are outline below as concepts 1, 2 and 3.

Etching Solution A

Concept 1 – Etching material X (unmodified UP resin) with etching solution A

This first etching solution tested was that recommended by on the website *www.finishing.com*. This solution was made by dissolving 200gm of NaOH in 800ml of cold tap water. Once cooled to room temperature 100ml of methanol was added.

A range of etching times from 2 to 120 minutes were tested in order to identify the optimum etching time and in the hope of illustrating under and over etching of the unmodified UP resin samples. All other variables remained constant, including the temperature of the solution, which was at 25°C (room temperature).

The results were analysed through viewing the etched surfaces through an optical microscope. It was found that the surfaces had been roughened proportionally with the etching time lengths. However, there were no 'key-holes' and none of the surfaces represented that which could be plated. It was concluded that this etching method was not satisfactory. Later attempts to plate metal onto these surfaces also failed, supporting the microscope results.

Etching Solution B

Concept 2 – Etching material X (unmodified UP resin) with etching solution B

Given the results of testing concept 1, Electroplating expert, Mr Bendary recommended doubling the concentration of etching solution A and raising the temperature of the etching solution to 70°C. This solution would attack the surface more vigorously. Solution B was made up using the same methodology as solution A.

Concept 2 was tested using the same methodology as concept 1 and with similar results. The stronger solution etched the surface more quickly but failed to produce the required keyholes necessary to plate the material.

Etching Solution C

Concept 3 – Etching material X (unmodified UP resin) with etching solution C

Mr Bendary used etching solution C for plating a similar resin material to that used by PHNZ. The solution is made up by dissolving the NaOH in purified water and carefully adding the Ethylene Glycol before lastly adding the TEA. This solution is to be heated to 70°C.

This experiment was run similarly to the methodology of concepts 1 and 2. Due to the increased strength and temperature of this solution, a smaller range of etching times was tested: 5, 10, 15, 20, 25 and 30 minutes.

The result was the formation of etch-holes on the surfaces that were etched for less than 20 minutes. It was identified that anything over 15 minutes was too destructive on the material surface, rendering it too rough to obtain quality plating. Further testing was required to identify the exact optimum etching time, which was suspected to be between 3 and 15 minutes. Experiments were carried out using etching times of 3, 5, 7, 10 and 15 minutes to find the optimum etching time. The results are tabulated below:

Table 4.8-1: Results of etching concept 1 test

Etching concept 1 results	
Etching Time (minutes)	**Etching Outcome**
3	Highly under-etched
5	Under-etched
7	Slightly under-etched
10	Good etch
15	Over etched

It was found that 10 minutes was the optimum etching time for the unmodified samples, and resulted in quality plating with good adhesion. Over-etching was identified by the roughness of the plated surface, and under-etching identified by peeling of the plating from the surface.

Outcome of testing hypothesis 1

The overall outcome of testing hypothesis 1 was that alkaline solution C resulted in etching the surface of unmodified UP resin in a manner that improved the plate-ability of the material. When the etching was carried out using the above methodology and conditions, the optimum etch time is 10 minutes. Solutions A and B did not etch the unmodified UP resin in a manner that improved plate-ability.

4.8.2 TESTING HYPOTHESIS 2

This section outlines concepts 4 through 9 in which the methodology for manufacturing materials X and Y are explored followed by test methods for etching said materials with etching solutions 1, 2 and 3.

4.8.3 Material Y - CaCo3 filled UP resin

Manufacturing material Y

The primary objective in the development of Material Y was to distribute fine CaCO3 particles as evenly as possible through the surface to be etched. The particles must be 'fine' so that when they are etched from the surface, the holes the CaCO3 removal results in are small enough to avoid the subsequent plating from peeling from the surface. In addition, the smaller the holes, the smoother the surface and the higher the quality and appearance of the final plating. The distribution of holes is important to ensure even plating without 'skip-plate' where peeling occurs where etch holes are not present or infrequent. Therefore it was important to carefully consider the quantity of CaCO3 added, and the method of mixing the CaCO3 into the UP resin prior to moulding in order to best achieve these objectives.

In developing Material Y, the following three major constraints were identified:

- The manufacturability of the UP resin part, specifically the manufacturability when using a resin transfer moulding (RTM) machine to mould the part
- The affect of CaCO3 on the mechanical properties of the material, specifically impact resistance
- The cost of additional production materials, labour and overheads incurred due to the additional activities in manufacturing material Y

As the CaCO3 quantity increases so too does the viscosity of the UP resin. This has a negative affect on the manufacturability because as the resin thickens it becomes more difficult for it to flow through the RTM machine. Additionally, CaCO3 has a negative affect on UP resins resistance to impacts. The higher the CaCO3 content, the lower the impact resistance. Cost of material would not be greatly affected due to the relatively low cost of CaCO3.

Therefore a trade-off existed between CaCO3 quantity and the resulting etch-hole quantity and the manufacturability and mechanical properties of the material. Taking these objectives, constraints and trade-offs into consideration, concepts for potential material manufacturing methods were developed. From these concepts the following were selected for testing:

1. Premix the CaCO3 into the resin prior to RTM.
2. Add the CaCO3 in the same way pigment is added to the resin – as a concentrated CaCO3/resin mixture through a shaft into individual mould (helmet) batches prior to moulding.
3. Apply a coating of CaCO3 powder to the inside of the helmet mould so that it is absorbed into the resin upon injection into the mould.
4. Apply the CaCO3 to the 'finishing tissue' material that is laid inside the mould prior to RTM and is closest to the outside surface of the helmet to be plated.

Variations of the above four methods of CaCO3 application were developed and tested on the RTM machine. It was found that both concept 3 (powder-coating) and concept 4 (finishing tissue) resulted in very uneven distribution of CaCO3 throughout the product. These methods also increased the overall cost of manufacturing, primarily through an increase in the production time and a decrease in the ease of manufacturability.

Concept 2, mixing a concentrated CaCO3/resin mixture through an additional 'pigment' shaft caused very unreliable quantities of CaCO3 in the material. In addition the relative viscosity of the CaCO3/resin mix meant that it was not possible to make a mixture with a high enough concentration of CaCO3 to make this method feasible. It was more efficient to use the first method of premixing the CaCO3 and resin.

Therefore the concept 1 was selected as the best method for mixing the CaCO3 into the resin. Two potential methods were developed from this concept. The first was to mix the CaCO3 and resin in a 44 gallon resin drum with a vertical 'drum-mixer' inserted from the top, continuously mixing the resin at a high speed, and feeding directly into RTM. The second method was to mix the CaCO3 and resin in a 'barrel-mixer' in which the whole barrel is continuously rotated, thereby mixing the resin during RTM. These methods were the quickest and easiest for manufacturing, created very little waste of materials, and were considered the best methods for even distribution of the CaCO3 powder throughout the moulded part.

Method of making material Y samples for testing Hypothesis 2

For the purpose of manufacturing the material Y for testing in the laboratory, it was not necessary to use actual helmet shells. It was sufficient to use flat resin-fibreglass samples produced by 'hand-lamination' using mixing and lamination methods that best replicates the premix manufacturing concept 1. This process was required to be very controlled, and was carried out as follows:

- The first Material Y was manufactured by adding 10% (weight) CaCO3 fine powder (between 1 and 3 μm) to the resin prior to curing as suggested by

Donovan III et al (1982). Further refinement may be required later in the process development.

- The CaCO3 was mixed into the resin for 15 minutes at a fast speed. This aggressive mixing with an electric air-mixer ensured the CaCO3 was very evenly distributed in the resin, and that the particles of CaCO3 were broken down to particles as small as possible.
- A mould cleaner, Loctite FMS Frekote was used to ensure the mould was free from any grease or foreign matter that might affect the samples plate-ability.
- A releasing agent used was Frekote 770-NC was applied to the mould prior to laminating to allow the sample to be removed easily. This particular releasing agent is known to have the least affect on the materials plate-ability.
- When laying the resin, an initial coat of CaCO3 resin was brushed onto the mould and allowed to partially cure before the fibreglass sheet was laid on top and more resin applied. This prevented fibreglass from roughening the outer surface of the sample, which negatively affects the plate-ability of the surface.
- After 24 hours the sheet of sample material was released from the flat mould and ready for use.

These samples of material Y were used to test concepts 4, 5 and 6.

Concept 4 – Etching modified material Y with Alkaline Etching Solution A

Concept 4 was tested by etching material Y for 10, 20, 30, 40, 50, 60 and 120 minutes to remove the surface layer of resin, followed by the HCl 'acid-etch'. Mr Bendary suggests one method of identifying when the acid etch process is complete is by monitoring the gas released by the reaction of the CaCO3 with HCl. The reaction causes the solution to effervesce which can be clearly observed. Once the effervescence has ceased, the reaction is complete, all CaCO3 has been removed from the surface of the material and the sample can be removed from the HCl and rinsed in preparation for activation. It was found that after 5 minutes in the acid etch, effervescence ceased. The part was rinsed in water between degreasing and pre-etching to wash the degreasing solution from the part and protect the pre-etch solution from contamination. After Pre-etching the part is rinsed thoroughly in tap water with agitation.

The E.D.X. results for this experiment concluded that the optimum pre-etching time was 50 minutes when using a 37% HCl solution (see Figure 4.8-1).

With the addition of the alkaline 'pre-etch' of the top surface of the resin, the acid-etch times were reassessed. A number of samples were therefore 'pre-etched' for 50 minutes in Alkaline Solution A and then acid-etched in HCl for between 20 and 600 seconds. The samples were analysed using EDX to count the amount of Ca remaining in the surface. The optimum acid-etching time was found to be 300 seconds (see Figure 4.8-2).

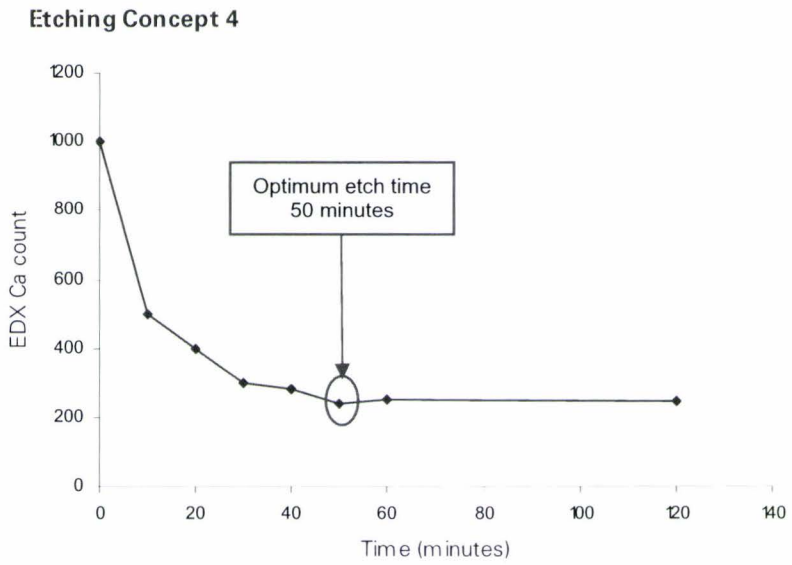


Figure 4-3: EDX Ca count over time; optimum alkaline etch time of 50 mins

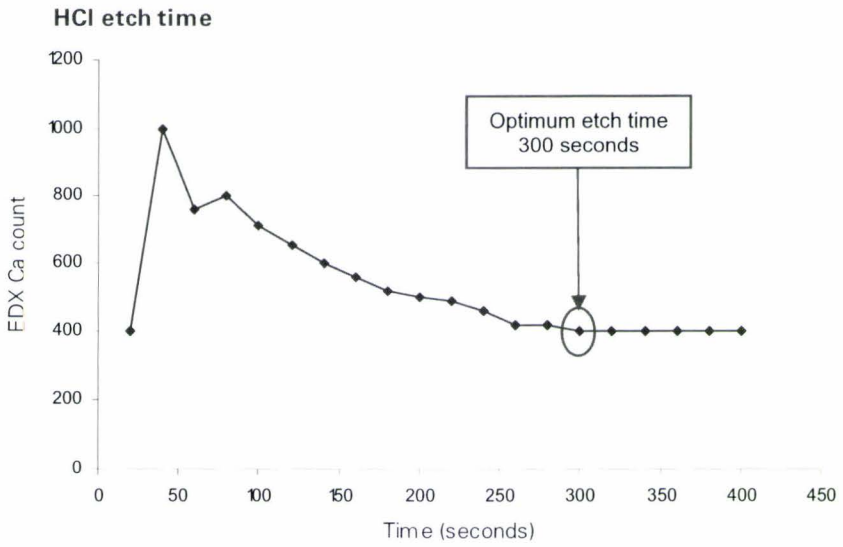


Figure 4-4: EDX Ca count over time, optimum acid-etch time of 300 seconds

Optical microscope photographs were consistent with the results of the above trials and illustrated holes similar in size and evenly distributed (see Figure 4.8-3). Therefore the desired affect of etching was achieved. These results were reinforced with the successful plating of samples etched using this method with good adhesion and appearance.

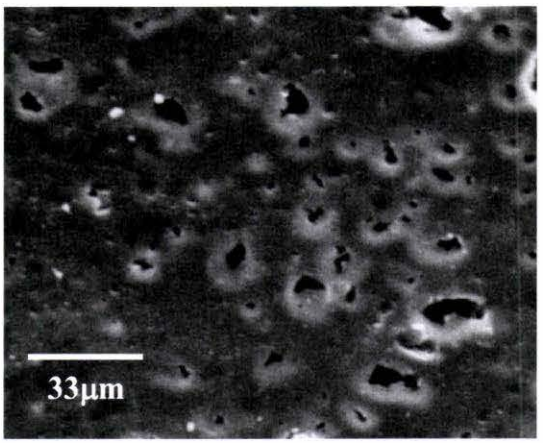


Figure 4-5: Optical microscopy photograph (mag. x 300) of CaCO3 modified UP resin etched for 10

However, an alkaline etch time of 50 minutes with an additional acid etch time of 5 minutes was considered far too long for industrial applications. It is hypothesised that solution B would reduce the etching time.

Optimisation of Material Y (CaCO3 filler)

Having successfully created etched keyholes into the modified UP resin surface, the next aim was to further develop the material by identifying the optimum amount of CaCO3 to be added to the resin. At this stage in the process it was not possible to test the modified materials ability to pass impact test standards because a finished product (helmet) is required for such tests. However, Donovan III et al (1982) recommended using 'not more than 10% CaCO3' to create good keyhole etching without dramatically affecting the physical properties of the resin. An experiment was therefore carried out to compare CaCO3 quantities of 6, 7, 8, 9 and 10%. Through comparing optical microscopy photographs of the samples it was found that as the percentage of CaCO3 increased, so too did the number of keyholes per unit area. It was also noted that 10% CaCO3 did not make the resin too viscous and was therefore still an easy consistency to work with. 10% CaCO3 was therefore chosen as the optimum CaCO3 quantity for use in the following steps of the process. Further development of the material may be required upon completion of the plating process in order to find a median between hole creation and physical characteristics of the material. Therefore the 10% CaCO3 samples became the standard for material modification Y.

Concept 5 - Etching Modified Material Y with Etching Solution B

It was hypothesised that etching solution B, pre-etch material Y in shorter time frame than solution A. Concept 5 was tested using the same methodology as in concept 4. The results found that 15 minutes was the optimum pre-etching time (see Figure 4.8-4). The HCl etching time remained the same as concept 4, at 5 minutes.

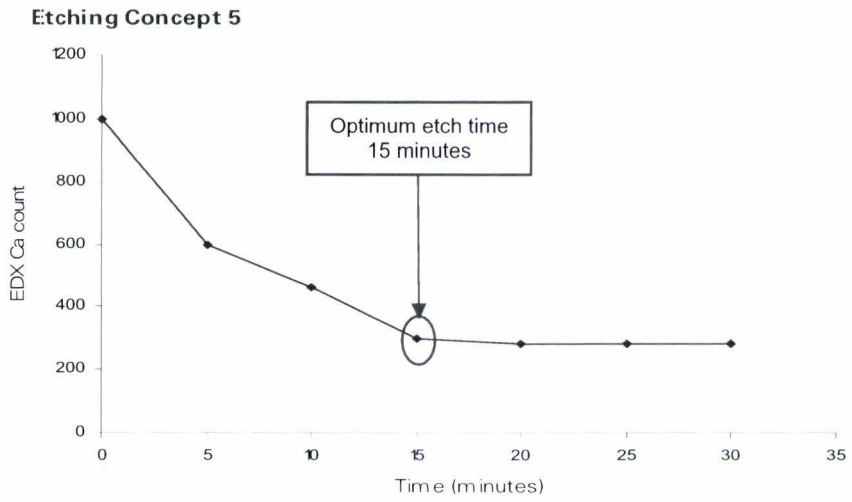


Figure 4-6: Concept 5 EDX Ca Count; optimum etch time of 15 minutes

With the etching of material Y with etching solution Y for 15 minutes followed by a 5 minute HCl etch; the desired 'holes' have been achieved within the specified marginal etch time of 20 minutes.

Concept 6 – Etching Modified Material Y with Etching Solution C

It was hypothesised that the etching solution C would 'pre-etch' modified material Y in even less time than the etching solution C, and would therefore be closer to meeting the specified target value of 10 minutes. The same methodology was used as that in concept 4, but with pre-etch times of 0, 2.5, 5, 7.5, 10, 12.5, 15 17.5 and 20 minutes. The optimum pre-etching time using etching solution C was identified as 10 minutes (See Figure 4.8-5); followed by a 5 minute acid etch in HCl resulted in a total etch time of 15 minutes, which met the specified target value of 15 minutes.

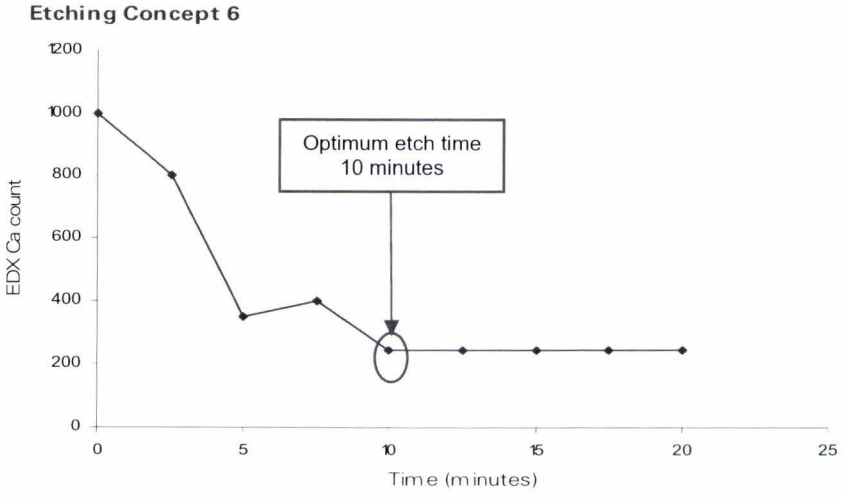


Figure 4-7: Concept 6 EDX Ca Count; optimum etch time of 10 minutes

4.8.4 Material Z - CaCo3 and Fumed silica filled UP resin

At this stage of the project, having successfully plated the modified polyester resin containing CaCO3 using a number of different methods, attention was turned to ensuring that the product would still pass international safety standards. Of the highest concern was the materials ability to conform to impact resistance standards. It was therefore necessary to explore methods of strengthening the material to counteract the CaCO3, which made the material increasingly brittle.

A number of material strengthening ideas were explored including the addition of a fine metallic woven sock inside the material. However by far the best method was the addition of fumed silica to the resin prior to curing. Fumed Silica is a non-crystalline (glass) form of silicon dioxide (quartz, sand) and has an exceptionally good thermal shock resistance. It is available in a 'powdery flake' form that can easily be mixed with the resin prior to curing. Once the resin is cured, the additional fumed silica works in a similar way to the fibreglass sheets within the material to strengthen it. The amount of fumed silica that can be added to the resin is restricted by the proportional increase in the resins viscosity.

Method of making material Z samples for testing Hypothesis 2

The aim was to identify the optimum quantity of fumed silica that could be added to a UP resin sample with 10% CaCO3 (weight). A trade-off existed between increasing the strength of the material (by adding more fumed silica), and manufacturability, which is affected negatively as the viscosity of the liquid resin increases as a result of adding more fumed silica.

Samples were made using the same method as creating material Y, and fumed silica added in weight % quantities of 2gm (0.7%), 4gm (1.3%), 6gm (2.0%), 8gm (2.7%),... 24gm (8%). Quantities above 8% (weight) fumed silica made the resin too thick for manufacturing in an RTM machine.

A methodology the same as that used in concept 6 was used to test the samples. It was found that as the viscosity of the resin increased, less CaCO3 was found at the surface of the material. That is, the thicker the resin, the more difficult it was for the CaCO3 particles to move towards the surface of the material, and therefore the etching was less effective. This was evident when trying to acid-etch the samples in HCl as there was no effervescence, indicating the surface in contact with the HCl was purely UP resin.

Therefore, 6gm of fumed silica per 300gm samples, approximately 2% weight, was found to be the optimum quantity as anything higher than 6gm significantly increased the viscosity of the resin and therefore affected the manufacturability and the ability for the

CaCO3 particles to reach the surface of the resin. Therefore the first sample had the following composition:

- 300gm unsaturated polyester resin
- 6gm fumed silica
- 33gm CaCO3
- 6ml hardener

It should be noted that although 2% seems a small quantity, the volume of the fumed silica and the affect on the materials strength was expected to be significant. This area of research may require further optimisation if selected for production.

Plating Methodology

The etch process tests for concepts 7, 8 and 9 were the same as those for concepts 4, 5 and 6 but using Modified Material Z filled with 10% CaCO3 and 2% Fumed Silica.

Concept 7 – Etching Material Z with Alkaline Etching Soln. A

Modified material Z was tested using the same method as concept 4. The creation of etch holes was successful after finding the optimum alkaline pre-etch, followed by a 5 minute acid etch in HCl. The alkaline etch took 60 minutes to pre-etch the surface of the material optimally (see Figure 4.8-6), 10 minutes longer than in Concept 4. The 'Ca' count prior to etching, and at optimum etch were both lower than the counts observed in concept 4. The most probable cause of this is that the resin became thicker due to the addition of fumed silica. The thicker resin would mean that less CaCO3 particles sink to the bottom (surface) of the material, resulting in lower 'Ca' counts in general. This etching method resulted in very good adhesion and appearance upon plating. However, the etch time was outside the marginal etch time value.

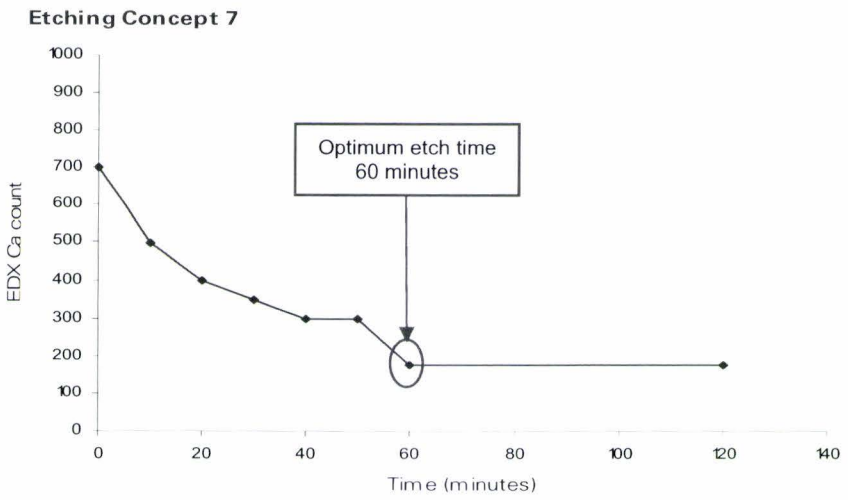


Figure 4-8: Concept 7 EDX Ca count; optimum etch time of 60 minutes

Concept 8 – Etching Material Z with Etching Solution B

Concept 8 had very similar results to concept 5, but with lower overall CaCO3 counts, as expected due to the results of concept 7, and as a result of the increased viscosity of the resin prior to moulding. It was found that the optimum 'pre-etching' time was 15 minutes. The resulting surfaces showed well distributed correct sized etch holes, which resulted in a quality plating with good appearance and adhesion.

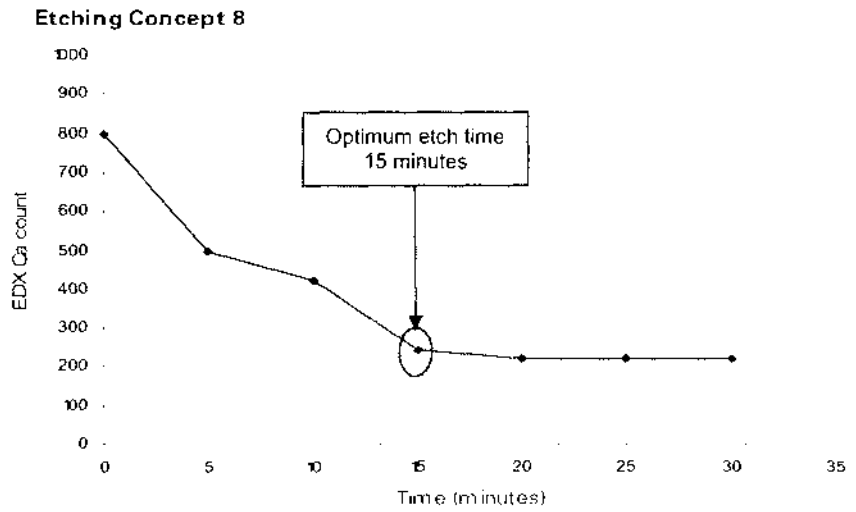


Figure 4-9: Concept 8 EDX Ca count; optimum etch time of 15 minutes

Concept 9 – Etching Material Z with Etching Solution C

Concept 9 was tested using the same method as concept 6 and with similar result but with slightly longer etch times, and lower overall 'Ca' counts. The optimum 'pre-etching' time (see Figure 4.8-8) was identified as 12.5 minutes (concept 6 was 10 minutes). After pre-etching the samples were acid-etched in HCl for 5 minutes, resulting in 'Ca' counts as low as 200. Microscopy photography showed the surface with well distributed, correct sized etch holes, which resulted in quality plating with good appearance and adhesion.

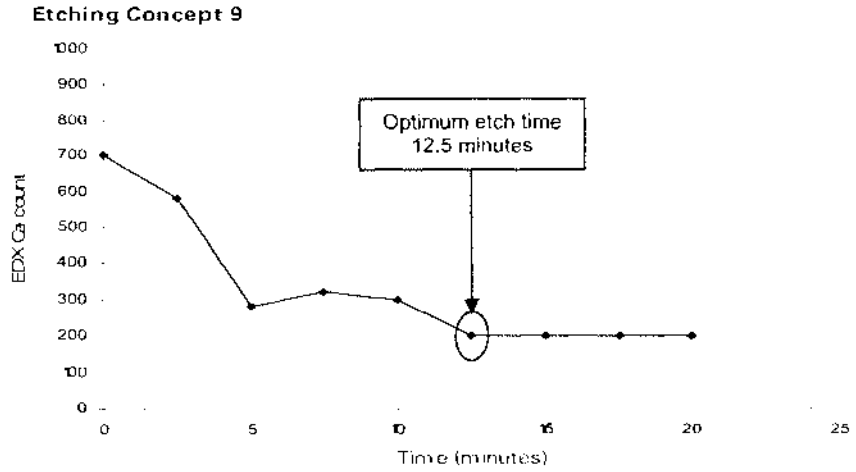


Figure 4-10: Concept 9 EDX Ca count; optimum etch time of 12.5 minutes

4.9 ACRYLATHANE PAINTED UP RESIN

During the testing of hypothesis 1, UP resin helmet shells were cut into samples for testing. In some instances the shells sent from the PHNZ factory were coated with Acythane paint. As a UP resin surface was required for the testing, these shells could not be used. However, instead of suspending testing as a result of having no suitable helmet shell samples, trials were carried out on the painted shells 'out of interest' to see if the material could be plated readily.

The results of the initial trials were surprisingly successful and lead to a third hypothesis: That modifying UP resin by adding a coating, specifically Acrythane paint, to the UP resin prior to etching will enhance plate-ability.

The same method of testing concepts 1, 2 and 3 were used to test the painted resin using each of the etching methodologies in concepts 10, 11 and 12.

Concept 10 – Etching Acrylathane Painted UP Resin with Alkaline Soln. A

Alkaline Solution A was used to attempt etching the painted material using the following times: 10, 20, 30, 40, 50 and 60 minutes. It was not necessary to test further than 60 minutes, because any time over this would be far too long, rendering the concept useless in manufacturing efficiency.

The result of the trials was that none of the etch times provided etch-holes for plating. Therefore this concept was not selected because it did not work.

Concept 11 – Etching Acrylathane Painted UP Resin with Alkaline Soln. B

The same trials were carried out for this concept as for Concept 10. The results were very much the same, with no etch-holes being created, and consequently the material failed to be plated with copper.

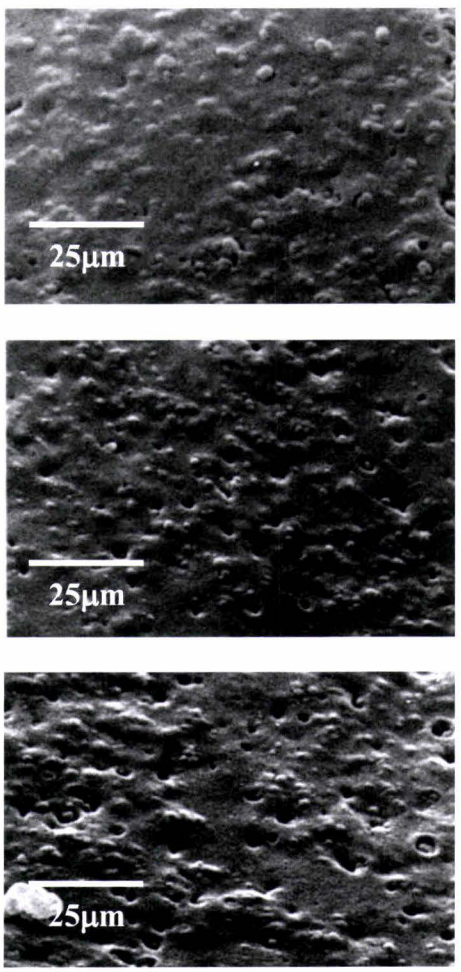
Concept 12 – Etching Acrylathane Painted Material with Alkaline Soln. C

The experiment was run using the following etch times: 3, 5, 7, 9, 11, 13 and 15 minutes. The results are tabulated below:

Table 4.9-1: Concept 12 optimum etch time analysis

Etching Concept 12 Results	
Etching Time (minutes)	**Etching Outcome**
3	Under etched
5	Good etching
7	Good etching, slightly over
9	Over etched
11	Over etched
13	Very over etched
15	Greatly over etched

The optimum etching time was established as being between 4 and 6 minutes. In order to identify the exact etching time, another experiment was run with times of 4, 5 and 6 minutes. The optical microscopy photographs are presented below (Figure 4.9-1) to illustrate the results.



a) 3 minute etch in solution C resulted in the surface being swollen to it appears bubbled. This indicates the etch time was too short to produce etch holes.

b) 5 minute etch in solution C resulted in some holes, with some bubbles remaining, indicating that 5 minutes was not long enough to develop all the bubbles into etch holes. However, the etch holes are evenly distributed and resulted in good plating.

c) 6 minute etch in solution C resulted in more etch holes with fewer 'bubbles' which represent developing holes. 6 minutes is a good etch time.

Figure 4-11: Optical microscopy photographs (mag x 500) of Acrylathane painted surface etched for 4, 5, and 6 minutes with etching solution C

Another advantage of this concept is that the etch holes produced were comparatively smaller than when etching the other materials. For example, the holes produced in modified material A were photographed at 400 x magnification, whereas the Acrylathane painted materials holes had to be photographed at 5000 x magnification to be visible. The smaller holes will result in a smoother plated surface, with a higher sheen.

The subsequent plating worked very successfully. In addition, the surface was smoother and shinier than the non-painted shells. The painted shells gave a greater plated appearance due to both the smaller etching holes and the original surface to be plated was smoother than the other materials. That is, the paint on top of the polyester resin was in fact smoother than the polyester surface, and therefore the final plated surface is smoother and shinier. Adhesion tests were carried out in the same manner as for the other samples, and seemed to have similar results. Final judgement of the comparative adhesion quality and durability of the plating on each material will be reserved until tests are completed on whole helmet shells in the testing laboratory at Pacific Helmets Ltd.

4.10 SELECTION OF ETCHING PROCESS CONCEPT(S)

Tables 4.10-1 and 4.10-2 illustrate the results of the etching concepts tested against both non-plating related and plated related specifications. Table 4.10-3 illustrates the ranking of the concepts based on these tests.

Table 4.10-1: Etching results – non plating related tests

Etching Target Specifications - non plating quality tests																	
Metric No.	Metric	Importance	Unit	Marginal Value	Target Value	Concept											
						1	2	3	4	5	6	7	8	9	10	11	12
1	Holes Achieved	5	Binary	Pass	Pass	F	F	P	P	P	P	P	P	P	F	F	P
2	Holes size	4	Subj	3	4	-	-	3	3	3	3	3	3	3	-	-	4
3	Hole distribution	4	Subj	3	4	-	-	4	4	4	4	3	3	3	-	-	5
4	Cost per Helmet	4	NZ$	0.5	0.3	0.13	0.19	0.23	0.27	0.33	0.37	0.27	0.33	0.37	0.19	0.19	0.23
5	Time to Etch	4	Min	20	10	-	-	10	55	15	15	55	15	15	-	-	5
6	Ease of Manufacture	4	Subj	3	4	5	5	5	3	3	3	2	2	2	3	3	3

Table 4.10-2: Etching results – plating quality tests

Etching Target Specifications - plating quality																	
Metric No.	Metric	Importance	Unit	Marginal Value	Target Value	Concept											
						1	2	3	4	5	6	7	8	9	10	11	12
5	Bend test	5	Subj	4	5	-	-	5	3	4	5	3	4	5	-	-	5
6	Sharp object resistance	4	Subj	4	5	-	-	5	3	4	5	3	4	5	-	-	5
7	Texture test	4	Subj	4	5	-	-	5	3	4	5	2	3	5	-	-	5
8	Shine test	5	Subj	4	5	-	-	5	3	4	5	2	3	5	-	-	5

Table 4.10-3: Etching concept selection ranking

Concept Selection Rank												
	Concept											
	1	2	3	4	5	6	7	8	9	10	11	12
Ranking	-	-	1st	7th	5th	4th	8th	6th	3rd	-	-	2nd

The following conclusions were drawn from the results:

- Concept 3, followed by Concept 12 were the two strongest concepts, as they best met the requirements.
- Concepts 1, 2, 10 and 11 were eliminated immediately because they failed to produce the 'holes' required to adhere the metal coating to the material.
- Concepts 4 and 7 were eliminated because the etch time was well above the target and marginally acceptable values.
- Concepts 5, 6, 8 and 9 were above the cost target range, but were within the marginal value range. Therefore these concepts were still potential options, but not preferred choices.
- These results illustrated that alkaline etching solution C was the most effecting etching solution.
- The unmodified material was considered the best material concept, as it requires the least time and money to manufacture, while still being able to achieve good results while being etched with Alkaline etching solution C.
- The painting of a shell is considered less expensive than the addition of fillers. Therefore this material concept is always second in preference.

4.11 OUTCOME OF PLATING PROCESS DEVELOPMENT

The major outcome of this section – the development of the etching process, was that a number of different methods of successfully etching the surface of UP resin were identified. Four methods of manufacturing the helmet shells were identified of which the following two concepts were selected:

- Unmodified Polyester resin.
- Polyurethane painted polyester resin.

The materials were then successfully etched with three etching solutions and related methodologies. The unrefined full four-step plating processes were then used to trial plating using the etching concepts. Concepts 3 and 12 were selected as the best etching methods to use during the project and went through to the refined concept sequence in the following chapters as outlined in Table 4.1-11

Table 4.11-1: Process concept matrix following etching concept selection

Process concept matrix																								
	Concepts																							
Material	X						Y						Z						PAINTED					
Etching solution	A		B		C		A		B		C		A		B		C		A		B		C	
Activation	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd
Electroless plating	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni
Electroloplating	Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu	

5 ACTIVATION METHODOLOGY

5.1 INTRODUCTION

After etching it is necessary to 'activate' the surface. The primary purpose of activation is to provide catalytic sites on the plastic surface to attract the electroless metal coating. This involves putting the material into an activation solution, where the 'activator' is attracted to the 'key-holes'. Following this, an 'accelerator' reduces the activator to a form that attracts the electroless copper onto the surface, where it is locked into place.

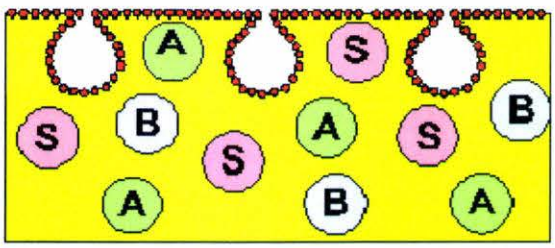


Figure 4-12: Cross section view of Acrylonitrile butadiene styrene (ABS) after Activation. (red dots are activator precious metal ions on the etched surface)
(Astro Electroplating, 2004)

5.2 BACKGROUND TO ACTIVATION

In order for the electroless copper plating to work the surface to be plated must be catalytic to attract the metal to it. For many materials (e.g., insulators), their surfaces are not inherently catalytic and must be activated prior to electroless plating (Liu, He et al. 2005). The metal, usually Cu or Ni, can then be deposited onto the catalytic sites formed on the objects surface. These sites usually contained palladium nuclei chemisorbed (to take up and chemically bind a substance onto the surface of another substance) from solution. Different methods have been proposed to perform the chemisorptions. Historically, the most widely used methods were the "two-step" process and "one-step" process. In the two-step method, the object was immersed successively in $SnCl_2$ and then in $PdCl_2$ solutions (Ebneth 1993).

The one-step process, on the other hand, uses a mixed $SnCl_2$ / $PdCl_2$ solution (Meek 1975). However, $SnCl_2$ is not an active catalyst for electroless plating. As a result, the growth of copper deposit was inhibited. Tin free electroless copper plating was realised by the introduction of amino groups which formed solid complexes with palladium ions (Liu, He et al. 2005). Nevertheless, palladium is a relatively expensive catalyst. In order to circumvent this problem, Hill, Foss et al. (1979) developed a procedure for making a coppered mirror through pre-treatment with Silver (Ag) slurry. Shukla et al. replaced successfully the costlier $PdCl_2$ activator with cheaper $AgNO_3$ (Liu, He et al. 2005).

Usually, the expensive noble metals such as Pd and Pt were chosen as seeds (in those techniques), or the precursors were organo-metal compounds, which were relatively expensive, or water-insoluble leading to environment problems when using organic solutions such as chloroform. So a cheap and water-soluble seed precursor is attractive (Chen, Li et al. 2004).

In the research of Chen, Li et al. (2004) Copper was selectively deposited on Polyimide (PI) surface catalysed by laser-induced deposition of Ag particles. The ablated surface was immersed in a silver diamine solution. $Ag(NH_3)_2^+$ ions were reduced to Ag at the ablated region on the film, and the Ag particles were deposited in situ. After rinsing the film, copper was deposited on the seeded film by electroless plating successfully (Chen, Li et al. 2004).

Similarly, Goosey, Graves et al. (1999) describe how conventional methods employed for metallising polymers (e.g. ABS) utilize aggressive oxidising agents such as chromic acid as part of the surface treatment prior to conditioning, catalyzation and electroless metal deposition. The result is a lengthy process which often utilizes undesirable chemicals that are unpleasant to handle, difficult to treat and increasingly environmentally unacceptable.

Goosey, Graves et al. (1999) found processes that include a surface treatment providing a substrate morphology leading, after further steps, to direct catalyzation of the substrate surface without the need for the traditional subsequent neutralization, conditioning and tin/palladium catalyzation steps. This is a major improvement since it removes several process steps, one of which is the use of chromic acid. The invention also obviates the need to use an expensive palladium based plating catalyst. The new processes are, in part, based upon the use of electrochemically or otherwise generating metal ions (e.g. Ag^{2+} or Co^{3+}), referred to as metal activators. Suitable metal activators include silver, cobalt, ruthenium, cerium, iron, magnesium, nickel, rhodium, and vanadium, with silver and cobalt being generally preferred. However, Chen, Li et al. (2004) believes that compared with Palladium and Platinum as seeds, Ag is less effective for catalysing electroless plating.

On the other hand, Mr Bendary believes that it was possible to use Ag based activators for plating UP resin, and claimed to be using such a solution to plate UP resin in Egypt for decorative purposes. Advantages to using an Ag activator include:

- Increased solution stability
- Reduction in cost
- Ease of use and maintaining optimum solution composition

Following activation, the part must come in contact with an accelerator. Accelerators are historically used to remove excess tin while leaving the palladium sites intact on parts that have been activated using a palladium-tin activator (Kuzmik 1990). However, when using the silver activator the accelerator acts as a reducing agent capable of reducing the oxidising the metal activator species to a lower oxidation state. Specifically the accelerator reduces the $Ag(NH_3)_2^+$ to Ag, which then attracts the electroless copper in the electroless plating solution.

5.3 THE ACTIVATION PROCESS SUMMARY

The activation process is made up of the following steps:

1. **Distilled Water Rinse** to remove any 'drag-out' of the etching solution, which would easily contaminate the activation solution.
2. **Activation** for approximately 15 minutes
3. **Accelerating** to either a) remove the stannous hydroxide from a $SnCl_2$ / $PdCl_2$ activated surface which inhibits the electroless bath or b) act as a reducing agent to reduce the oxidized metal activator species to lower oxidation state.
4. **Final Rinse** in distilled water to remove excess activator and accelerator.

5.4 ACTIVATION PROCESS DEVELOPMENT STRATEGY

The flow diagram summarises the activation process development strategy:

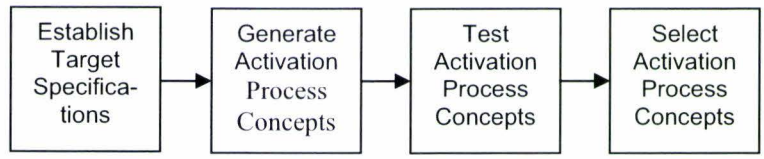


Figure 4-13: Flow diagram of the Activation process development strategy

5.5 IDENTIFACTION OF ACTIVATION SPECIFICATONS

The primary activation specification is that the part is catalysed to achieve quality plating adhesion. The simplest and most reliable method of testing the activation is to analyse how well the subsequent plating adhesion. Assuming the electroless plating is being carried out correctly, it is probable that one of the following problems has occurred with the activation:

- Solution is too dilute
- Activation time is too short.
- Accelerator is contaminated

In the case where no plating has occurred it is possible to use scanning electron microscopy (SEM) to identify if Palladium, Tin or Silver were found on the surface of the material. If limited or no traces of either element are found on the sample, then there is something fundamentally wrong with the solution or process.

5.6 ESTABLISHING TARGET SPECIFICATIONS

Table 5.6-1 outlines the target metrics, importance and marginal and target values of the non-plating related specifications:

Table 5.6-1: Activation Target specifications

Activation target specifications					
Metric No.	Metric	Imp.	Unit	Marginal Value	Target Value
1	Activated Successfully	5	Binary	Pass	Pass
2	Time to activate	4	Minute	20	15
3	Cost of Solution	4	NZD$	2	1
4	Stability of Solution	4	Subj.	3	4

In addition, the same plating quality specifications, with the same target and marginal values were used as those used in the etching process.

5.7 HYPOTHESIS GENERATION

A review of the relevant literature, and discussions with Mr Bendary identified two methodologies that might potentially activate the UP resin:

1. The palladium/stannous chloride solution commonly used to activate ABS was the only solution readily available within the NZ plating industry.
2. Mr Bendary recommended a silver based solution which offered several advantages over the Palladium based solution.

5.7.1 Activation Hypothesis 1 - Palladium Activator

The literature identified a number of palladium activator compositions generally containing Stannous Chloride, Palladium Chloride and Chloride ion in varying ratios.

The chloride ion is usually maintained using hydrochloric acid, but sodium chloride may also be used. This solution causes the Pd^{+2} ion to be reduced to Pd^{0} according to the reaction below. The Pd sites form the catalytic surface needed to deposit the chemical plating (Ferrier, 1995).

$$Sn^{+2} + Pd^{+2} \rightarrow Sn^{+4} + Pd^{0}$$

The operating conditions for the activator bath are dependent on the solutions concentration and the earlier referenced literature identified temperatures between 85°F and 130°F (approximately 30°C to 55°C) for times between 2 and 5 minutes.

After rinsing the part following the activator, metallic palladium is present on the surface of the part surrounded by hydrolysed stannous hydroxide. The excess stannous hydroxide must be removed from the part before the palladium can act as a catalyst. This is the role of the accelerator. The accelerator removes the excess tin from the part, which would otherwise inhibit the action of the electroless bath, while leaving the palladium sites intact for the deposition of the electroless bath (Ferrier, 1995).

5.7.2 Activation Hypothesis 2 - Silver Activator

Although the Palladium/Tin type of activation solution is currently the most commonly used activator in the electroless plating on plastics industry, it is very expensive and easily destroyed through contamination. Very recent developments by Mr Bendary have identified an alternative activation solution that has many advantages over the Palladium/Tin type. That is a solution that uses Silver (approximately 0.1mol/L) instead of Palladium (approximately 0.02mol/L) as the precious metal.

5.8 HYPOTHESIS TESTING

Following the outcome of the etching refinement process and the selection of concepts 3 and 12 the activation concepts were tested using material X (unmodified UP resin) and the painted UP resin materials with etching concept C. The unrefined electroless copper and electroplating methodologies were used as in the etching trials. Table 5.8-1 illustrates the sequence of the individual process step concepts used to test the activation concepts. All variables remained constant except the activation process.

Table 5.8-1: Process concept matrix for Activation hypothesis testing

Process concept matrix																								
	Concepts																							
Material	X						Y						Z						PAINTED					
Etching solution	A		B		C		A		B		C		A		B		C		A		B		C	
Activation	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd
Electroless plating	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni
Electroloplating	Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu	

5.8.1 Palladium Activation Methodology A - Commercial Palladium Activation

An experiment was carried out in which a commercially available palladium activation solution supplied by MacDermid Plating. The MacDermid 'pre-activation dip' followed this for one minute, agitated, at room temperature as described in the MacDermid

Technical Data Sheet. Then, the MacDermid HM activator was used for 8 minutes at 35°C (as described) and the MacDermid HM accelerator solution for 2 minutes at 50°C (as described). Half the samples were then agitated in the MacDermid HM electroless copper solution for between 20 and 30 minutes at 70°C. This resulted in no visible plating.

The EDX analysis showed no traces of copper, palladium or tin on the samples on which plating was attempted. The samples on which no plating was attempted did not show any traces of palladium and only very small amounts of tin.

It was concluded that the activation using MacDermid solutions was most probably unsuccessful because the solutions are made specifically for plating ABS, not UP resin. Due to having no success with existing Activation solutions readily available in New Zealand, expert advice was sought from Mr Bendary in Egypt, who recommended a different palladium activation solution, made up in the laboratory.

The composition and methodology is as follows:

1. Dissolve 200gm $SnCl_2$ in 150mL of 37% HCl solution, stir over heat until colourless.
2. Dissolve 3gm $PdCl_2$ in 100mL of 37% HCl solution, stir over heat until the solution looks like strong black coffee.
3. Cool both solutions; combine and make up to 1 litre with distilled water. This solution is not stable and is easily contaminated. Therefore it is essential that parts activated are rinsed in distilled water directly before activation.
4. Activation is run at room temperature for approximately 15 minutes.
5. Rinse the part in distilled water to remove any excess solution. It is imperative the water be distilled to protect the sensitive activated sites.

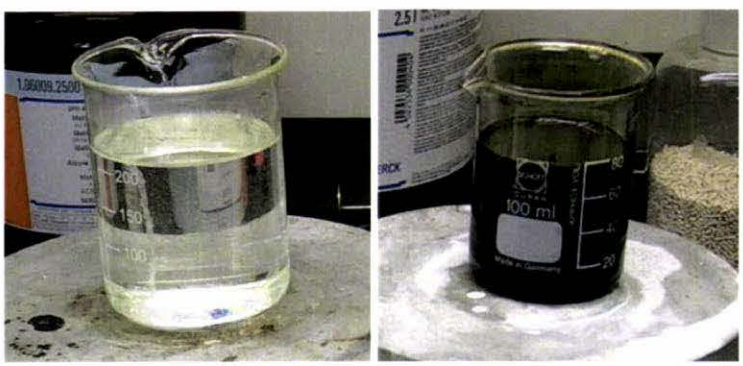


Figure 4-14: a) Clear solution of SnCl2 dissolved in HCl. b) Black coffee coloured PdCl2 dissolved in HCl.

Following the activation the part was accelerated to remove the excess tin from the part while leaving the palladium sites intact. For this process the accelerator was a 10%

NaOH solution. That is, 100gm NaOH dissolved in distilled water, made up to one litre. The accelerator is run at room temperature for between 2 and 5 minutes.
It is during the acceleration of the part that the first visual change of the material occurs. The reduction of the activator darkens the material to a tan to brown colour. This colour change is a visible sign that the activation and acceleration has worked well. The part is rinsed in distilled water before progressing to electroless plating.

The outcome was that samples were successfully plated with a high quality copper coating. The cost of using this activation process was calculated at $2.54 per helmet. It could be activated in 15 minutes with 2 minutes acceleration.

5.8.2 Activation Hypothesis 2 – Silver Activator

The Silver activation solution is prepared with a much simpler method than the Palladium activation solution. It is also much more stable, and resistant to contamination, and is cheaper to make up and maintain. The only disadvantage of the silver activator is that it can only be used in the electroless Copper plating process. It is possible to use this activator for electroless nickel plating if the reducing agent in the electroless nickel solution is modified.

The preparation of the Silver activation solution is as follows:

- Place 800mL distilled water in a 1L beaker.
- Add 20gm Silver Nitrate.
- Stir to dissolve (heat not necessary).
- In a separate beaker dissolve 2-3gm of Sodium Borate in 100mL distilled water.
- Add the sodium borate solution (which acts as a buffering agent) slowly to the Silver Nitrate solution; drop-by-drop is best, stirring to dissolve each drop, until one drop does not dissolve. STOP! The solution is saturated. The finished solution should be just cloudy, with a small amount of turbidity, and only just no longer colourless.

Once prepared, the solution was tested using the same methodology as outline for the Palladium activator. The results were very successful, as the sample parts were plated to a similar quality as when using the Palladium activator.

In addition the Silver activator cost less at $0.12 per helmet shell, and takes the same length of time as the Palladium activator (15 minutes, with 2 minutes acceleration).

5.9 SELECTION OF THE BEST ACTIVATION METHODOLOGY

Table 5.9-1 illustrates the results of the activation concept testing against the activation specifications. The plating quality resulting from the activation concepts was the same, both performing very well scoring 5 in all test, and thus are not presented.

Table 5.9-1: Activation methodology selection matrix

Activation target specifications							
Metric No.	Metric	Imp.	Unit	Marginal Value	Target Value	PdCl2 soln.	Ag soln.
1	Activated Successfully	5	Binary	Pass	Pass	Pass	Pass
2	Time to activate	4	Minute	20	15	15	15
3	Cost of Solution	4	NZD$	2	1	2.54	0.12
4	Stability of Solution	4	Subj.	3	4	2	4

The Silver activator was selected as a superior methodology, because it offered all the same quality plating benefits as the Palladium activator with the added advantages of being cheaper, more stable and resistant to contamination. However, due to the incompatibility of the Silver activator with the Nickel electroless plating concept, both the Silver and the Palladium activation concepts progressed into the electroless plating trails.

5.10 OUTCOME OF THE ACTIVATION PROCESS DEVELOPMENT

Table 5.10-1 illustrates the refined process sequence that would go forward into the electroless plating development phase following the selection of the Silver activation concept.

Table 5.10-1: Process concept matrix following activation concept selection

Process concept matrix																								
	Concepts																							
Material	X						Y						Z						PAINTED					
Etching solution	A		B		C		A		B		C		A		B		C		A		B		C	
Activation	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd
Electroless plating	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni
Electroloplating	Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu	

6 ELECTROLESS PLATING METHODOLOGY

6.1 INTRODUCTION

Activation is followed by electroless plating, the final step of the 'pre-plate' cycle. This section will outline the prior art, along with the methodology and outcome of this study. The main focus of the study was on electroless copper plating, as this was considered the most suitable method of plating. However, a less detailed look at Nickel electroless plating is also outlined, and was tested as a second potential electroless plating method.

6.2 BACKGROUND TO ELECTROLESS PLATING

6.2.1 Electroless Copper plating

After activation, the part is rinsed and put into the electroless bath, which deposits a thin, adherent metallic film, in this case copper, on the plastic surface by chemical reduction. This is accomplished by using a semi-stable solution containing a metal salt, a reducer, a complexor for the metal, a stabilizer and a buffer system. When idle, the baths are stable, but when the catalytic surface is introduced into the solution, a chemical reduction of metal occurs on the catalytic sites and through autocatalysis continues until the part is removed (Kuzmik 1990).

The deposition rate and deposit properties of electroless copper plating depend on the copper complexing agent, reducing agent, bath temperature and pH (Duffy, Pearson et al. 1983). In addition, additives such as stabilizers, accelerators and brighteners are used (Oita, Matsuoka et al. 1997).

Deckert (1993) states that the minimum necessary components of an electroless plating solution are the metal salt and a reducing agent. The source of copper is a simple cupric salt such as copper sulphate, chloride or nitrate. Pearlstein (1974) suggests various common reducing agents for use in electroless copper baths, namely formaldehyde, dimethyl-amine borane, boro-hydride, hypophosphite, (Gulla and Dutkewych 1984) hydrazine sugards (sucrose, glucose etc) and dithionite. In particular, however, virtually all commercial electroless copper solutions have utilized formaldehyde as reducing agent. This is a result of a combination of cost, effectiveness, and ease of control of formaldehyde systems, and is particularly remarkable in view of considerable and continual pressures exerted on the plating industry by environmental and regulatory agencies because of health concerns regarding formaldehyde exposure.

The relevant half-cell reaction for electroless copper deposition is:

$$Cu^{2+} + 2e \rightarrow Cu^{0} \qquad E^{\circ} = +0.340\ V$$

For formaldehyde, E° depends on the pH of the solution. For example:

$$HOOH + 2H^{+} + 2e^{-} \Leftrightarrow HCHO + H_2O \ (pH = 0, E^{\circ} = +0.056)$$
$$HCOO^{-} + 2H_2 + 2e^{-} \Leftrightarrow HCHO + 3OH^{-} \ (pH = 14, E^{\circ} = -1.070)$$

Therefore electroless copper solutions utilize formaldehyde as reducing agent and employ high pH, above 12. Because simple copper salts are insoluble at pH above 4, the use of alkaline plating media necessitates use of a complexing, or chelating component. Historically, complexing agents for electroless copper baths have almost always fallen into one of the following groups of compounds (Deckert 1993):

1. Tartrate salts
2. Alkanol amines
3. EDTA (ethylenediamine tetra-acetic acid) or related compounds.

The complexing agent stabilizes the bath, making the selection of the reducing agent critical. It also affects the rate of crystal formation (Li and Kohl 2004).

Ethylenediaminetetraacetic acid (EDTA) and sodium potassium tartrate have been widely used as complexing agents in conventional electroless copper plating solutions with formaldehyde as the reducing agent. These plating solutions exhibit low deposition rates because of the high formation constants of the cupric complexes and the shift in reduction potential toward negative values with stability constants (Li and Kohl 2004). Recently, complexing such as Triethanolamine (TEA) and triiosporpanolamine have been used to yield high deposition rates (Lin and Yen 2001). However, high deposition rates are associated with bath stability and deposition quality problems (Li and Kohl 2004).

In electroless plating, there is always a tug-of-war between the deposition rate and bath stability. A stable bath is slow, but a higher rate bath can decompose at the drop of a hat (Li and Kohl 2004).

The reductive behaviour of cupric ions in a strong base depends on the complexing agents because of the formation constant of the complex, which affects the mixed potential and thus the deposition rate of electroless copper. At the mixed potential, the oxidation of formaldehyde is independent of the copper complexing agents, but can be

accelerated by increasing the pH of the bath. The EDTA-based electroless copper solution has a relatively low deposition rate and high bath stability because EDTA forms a strong complex with cupric ions. TEA adsorbs on palladium and can poison the oxidation of formaldehyde and thus inhibit the initial copper deposition on the active palladium. Although TEA forms a weaker complex with cupric ions than EDTA, the TEA-based electroless copper solution achieves a higher deposition rate only after the active palladium surface is covered with fresh copper(Li and Kohl, 2004).

The TEA-EDTA dual-complexing agent electroless copper solution provides reasonable deposition rate and bath stability. The deposition rate increases as the mole ratio of TEA to EDTA increases and the bath stability holds. The uneven surface coverage of copper deposition on the palladium activated surface decreases with an increase in the TEA to EDTA mole ratio. It can be improved, however, by adjusting the operating temperature and pH of the bath (Li and Kohl, 2004).

In addition, EDTA has certain desirable characteristics based on waste treat-ability; specifically, EDTA can be more easily separated (precipitated) from waste solutions by pH adjustment. Starting in the 1970s, bath additives for EDTA systems were developed that allowed excellent control of plating rate, grain structure, and other important factors (Deckert 1993).

In addition to the copper salt, reducing agent, source of alkalinity and chelate, other important components are present in commercial electroless copper solutions. These components are generally considered the proprietary portion of the formulation, and control such parameters as initiation and plating rate, stability, deposit strength, colour, ductility, etc (Deckert 1993).

Additives that stabilize the bath against various manifestations of undesired plate-out are referred to as stabilizers. They are usually employed at low concentrations, typically 100 ppm. It is noteworthy that perhaps the most common stabilizer for electroless copper baths is a steady stream of air (i.e. oxygen) bubbled through the solution (Deckert 1993).

Julve (2001) describes the main reaction taking place in electroless copper deposition are represented in the following simplified form:

(1) Cathodic partial reaction: $Cu^{2+} + 2e \rightarrow Cu^{0}$

(2) Anodic partial reaction: $2\ HCHO + 4\ OH^{-} \rightarrow 2\ HCOO^{-} + H_2 + 2\ H_20 + 2e$

The global reaction will be the following:

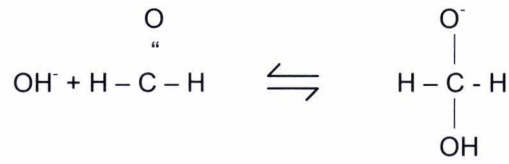
(3) $Cu^{2+} + 2\ HCHO + 4\ OH^- \rightarrow Cu^0 + 2\ HCOO^- + H_2 + 2\ H_20$

For each mole of copper deposited, two moles of formaldehyde and four moles of hydroxide ion are consumed. And for each mole of copper deposited, one mole of hydrogen gas is evolved. In practice, more formaldehyde and alkali are required, indicating that side reactions take place. One of these reactions is the disproportionation of formaldehyde with alkali to form methanol and formate ions (Cannizzaro reaction), which also consumes HCHO and OH^-:

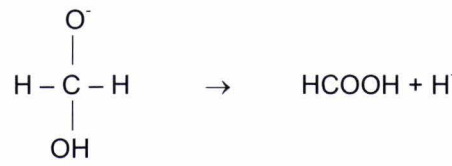
$$2\ HCHO + OH^- \rightarrow CH_2OH + HCOO^-$$

This consumption of OH^- is partially responsible for the decrease in pH.

In respect to the reduction mechanism of cupric ion to copper metal, as formaldehyde exists in the following state of equilibrium:



A hydride ion is transferred from the alcoholate ion by means of an electron shift to the catalytic surface (anode):



And in this catalytic surface the hydride ion reduces the cupric ion to metallic copper:

$$Cu^{2+} + 2\ H^- \rightarrow Cu^0 + H_2$$

$$\text{Or} \quad 2\ Cu^{2+} + 2\ H^- \rightarrow [2\ Cu^{2+} + H_2] \rightarrow Cu^0 + Cu^{2+} + H_2$$

The rate of the mentioned cathodic partial reaction (Eq.1) is proportional to the Cu^{2+} concentration and the rate of the anodic partial reaction (Eq.2) is proportional to the HCHO concentration and to the OH^- concentration.

So the plating rate (or deposition rate) for producing copper layers of good quality depends on the concentration of these bath constituents.

On the other hand, in the Eq.3, free formaldehyde must be maintained at low concentration in order to suppress the tendency for other reaction to take place:

$$2\ Cu^{2+} + 5\ OH^- + HCHO \rightarrow Cu_2O + HCOO^- + 3\ H_2O$$

$$Cu_2O + HCHO + OH^- \rightarrow 2\,Cu^0 + HCOO^- + H_2O$$

The function of the stabilizer is to prevent reaction of Eq.3 from depositing copper within the solution or on surfaces that are not activated.

In the research carried out by Julve (2001), Glycine is used as a stabilizer. Glycine reacts with formaldehyde to form a condensation product:

$$NH_2\,CH_2\,COOH + HCHO \Leftrightarrow H_2C = NCH_2COOH + H_2O$$

And due to the equilibrium of this reversible reaction the free formaldehyde is maintained at low concentration. So, the concentration of stabiliser also affects the plating rate and must be controlled.

Electroless plating has a deposition rate of between 1 to 3 μm/hr; ~ 40 to 120μ-in./hr (Eveleth and Mayer 1985) (Oita, Matsuoka et al. 1997). Furthermore, electroless plating requires rigorous control because of transient bath changes, and the deposit mechanical properties are highly process-dependant (Li and Kohl 2004).

NB: All details of process chemical reactions are quoted from Julve (2001)

6.2.1.1 Electroless Copper Bath Maintenance

Bath Chemistry

Though it is difficult to predict the life of an electroless copper solution, the rise in specific gravity is an indication of when the solution is spent. When the specific gravity reaches 1.12 - 1.14 at 24°C (75°F), a decrease in bath performance can be expected. At this point, the bath should be diluted by 50% or changed entirely (Electrochemical Inc 2006).

In addition the electroless copper solution requires a variety of controls, all directed toward maintaining steady-state performance in terms of plating rate, deposit physical properties and bath stability (both during operation and in storage). First and foremost, the principal chemical parameters (copper, formaldehyde and caustic content) must be kept within specification. Normally, by following replenishment and bail-out instructions with respect to these primary components, all other bath chemical components will remain within the recommended ranges; however chelate and stabilizer levels will occasionally need independent control (Deckert 1995).

Temperature

Other than the chemistry, temperature is the most critical operating parameter – too low and the plating will be shut off; too high may cause excessive plating rate and instability. Other key parameters include specific gravity, air agitation, filtration, circulation, panel loading, and others (Deckert 1995).

Wells (1969) suggests, but does not restrict the temperature of the electroless copper bath should be run at 75°F. Goosey, Graves et al. (1999) states electroless plating may be conducted at elected temperatures from about 40 to 50°C. Shirota and Okada (1997) suggests between 20 to 70°C.

Deckert (1993) suggests that the type of plating 'build' dictates the operating temperature of the bath. A low build of one half (or less) μm can be achieved in 20 minutes and is typically operated at ambient temperature. A high (heavy) build of two to three μm in about 20 minutes typically operates at elevated temperatures of 35 to 55°C, but room temperature formulations are available. A full build of 25 μm or more are typically run at 55 to 80°C.

A study by Hanna, Hamid et al. (2003) on the controlling factors affecting the stability and rate of electroless copper plating found that for an electroless copper solution with an EDTA complexing agent such as that used in this project, the deposition rate increases with the increase of bath temperature up to 50°C. Above 50°C the bath remains stable to 70°C, but between 50°C and 70°C the deposition decreases slightly (see Figure 6.2-1).

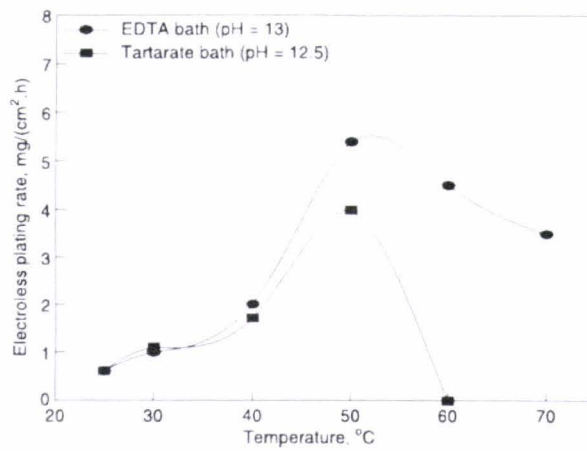


Figure 4-15: Effect of temperature on plating rate (Hanna, Hamid et al. 2003)

Deckert (1993) also notes that although these are the typical temperatures, it is possible to formulate the solutions so that they can be run at room temperature. If it is possible to

run a bath at room temperature it removes the need to heat the solutions, which adds both time and cost to production.

Mr Bendary agreed on the benefits of raised temperatures to increase production rates in a commercial setting, however notes that for research purposes or small scale operations room temperature solutions pose advantages such as better variable control and cost savings.

pH

Copper deposition is thermodynamically more favourable in alkaline solutions (Bindra and White 1990). Shirota and Okada (1997) suggest the electroless plating solution have a pH of 10 to 14. Mr Bendary suggested pH levels between 12.5 and 13 are common, but that he had found a range of 12.5 to 13 was most optimum.

Hanna, Hamid et al. (2003) carried out a study that suggested deposition rate increases markedly with the increase of pH value up to 13.0 for electroless copper baths with EDTA complexing agent. Above this value, the rates of electroless plating decrease. Electroless copper baths are characterised by a plating rate that firstly increases and passes through a peak then begins to decrease as a function of pH (see Figure 6.2-2).

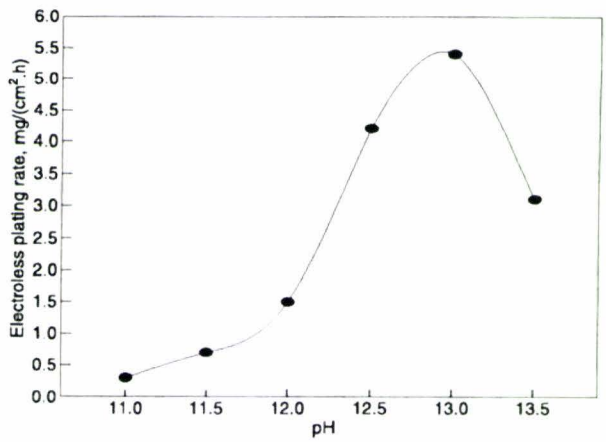


Figure 4-16: Effect of pH values on deposition rate (Hanna, Hamid et al.2003)

In any case it would appear that the optimum pH of any electroless copper solution is dependant upon its individual make-up. The pH can be altered accordingly by the addition of hydroxyl ions often in the form of NaOH solution.

Agitation

A number of experts including Deckert (1993), Mandich and Krulik (1993) and Bindra and White (1990) outline the need for agitation to aid stability in electroless copper solutions which results in a more even copper deposition. However, Mr Bendary

suggested agitation was not necessary for successful electroless copper plating. It appears once again that the need for agitation during electroless copper deposition depends on the unique solution being used.

6.2.2 Electroless Nickel Plating

During this project electroless copper plating was considered the preferred technology. However, limited research was also made into the mechanisms of nickel electroless plating.

There is a large family of EN coatings, typically defined by their alloy. The most common form of Electroless nickel plating produces a nickel phosphorus alloy coating. Nickel deposition by hypophosphite is usually represented by the following reactions (Barnstead and Morcos, 2007):

$NiSO_4 + H_2O \rightarrow Ni^2 + SO_4{}^2 - + H_2O$
$NaH_2PO_2 + H_2O \rightarrow Na+ + H_2PO_2 - + H_2O$
$Ni^2 + + H_2PO_2 - + H_2O \rightarrow Ni^0 + H_2PO_3 - + 2H+$
$H_2PO_2 - + H_2O$ (CATALYST)$\rightarrow H_2PO_3 - + H_2$

Typically, an electroless nickel plating bath consists of a source of soluble nickel ions, a reducing agent, complexors, neutralizers/buffers, stabilizers, and (in some systems) brighteners (Barnstead and Morcos, 2007).

There is one major disadvantage of the electroless nickel plating bath, and that is, it does not work with the silver activator, only the palladium activator. This is because silver is not catalytic to the electroless nickel because it uses sodium hypophosphite as a reducing agent.

6.3 THE ELECTROLESS PLATING PROCESS SUMMARY

Following activation the part is rinsed in distilled water to protect the catalyst sites and remove excess activation solution from the part. The part is then immersed in the electroless plating solution until the part is sufficiently plated with electroless copper or nickel. The part is then rinsed in water to remove excess electroless plating solution prior to the electroplating step.

6.4 ELECTROLESS PLATING PROCESS DEVELOPMENT STRATEGY

The flow diagram below summarises the stages of the activation development strategy:

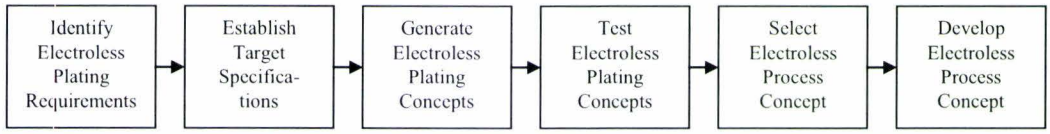


Figure 4-17: Electroless-plating process development strategy flow diagram

6.5 ELECTROLESS PLATING REQUIREMENTS

The most important requirement was that the solution successfully applies an electroless metal coating which enables a quality electroplated coating to be applied. The aforementioned plating quality specifications were also used to assess plating quality. In addition, the electroless plating process was required to be cost effective, stable, timely and meet environmental requirements. Table 6.5-1 below outlines the electroless plating marginal and target specifications.

Table 6.5-1: Electroless plating target specifications matrix

Electroless plating target specifications					
Metric No.	Metric	Imp.	Unit	Marginal Value	Target Value
1	Electroless Plated Successfully	5	Binary	4	5
2	Time to plate	5	Minute	<20	<15
3	Cost of Solution	5	$NZD	<$30	<$25
4	Stability of Solution	3	Subj.	3	4
5	Environmental Issues	3	Subj.	3	4
6	Plating Quality:				
a	Bend test	5	Subj	4	5
b	Sharp object resistance	4	Subj	4	5
c	Texture test	4	Subj	4	5
d	Shine test	5	Subj	4	5

NB: The 'Cost of solution' values are conservative as they are based on the cost in a pilot plant where a maximum 27 helmets are produced per 8-hour day.

6.6 HYPOTHESIS GENERATRION

The review of relevant literature and expert advice led to the identification of two common electroless plating processes used throughout the world to plate plastics. This section outlines how each solution was made up in the laboratory, and used to plate samples as follows:

1. Electroless copper plating on silver activated surface.
2. Electroless nickel plating on palladium activated surface.

6.7 HYPOTHESIS TESTING

Following the outcome of the etching and activation refinement process the electroless plating concepts were tested using material X (unmodified UP resin) and the painted UP resin materials with etching concept C. The electroless Copper plating concept was tested using the silver activator described in section 5.8.1 and the electroless Nickel plating concept was tested using the palladium activator also described in section 5.8.2.

Table 6.7-1 illustrates the sequence of the individual process step concepts used to test the activation concepts. All variables remained constant except the activation concepts.

Table 6.7-1: Process concept matrix for Electroless plating hypothesis testing

Process concept matrix																								
	Concepts																							
Material	X						Y						Z						PAINTED					
Etching solution	A		B		C		A		B		C		A		B		C		A		B		C	
Activation	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd
Electroless plating	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni
Electroloplating	Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu	

6.7.1 Concept 1 - Electroless Copper Plating Process

As with the activation solution, the method of making up the electroless copper plating solution was very precise, and required expert knowledge to be completed successfully. The development of this solution took several attempts to create a bath that was not too active or under-active, by iteratively decreasing the reducing agent and NaOH, and increasing the complexing agent and stabilizer. This is described in more detail later in the chapter. The perfected electroless copper solution was made up as follows:

1. Pour approximately 800mL of water into a 1L beaker
2. Adds 5gm copper sulphate (metal source), stir to dissolve (may require heat).
3. Add approximately 3-5mL tri-ethanol-amine (T.E.A.) (stabilizer) and stir until the solution turns a dark blue colour, commonly referred to throughout the project as 'to taste' (see Figure 6.7-1).
4. Add 80gm EDTA (ethylene-diamine-tetra-acetic) (complexing agent), which will turn the solution cloudy. Then stir to dissolve, and cloudiness disappears.
5. Dissolve 40gm of NaOH in 100mL of water.
6. Add NaOH solution to copper solution. The solution is now a darker teal blue (see Figure 6.7-2)
7. At the last minute before plating Add 4mL of formaldehyde (reducing agent). This will cause the copper to reduce onto the activated surface.

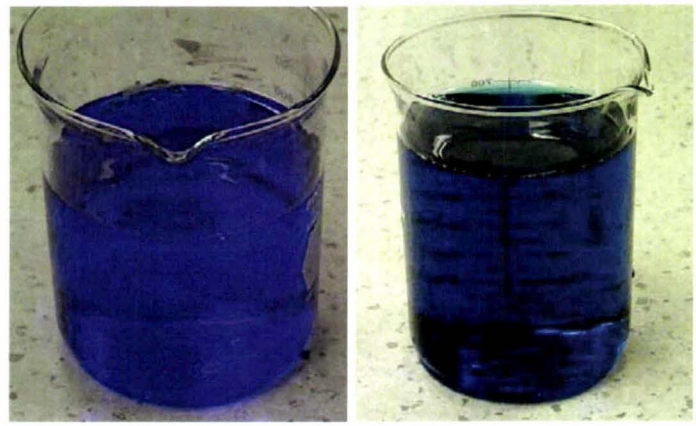


Figure 4-18: Colour of the electroless copper solution at step 3 upon the correct amount of TEA being added 'to taste' to the CuSO4 solution.

Figure 4-19: Colour of solution at step 6 after NaOH has been added.

In order to plate the part, it is simply immersed in the electroless solution, and the copper is plated onto the activated surface through a reduction reaction. It is beneficial to continually agitate the part in the solution to encourage even plating, increase plating deposition and decrease faults. The plating deposition rate depends on many variables including:

- The size of the part relative to the size of the solution.
- How active the solution is.
- Bath temperature and concentration.

The part can be removed from the electroless-plating bath when the copper coating is thick enough to be plated on with acidic copper electroplating. During this project sufficient plating thickness was estimated by analysing the colour change of the part. Figure 6.7-3 illustrates the colour the part should be when electroless plating is adequate. However in a production situation, the copper thickness can be calculated through working out the deposition rate and the plating time, or through weight calculations.

The result of the electroless copper plating concept was that both samples were plated with a very high quality electroless copper coating, followed by successful acidic copper coating. The resulting plating was rated 5 out of 5 for plating quality in all tests.

Figure 6.7-3: Colour of copper sufficiently coated copper part

6.7.2 Concept 2 - Electroless Nickel Plating Process

An alternative to plating plastics with electroless copper is to plate with electroless nickel. This plating technique uses a similar method to that of electroless copper with some differences outlined below.

To make the solution the following chemicals were mixed into approximately 800mL water over heat:

- 20gm/L Nickel sulphate
- 80gm/L Sodium citrate
- 20gm/L Sodium hypophosphite
- 18gm/L Ammonium chloride

At this stage the solution is green.

- Add ammonium hydroxide until the solution turns blue (approximately 100mL/L).

The full electroplating process was carried out using the same method as the electroless copper concept except for the Palladium activator. The results were identical to the plating achieved with the electroless copper plating solution, that is, the samples were plated with a very high quality electroless copper coating, followed by successful acidic copper coating. The resulting plating was rated 5 out of 5 for plating quality for all tests.

6.8 SELECTION OF ELECTROLESS PLATING CONCEPT

This section discusses how concepts 1 and 2 performed under the specifications that were not based on plating quality. Both concepts are then rated on how well they meet all target specifications in a selection matrix. Table 6.8-1 outlines how the electroless plating concepts faired against the specifications.

Table 6.8-1: Electroless plating target specifications matrix

Electroless plating target specifications							
Metric No.	Metric	Imp.	Unit	Marginal Value	Target Value	Nickel activator	Copper activator
1	Electroless Plated Successfully	5	Binary	4	5	5	5
2	Time to plate	5	Minute	<20	<15	15	15
3	Cost of Solution	5	$NZD	<$30	<$25	$38.83	$22.42
4	Stability of Solution	3	Subj.	3	4	4	4
5	Environmental Issues	3	Subj.	3	4	3	3
6	Plating Quality:						
a	Bend test	5	Subj	4	5	5	5
b	Sharp object resistance	4	Subj	4	5	5	5
c	Texture test	4	Subj	4	5	5	5
d	Shine test	5	Subj	4	5	5	5

Time to plate

Both solutions (concepts 1 and 2) plated the samples within 15 minutes, thereby meeting the target specification.

Cost

The electroless plating solution, although not the most expensive by volume, it is the most expensive solution to maintain. This is because it is exhausted quickly during use, and must be replenished more frequently than any other solution. Therefore the cost of maintaining the solution is an important variable in the selection process. Pricing information was gained from Merck Ltd (chemical supplies) in order to compare the cost of each solution. The pricing information was only available for smaller quantities. It is therefore expected that the cost per solution when ordering in bulk for a production situation will be heavily decreased. However these values can be used as a comparative measure. It was found that in a pilot plant situation, the cost of electroless plating per helmet was as follows:

Table 6.8-2: Cost analysis of electroless plating concepts

Electroless Plating cost analysis	
	Cost/helmet
Concept 1: Electroless Nickel	
Electroless nickel solution	$36.27
Palladium activator solution	$ 2.54
	$38.83
Concept 2: Electroless Copper	
Electroless copper solution	$22.42
Silver activation solution	$ 0.12
	$22.54

Stability of Solution

The solutions were equally stable, and both met the target specification of 4 out of 5. It was noted that the electroless copper solution had a higher pH of between 12 to 13, compared to the nickel solutions ph of 9, this does not alter the selection process.

Environmental Issues

Again, both solutions fared very equally in this specification.

Despite the advantages of knowing an alternative method of plating UP resin with electroless nickel, there are obvious disadvantages of the nickel-plating that render the electroless copper a more desirable method. The major deterrence is the increased cost of the solution, and its inability to be plated onto the favoured silver activator. An additional disadvantage is the use of sodium hypophosphite, a chemical, which is not only expensive but also difficult to obtain.

Therefore the electroless copper solution was selected to go through to the development phase of the project. Table 6.8-3 illustrates the refined process sequence that would go forward into the refinement of the electroless plating process.

Table 6.8-3: Process concept matrix for Electroless plating refinement

Process concept matrix																								
	Concepts																							
Material	X						Y						Z						PAINTED					
Etching solution	A		B		C		A		B		C		A		B		C		A		B		C	
Activation	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd
Electroless plating	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni
Electroloplating	Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu	

6.9 FURTHER REFINEMENT OF THE ELECTROLESS PLATING PROCESS

The complex chemistry of the electroless plating process required more refinement than the preceding steps. This section outlines the development of the electroless copper plating process with the aim of optimising the deposition rate and deposit properties.

Deposition Rate

The rate at which the plating solution deposits electroless copper is an important variable. It is desired that the deposition rate be such that the surface of the part is plated in between 10 to 15 minutes. A slow deposition rate will result in wasted time, especially in a production situation. In addition, a very slow deposition rate (barely active solution) can result the failure of the reduction reaction altogether.

On the other hand a fast deposition rate can be equally disruptive to the plating process. If the deposition rate is too fast, it means that the solution is too active. This results in the copper crystals being deposited too randomly, resulting in an uneven distribution of the electroless copper layer, that does not produce a conductive surface, and thereby cannot be subsequently electroplated.

Deposition Properties

Deposition properties refer to the shape, size and distribution of the copper crystals that form the electroless copper plated layer. The aim is to achieve short, flat shaped crystals that are small in size and distributed evenly across the material so that it is completely covered.

If the crystals are large and cone shaped instead of flat then the cover is random and unevenly distributed. This results in a non-conductive surface that will not be able to be subsequently electroplated.

The following variables were identified throughout the review of the literature as having effects on deposition rate and deposition properties:

- Composition (solution make-up)
- pH
- Temperature
- Agitation
- Contamination

The complex chemistry of the electroless copper plating solution meant that a change in any variable in the solution might dramatically alter the solutions ability to work properly. A deeper understanding of the mechanisms of electroless copper plating is outlined in Chapter 3.

pH

During this project, a digital pH meter was used to measure the pH of the various electroless copper solutions throughout the plating trials. The quantity of NaOH added to the solution was changed accordingly to maintain a pH between 12.5 and 13.0. It was found that 40g/l NaOH gave a pH of 12.5. This development is described in more detailed later in the chapter.

Temperature

In this project, the electroless copper baths were run at room temperature of 25°C. This decision was based on advice from Mr Bendary who advised that while in a commercial situation, a raised temperature was preferred for increased production rates. However, in a laboratory situation, a room temperature solution is sufficient.

An additional advantage was that the laboratory room temperature was at a relatively constant temperature of 23°C (±1°C). Therefore it was easy to maintain a constant temperature throughout experimentation.

It was important, however to ensure the temperature of the solution was within this range, as other factors affected temperature, such as the time between making up the solution and using it. That is because the NaOH dissolution is exothermic, that is, when the NaOH is dissolved in water, the solution becomes hot. To ensure the electroless copper plating solution is at the constant 23°C (±1°C) the NaOH solution (or the electroless copper plating solution containing the NaOH solution) must be allowed to come down to 23°C (±1°C) before plating is started.

Unless otherwise stated, the electroless copper plating solution temperature was measure during experimentation, and was at the stated temperature of 23°C (±1°C).

Agitation

The most common stabilizer for electroless copper baths is a steady stream of air bubbled through the solution (Innes, Grunwald et al. 1969). Mild air agitation increases the bath stability 20 times over baths without aeration (Hanna, Hamid et al. 2003). Therefore aeration also aids in increasing the bath life.

In this project it became quickly clear that samples plated without agitation in the electroless copper plating solution were of lower quality. In many cases, the electroless coating was very poor, resulting in the following acidic copper plating being patchy and spidery. It was also found that without air agitation the baths expired more quickly.

For the majority of the experimental work, agitation was created mechanically. That is, the part was dipped into the solution on a piece of string and jiggled up and down by hand. Although this method did not allow for the amount of agitation to be quantitatively measured, efforts were made to maintain a constant and consistent mechanical agitation of the part. Although this mechanical agitation did not increase the stability of the solution as much as air agitation, it did improve the quality of the electroless plating by increasing the dispersion of copper crystals on the surface, resulting much smoother acidic plating.

Later in the project, an air-agitation system was constructed using the Massey University laboratory air supply, and attaching plastic tubing with 'fish tank' air dispersion stones at the end. This allowed the electroless copper solutions to be continuously air agitated at the same rate every time. This system allowed the air agitation to be increased and decreased as necessary (for varying sized solutions). This resulted in extended bath life, and more consistently high quality electroless plating.

Figures 6.9-1 and 6.9-2 illustrate the electroless copper structure of deposition with and without solution agitation. The deposition is much more even when agitated, resulting in a higher plating quality.

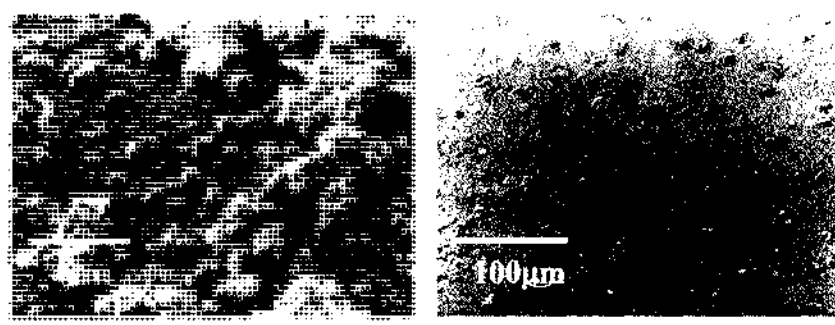


Figure 4-21: Electroless copper structure with no agitation

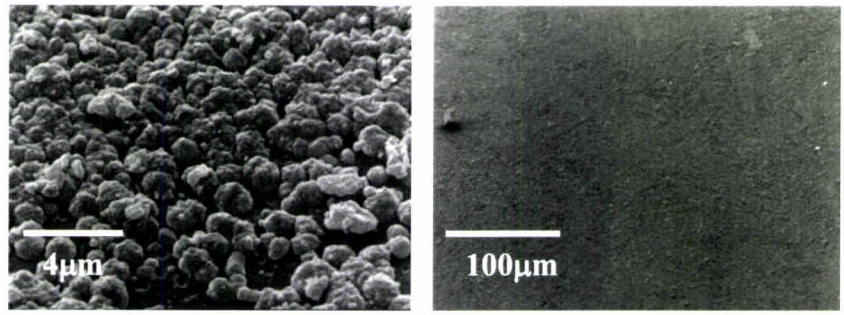


Figure 4-22: Electroless copper structure with air agitation

Contamination

Although contamination was not documented in the literature, it was found to be a variable that affected the process greatly. Any contamination of the solution has an effect on either the deposition rate and/or the deposition properties. That is because contamination may result in a change in the pH. Contamination was identified as a variable throughout the development of the electroless copper solution due to observations such as:

- Unusual colour of electroless copper solution, which appeared tainted.
- Bubbles in the solution indicating residual detergent in the beaker.

And usually resulted in:

- Unusual colour of resulting electroless copper plating.
- The resulting electroless copper plating having an inability to be electroplated with acidic copper due to uneven electroless copper dispersion.

In some cases, a seemingly contaminated electroless copper solution would result in an unusual coloured electroless copper plating that would have no difficulty in being successfully electroplated. This lead to the conclusion that contamination was a variable that was difficult to control. Although efforts could be made to reduce the risk of contamination, as a result of human error, it did occur on occasion. The results of contamination in each situation were dependant on the level of contamination, and therefore its affects on the pH of the solution.

Optimisation of solution constituent quantities

This section outlines the process of developing the electroless plating process by optimising these constituents.

Li and Kohl (2004) describe how in electroless plating, there is always a tug-of war between the deposition rate and bath stability. A stable bath is slow, but a higher rate bath can decompose at the drop of a hat. The deposition rate and deposit properties of electroless copper plating depend on the copper complexing agent, reducing agent, bath temperature and pH (Duffy, Pearson et al. 1983).

This part of the electroless copper solution development was carried out through trial and error. The first solution was that recommended by Mr Bendary. Table 6.9-1 shows four test solutions were composed, followed by descriptions of how each solution was further developed until the optimum chemical quantities were identified.

Table 6.9-1: Solutions 1-4 chemical composition and outcome of analysis.

	Chemical make-up					Outcome	
Soln. No.	$CuSO_4$ (g)	TEA (ml)	EDTA (g)	NaOH (g)	Formaldehyde (ml)	Solution Activity	Soln. pH
1	5	To dark blue	40	80	10	Over-active	13.0
2	5	To dark blue	80	80	7	Over-active	12.9
3	5	To dark blue	80	40	5	Over-active	12.6
4	5	To dark blue	80	40	4	Correct activation	12.5

Solution 1 was found to be highly over-active. Therefore the deposition speed was too high. To reduce the activeness of the solution, we must reduce the amount of sodium hydroxide and formaldehyde.

Solution 2 was still found to be fairly over-active. Instead of reducing the NaOH quantity further, another was of decreasing activity of the solution is by increasing the EDTA quantity to counteract the NaOH. Decreasing the formaldehyde further would also decrease the activity.

Solution 3 was found to be slightly over-active, which was considered easily to solve by further reducing the formaldehyde quantity to 4ml/l.

Solution 4 was not over-active or under-active, and was selected as the optimum electroless copper solution make-up.

For some time it appeared that the method of measuring TEA by colour change worked well. However, this was not the case, as more experimentation discovered that human error was resulting in some solutions not producing plating of a high enough quality. The next step was to optimise the TEA quantity.

6.9.1 Optimisation of T.E.A. in electroless copper plating solution

One of the major problems with the electroless copper plating solution was that the TEA quantity was subjective, and therefore inconsistent. TEA was measure out by 'colour change' to the solution, instead of by quantity. This left a lot of room for error, and through literature review and experimentation it was found to dramatically affect the plating quality. A particular point of difference identified between the initial TEA quantity

stated at the beginning of the chapter was that 3-5ml was a very conservative measure, and in order to achieve the desired blue colour, a larger quantity of 10ml or more was generally required. This may have been due to small differences in the chemicals used in the Massey University laboratories than those used in a production situation. It was necessary to define the optimum TEA quantity for the best electroless plating solution.

TEA is a complexing agent and is therefore used to control the deposition rate of the solution. Varied TEA quantities were tested on samples of Acrylathane painted helmet shells in order to analyse what difference to the plating occurred. An Acrylathane painted sample was etched with etching solution C and activated with the silver activator before being plated with electroless copper. Except for the varied TEA levels, the existing process was used to plate the samples throughout this section.

TEA quantity trial 1

The hypothesis was that TEA quantities of 5, 10 and 15 ml would affect the electroless copper solution, and thus the electroless plating process. Two painted UP resin samples were used in each electroless copper solution, one of which continued through to be acid coppered, only to electroless plating as to be analysed using electron microscopy.

As outlined earlier in the chapter, the shade of the blue colour of the solution becomes deeper as more TEA is added. Therefore it was expected that the 5, 10 and 15ml 'TEA' solutions would go from lightest to darkest successively. The 5ml TEA solution was the lightest. However the 10ml TEA solution was far darker than the 15ml TEA solution. It was also a noticeably duller shade of blue than the other solutions (Figure 6.9-3).

Figure 4-23: Illustration of how TEA levels affect the colour of the electroless copper solution: from left to right 5, 10 and 15 ml TEA solutions

Contamination was considered the most likely cause of the colour difference, and may have been caused through the use of dirty equipment. At this stage the effect of such contamination was unknown.

During electroless deposition, the following observations were made:

- Effervescence increased in the 5ml, 10ml and 15ml solutions successively.
- However plating occurred fastest in the 10ml solution and was completed in approximately 25 minutes, coated with a very bright coloured copper.
- The 15ml solution took 45 minutes and was a light copper colour.
- The 5ml solution was the slowest and was a dull copper colour.

The samples that were acid coppered came out as follows:

- The 5ml TEA sample coppered slowly but well in 30 minutes.
- The 10ml TEA sample coppered badly, with minimal and spidery.
- The 15ml sample coppered quickly and well in only 5 minutes.

Unfortunately, although the appearance is one method of estimating if a good thickness of electroless copper has been applied to the surface of the part, it is not necessarily a measure of the quality of that coating. The best method of measuring the quality of the electroless copper coating is by attempting to electroplate the surface with acidic copper. A quality electroless plating will result in a quality acidic copper electroplated layer that is plated quickly and smoothly.

In this example, all three samples appeared to be electroless plated (see Figure 6.9-4), and it was assumed they would all be successfully electroplated with acidic copper. However, the results were that only the samples with 5 and 15ml TEA were successfully electroplated, while the 10ml TEA solution failed (see Figure 6.9-5). This was attributed to the 'contamination' of the 10ml TEA solution. The assumption that the 10ml TEA solution was contaminated meant that a trend between TEA quantity and electroless plating quality was difficult to identify.

Figure 4-24: Left: Electroless Coppered samples (5, 10, 15ml TEA solutions)
Figure 4-25: Acid copper plated samples (5, 10, 15 ml TEA solutions)

The copper crystal structures of the electroless coatings were analysed using SEM (See Figures 6.9-6, 6.9-7, 6.9-8)

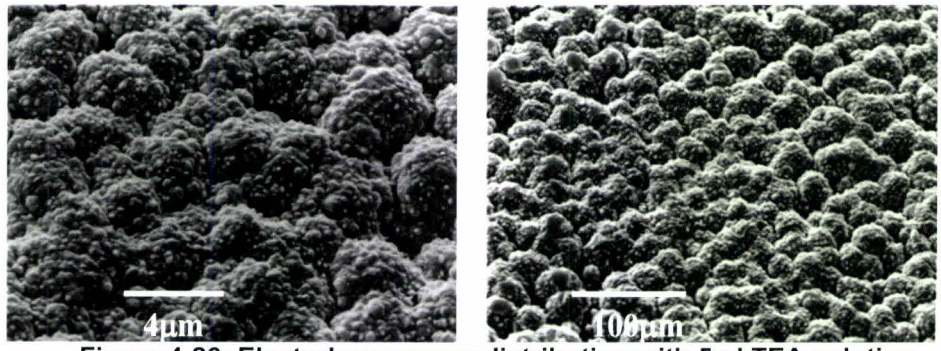


Figure 4-26: Electroless copper distribution with 5ml TEA solution

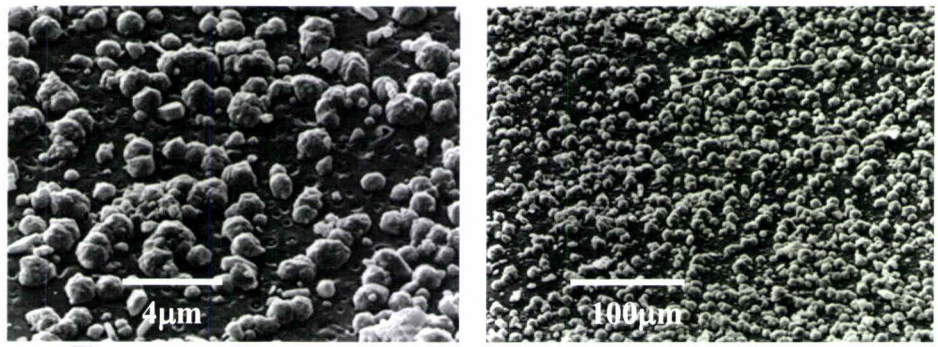


Figure 4-27: Electroless copper distribution with 10ml TEA solution

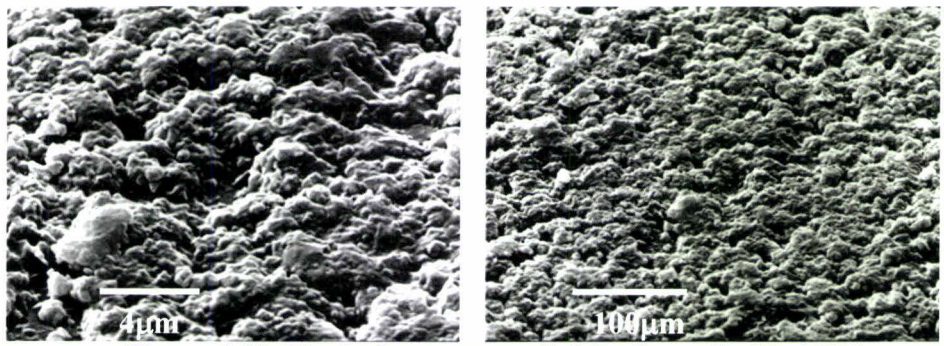


Figure 4-28: Electroless copper distribution with 15ml TEA

These photographs show that the 10ml TEA sample had unevenly distributed electroless copper crystals. The crystals were sparsely spread with gaps between them, and a different shape to the other samples crystals. In comparison, the 5ml and 15ml samples are evenly covered with copper crystals, and hence would provide the completely conductive layer required for acidic copper electroplating to take place. Hence, the electroplating circuit for the 10ml sample would have been incomplete due to the gaps in the electroless copper coating, resulting in failure to electroplate with acidic copper.

It was concluded that not only the quantity of TEA in the electroless copper solution affected the plating success, but also variables such as contamination of the electroless copper solution should be considered. TEA quantity and contamination are both factors that affect the pH of the solution, which in turn greatly affects the solutions plating ability.

A second experiment similar to trial one was carried out repeating the TEA quantities to identify trends in the electroless copper solution, and identify the optimum TEA quantity.

TEA quantity trial two

There trials were identical to trial one with the addition of an electroless copper solution with 20ml TEA. This was in order to confirm the result of trial one while increasing the range of TEA quantities. The 5, 10, 15 and 20ml TEA solutions were made up as precisely as possible to avoid contamination or inconsistencies.

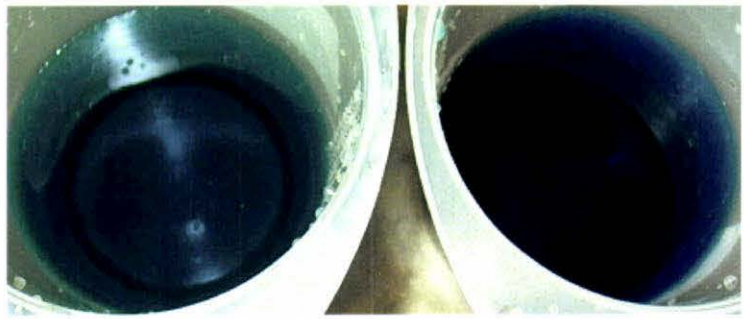


Figure 4-29: Colour difference between 5ml and 20ml TEA solutions

The above diagram illustrates the colour difference between the 5ml TEA and the 20ml TEA solutions. The 20ml solution is noticeably darker blue. It should be noted at this time that the 5ml TEA solution would have been considered too light in previous experiments, and more TEA would have been added until the colour of the solution was similar to that of the 20ml TEA solution. This experiment will identify if it is indeed too small a quantity of TEA, or if it is sufficient.

Each sample was run through the same process of electroless plating as in part one. All the samples were plated for 20 minutes before being removed from the electroless solution having been plated with a satisfactory coating thickness. The result of the experiment was that all four samples were plated with a rough / grainy electroless copper coating (see Figure 6.9-10 and 6.9-11).

Figure 4-30 (top): Electroless plated samples (5, 10-, 15, 20ml TEA solution)

Figure 4-31 (bottom): Electroplated samples (5, 10, 15, 20ml TEA solutions)

The consistently grainy surfaces lead to that there is a problem with the electroless coppering which varying level of TEA does not alter. The SEM photograph below (Figure 6.9-12) illustrates why the surfaces were so grainy. The copper was being deposited onto the surface in unevenly distributed clumps.

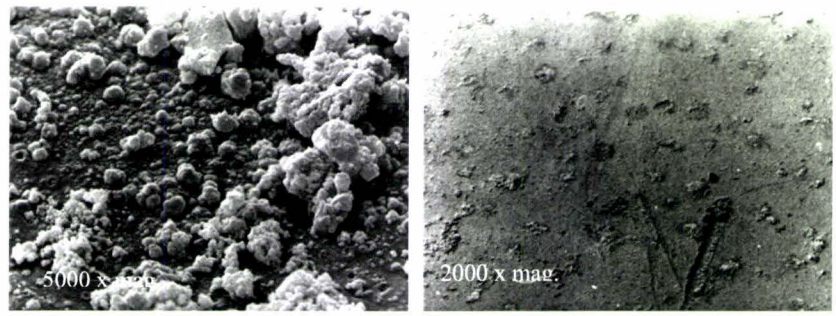


Figure 4-32: SEM photograph illustrating comparatively rough surface with clusters of electroless copper crystals

One possible reason for this outcome was that the solutions required agitation. It had been advised by Mr Bendary that agitation was not necessary for this electroless copper solution. However, some evidence supported otherwise. The next step of the electroless copper solution development was aimed at testing agitation of the solution, in the hope of either eliminating it as the problem causing the rough surface, or to identify it as the problem and change the process to incorporate it, thereby removing the problem.

6.9.2 Optimisation of Agitation

This part of the development aimed to identify if agitation of the solution through aeration was the problem causing a low quality of electroless copper plating. In order to create a constant and consistent method of agitating the electroless copper solutions using air, an air agitation system was constructed in the laboratory using the laboratories air supply, plastic tubing and 'fish tank' bubble rocks. These bubble rocks act to disperse the airflow from the hose throughout the solution. Apart from the addition of air agitation to the solutions, this experiment was identical to TEA quantity trial two.

In this experiment all the samples plated with electroless copper for 25 minutes, and plated easily and successfully with acid copper in 5 minutes (see Figure 6.9-13).

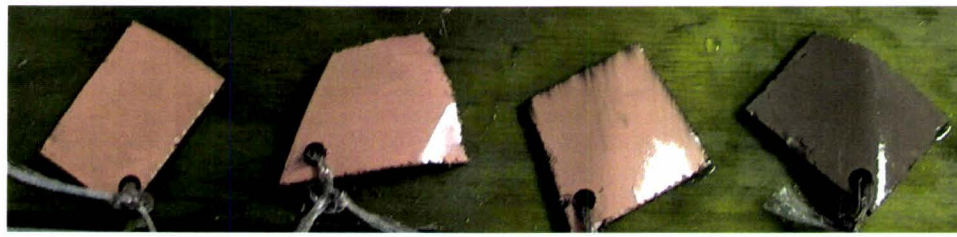


Figure 4-33: Electroless coppered samples from 5, 10, 15 and 20 ml TEA solutions consecutively. Notice colour of 4th sample is duller.

Despite the assumption that the contamination of the 20ml TEA solution would result in a failure to be electroplated with acidic copper, the experiment resulted in all four samples being very successfully electroplated (see Figure 6.9-14). These results were the best thus far, and were as a result of one variable – agitation.

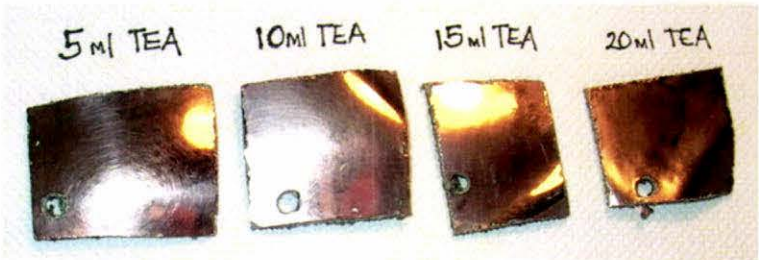


Figure 4-34: Electroplated samples from 5, 10, 15 and 20ml TEA solution.

All four samples were plated with a shiny metal coating, which performed extremely well in adhesion tests. The EDS (Figures 6.9-15, 6.9-16, 6.9-17, 6.9-18) results of the electroless coppered samples reflected why. All four samples were evenly distributed with small evenly sized copper crystals.

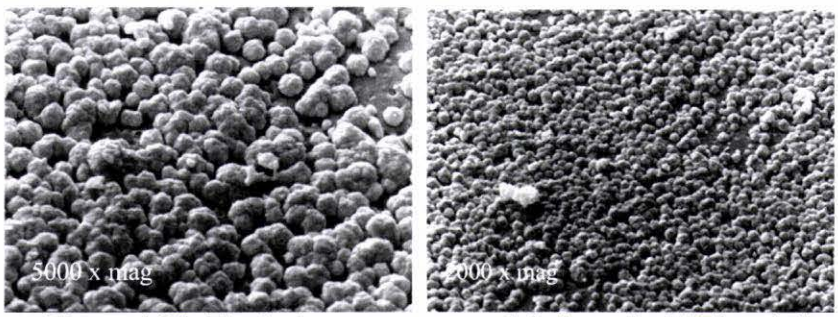


Figure 4-35: Electroless copper crystals from 5ml TEA solution

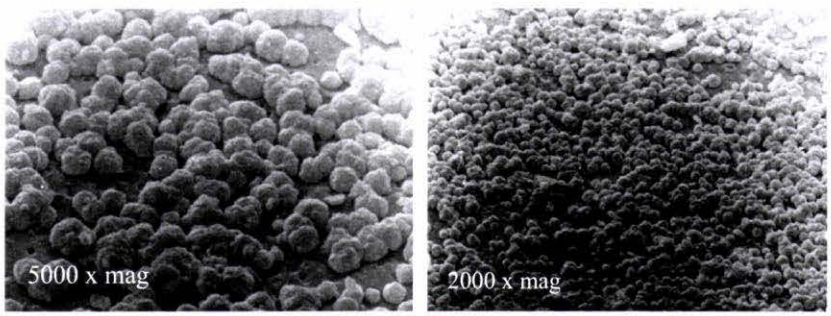


Figure 4-36: Electroless copper crystals from 10ml TEA solution

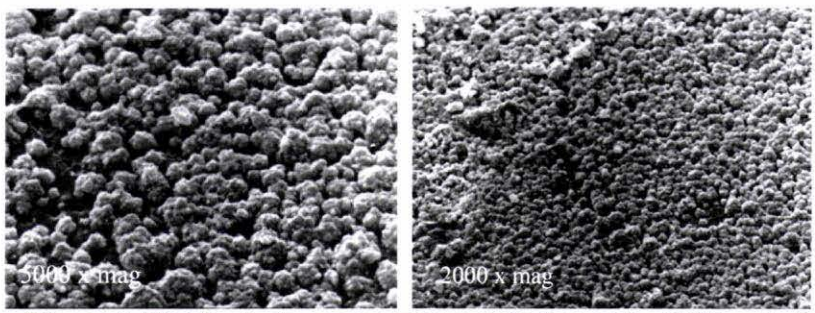


Figure 4-37: Electroless copper crystals from 15ml TEA solution

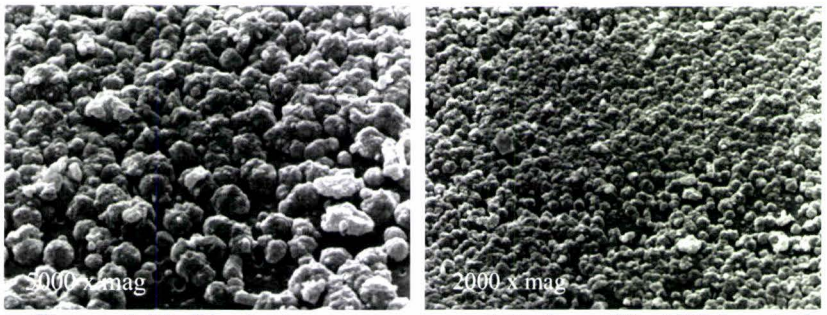


Figure 4-38: Electroless copper crystals from 20ml TEA solution

6.10 OUTCOME OF ELECTROLESS PLATING PROCESS DEVELOPMENT

The following major variables within the electroless copper plating conditions were identified as the problems causing failure of the process. They were identified, controlled and the problems eliminated:

- AGITATION
- TEMPERATURE
- PH
- Contamination
- Composition

It was found that these variables affected the deposition rate, which affects the shape and distribution of the copper crystals, which affects the plating quality, which affects the ability to conduct electricity, which affects the ability to acid copper plate.

The optimum electroless plating solution is outlined below:

- 5g/l $CuSO_4$
- 10ml/l TEA
- 80g/l EDTA
- 40g/l NaOH
- 4ml/l Formaldehyde

Bath conditions:

- Temperature 23°C (±1°C)
- pH 12.5 – 13.0
- Agitation mild air agitation (Important!!!)
- Plating time approx 15 mins (dependant on part to solution ratio)

Overall, the development of the electroless copper plating process was successful. The next aim of the project was to refine the acid copper electroplating process. Table 6.10-1

illustrates the refined process sequence that would go forward into the electroplating development phase following the selection of the copper electroless plating concept.

Table 6.10-1: Concept matrix following electroless plating concept selection

Process concept matrix																								
	Concepts																							
Material	X						Y						Z						PAINTED					
Etching solution	A		B		C		A		B		C		A		B		C		A		B		C	
Activation	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd
Electroless plating	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni
Electroplating	Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu	

7 ELECTROPLATING METHODOLOGY

7.1 INTRODCTION

Following electroless copper plating, the part can be electroplated with acidic copper using the 'acidic copper electroplating' process, which can be carried out on any conductive metal surface. It was therefore assumed that it was possible to electroplate on to the electroless plated UP resin achieved in this project. Following acidic copper electroplating, the conductive copper surface is both permanent and durable, and can be plated with Nickel using conventional Nickel electroplating techniques at any time.

7.2 BACKGROUND ON ELECTROPLATING

This chapter describes the construction, bath conditions and maintenance of the acidic copper electroplating bath used in the development of the 'plating on UP resin' process.

The electroplating of copper onto conductive surfaces is a very well developed science. Major international chemical manufacturing companies such as Atotech, Copper Plating Inc. and Technic Inc. are among a large number of companies in New Zealand who manufacture ready to use electroless plating solutions for the industry. There are a range of products depending on the plated finish required and operating conditions one wishes to operate within. Similarly each electroless copper solution is made from more than two components that are controlled according to strict user data sheets. In addition, each solution has a range of operating conditions set by the manufacturer.

In this project, Atotech's 'Cupracid 210' was used with operating conditions as follows: bath density of 1.17 g/cm^2 at 20°C, a pH less than 1, a preferred bath temperature of between 24 and 28°C and a deposition rate of 0.7 μm at 3 A/dm^2.

Therefore it was not necessary to develop a methodology of electroplating, and no development strategy was required for this section.

The hypothesis is that the Autotech solution will plate the electroless copper plated UP resin. Therefore the technical aim of this section is to optimise the copper plating bath running conditions.

7.3 OUTLINE OF COPPER ELEECTROPLATING PROCESS

Canning's describes Electro-deposition as "the application of metallic coatings to metallic or other conductive surfaces by electrochemical processes". Electroplating usually takes place in a "tank" of solution containing the metal to be deposited on an object. This metal is in a dissolved form called ions. An ion is an atom that has lost or gained one or more electrons and is thus electrically charged.

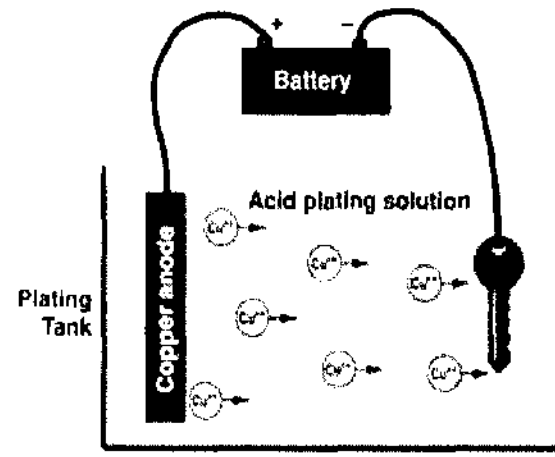


Figure 7-1: Typical Electroplating Bath (A.E.S.F.2004)

When certain metallic chemicals dissolve in water, the metal atoms of these chemicals are freed to move about, but lose one or more electrons (negative charges) and, as a result, are positively charged. The object to be plated is negatively charged and attracts the positive metal ions, which then coat the object to be plated and regain the lost electrons to become metal again.

7.4 HYPOTHESIS TESTING

7.4.1 Acid Copper Bath Equipment

Unlike the electroless copper bath, which required no current source to plate, the acidic copper bath required a current to run through the part for deposition to occur. Therefore the following equipment was required, and set up (see Figure 7.3-1):

- 10L plastic bucket (the tank)
- 20A rectifier (the D.C. source)
- Copper wiring and clips
- Copper Anode (100% copper sheet)

Figure 7-1: Acidic Copper Electroplating Bath

The plastic tank was lined with the copper sheet (anode). The anode is connected to the positive lead of the rectifier (D.C. source), while the red clip on the left is attached to the negative lead, which holds the part, (cathode) and completes the circuit once it is immersed in the solution

7.4.2 The Acidic Copper Solution

The solution was made by dissolving each of the following ingredients in tap water, one at a time, in the order presented below (as described in the technical datasheet):

- 200gm/L copper sulphate
- 25mL/L sulphuric acid (concentrated)
- 10mL/L acidic copper brightener make-up solution
- 0.5mL/L acidic copper brightener part A
- 0.5mL/L acidic copper brightener part B

7.4.3 Current Density

Output voltage and current depend on the surface area of the sample and the rate of deposition you wish to achieve. Commercial acidic copper plating solutions come with technical data sheets that tell the user what the optimum current density is for the solution. Current density (c.d.) is how many Amps/Dm^2. The surface area of the piece is used to calculate the c.d. (A/dm^2). The c.d. and coating thickness in μm is then used to calculate the plating time.

In the laboratory experiments the current density 'optimum range' was 0.5 to 2.5 A/ Dm^2. Therefore for every $1Dm^2$, a current of 0.5 to 2.5A must be applied. As we increase current density, we increase deposition rate. If the c.d. is too high then the metal finish will be poor due to the copper atoms forming on the surface randomly instead of ordered, resulting in bad adhesion. If the current density is to low then the plating takes too long and is not suitable or efficient for production purposes.

7.4.4 Electroplating Methodology

The processes for etching, activating and electroless plating the material samples were carried out as outlined in the previous chapters (using the selected concepts for each process). Following this the sample was 'wired' (wrapped in copper wire (see Figure 7.3-3) to promote even deposition of copper. The wire was then clipped onto the positive lead (cathode). The output voltage of the rectifier was adjusted according to the surface area of the part, and the part immersed in the solution. Agitation of the part while being plated aided even deposition and prevented faults such as skip plate from occurring.

To agitate the bath in the laboratory situation something similar to a fish tank air bubble supply can be used. The more bubbles, the more agitation, the more agitation, and the brighter the metal finish. In these trials the solutions were agitated mechanically by stirring the part by hand. Without agitation, the current density may become too high on areas of the sample and result in 'burning'. This is where the copper becomes dark and shine is not good.

The part remained immersed in the solution until the copper coating was thick enough to maintain a quality adhesion and shiny copper appearance. Although the plating thickness can be calculated using Current Density equations, in this project visual indicators were used, most commonly the 'colour' and 'shine' of the coating indicated when the plated coating was sufficiently thick, and plating completed.

Figures 7.3-3 and 7.3-4 illustrate the appearance of a part that has been sufficiently plated with acidic copper. Once this part has been buffed and shone it is possible to see ones own reflection in the surface.

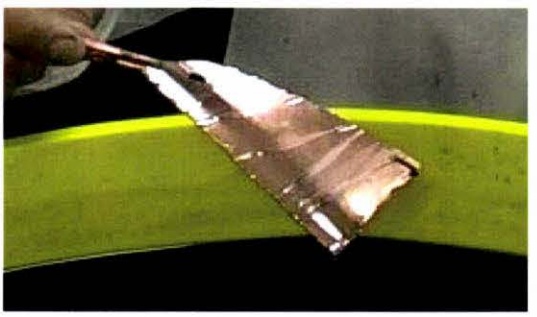


Figure 7-2: Acid Copper Plating bath with wired copper plated part.

Figure 7-3: Close-up of shine and colour of acid copper plated part.

7.5 OUTCOME OF ACIDIC COPPER ELECTROPLATING DEVELOPMENT

The overall outcome of the acidic copper electroplating process was that quality copper plated samples were produced. A number of trials were carried out to optimise current density. The quality of the adhesion and appearance of the acid copper coating is directly affected by all the preceding stages of the process. The quality of the plating in each experiment was analysed and tested as outlined in chapters 4, 5 and 6.

Table 7.5-1 outlines the results of the refined electroplating process against target specifications. The process was successful in meeting specification for all requirements.

Table 7.5-1: Electroplating specifications matrix

Electroplating target specifications						
Metric No.	Metric	Imp.	Unit	Marginal Value	Target Value	Acid Copper solution
1	Electroplated Successfully	5	Binary	4	5	5
2	Time to plate	5	Minute	<20	<15	15
3	Cost of Solution	5	$NZD	<$30	<$25	$16.01
4	Stability of Solution	3	Subj.	3	4	4
5	Environmental Issues	3	Subj.	3	4	4
6	Plating Quality:					
a	Bend test	5	Subj	4	5	5
b	Sharp object resistance	4	Subj	4	5	5
c	Texture test	4	Subj	4	5	5
d	Shine test	5	Subj	4	5	5

7.6 NICKEL ELECTROPLATING

Following successful acidic copper plating the UP resin samples can be plated using a conventional acidic nickel-plating methodology. It was important to ensure that the achieved acidic copper plating would a) withstand the conditions of nickel plating and b) would enable nickel plating to occur. For the purposes of this test, local electroplaters Manawatu Electroplaters were employed to plate the samples with nickel using their existing methodology. The outcome was that the samples were successfully plated with nickel illustrating that the development of a process for electroplating UP resin with nickel had been achieved. Figure 7.4 below demonstrates the nickel-plated UP resin sample.

Figure 7-4: Nickel-plated UP resin sample (small construction half helmet)

7.7 CONCLUSION

This chapter concludes the successful development of the 'electroplating UP resin' process. Table 7.6-1 illustrates the final selected sequence of the process steps that would progress too the scaled up pilot plant:

- Material concept selection: unmodified UP resin and painted UP resin
- Etching concept C: 250gm/L NaOH, 150ml/L TEA, 100ml/L E.Glycol, at 70°C
- Silver activation concept
- Copper electroless plating concept
- Acidic Copper electroplating concept (followed by conventional nickel plating)

Table 7.7-1: Process concept matrix of process selected for use in the pilot plant

Process concept matrix																								
	Concepts																							
Material	X						Y						Z						PAINTED					
Etching solution	A		B		C		A		B		C		A		B		C		A		B		C	
Activation	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd	Ag	Pd
Electroless plating	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni
Electroloplating	Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu		Acid Cu	

8 PILOT PLANT

8.1 INTRODUCTION

Following successfully plating small samples of UP resin in a laboratory it was necessary to scale up the operation to a pilot plant large enough to electroplate a whole PHNZ helmet shell.

The primary aim of constructing the pilot plant was to successfully plate a whole helmet shell. It was understood that the complex shape of the helmet shell would pose some challenges to electroplating. The secondary aim was to use the plated helmet shells to:

a) Test the quality of plating across the helmet shell
b) Construct a works-like prototype for use in regulatory product testing

It was also hoped that the pilot plant would be suitable for showing other industry experts how the process works. This was important if PHNZ were to form a relationship with an existing electroplating firm to carry out the plating of helmet shells for them.

This chapter outlines the construction of the pilot plant, methodology of trials used to plate helmet shells and the testing of the helmet shells and prototypes.

8.2 BACKGROUND

The convex shape of the helmet, with small indents (see Figure 8.2-1), makes the surface more difficult to plate than a flat object. While in the electroplating bath, the current prefers to go over curves as opposed to under and results in difficulty plating concave areas of the shell. This also affects the placement of the jig contact points (anodes), as positioning can increase its chances of overall plating.

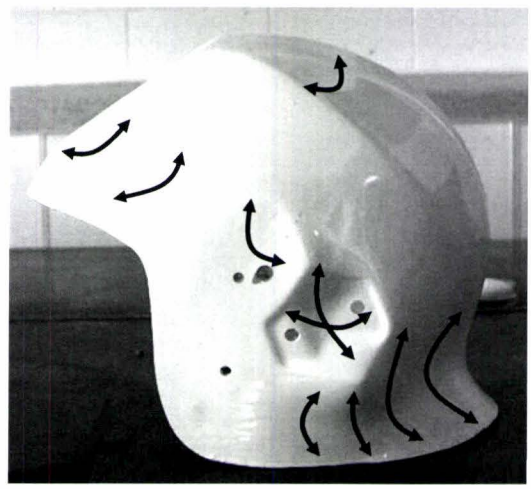


Figure 8-1: F7A helmet shell. Arrows indicate concave parts of the surface that are difficult to plate.

8.3 PILOT PLANT DEVELOPMENT STRATEGY

The pilot plant development strategy was an iterative process in which potential pilot plant methodologies and running conditions were attempted, and the resulting plated helmet shell then tested: a) plating quality and b) product testing to ensure it passes safety standards (see Figure 8.3-1). If either the product or consumer tests are failed, a return to the product development stage of the process may be required.

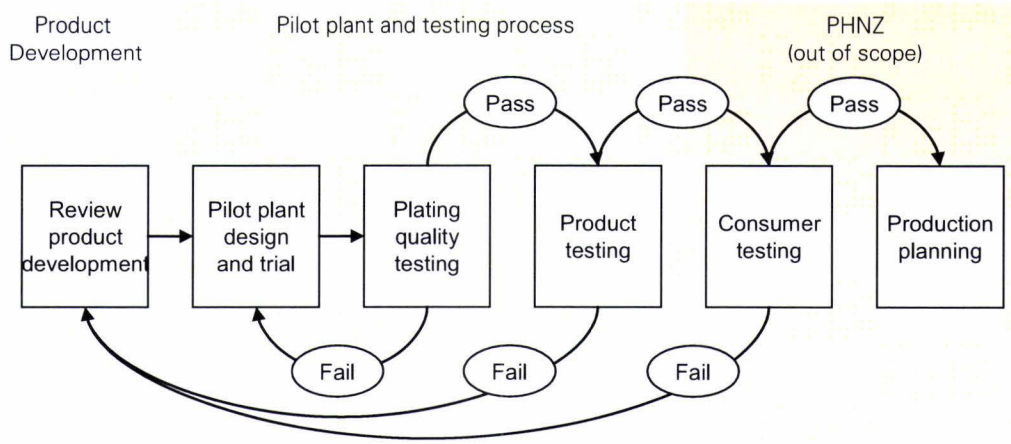


Figure 8-2: Pilot plant development strategy

Upon meeting the product test specifications, the prototype will be used by PHNZ to carry out consumer testing and production planning.

8.4 IDENTIFICATION OF PILOT PLANT REQUIREMENTS

In order to prove that the process could be used to plate the whole helmet shell it was only necessary to plate the shell with the acidic copper plating. The application of nickel-plating to acid copper is not new technology, and was considered a time consuming, high cost additional to the pilot plant. Therefore for the purposes of this pilot plant experiment, the nickel-plating step was not included.

8.4.1 Plating Quality Testing

In order for the plating to be sufficient to be used for product testing a quality coating that covered the majority of the helmet was required. Although a 100% coating was preferable, it was not necessary that the areas of the shell that are later covered with extrusions or accessories such as light clips be coated, but all areas visible to the consumer must be coated. Therefore the first test was a visual indicator, which identified plating coverage and quality.

Following this, the plating was tested using the quality measures outlined in chapters 4 through 7:

1. Bend test (adhesion)
2. Sharp object resistance
3. Texture test
4. Shine test

8.4.2 Product Testing

The second aim is that the plated helmet shell passes the product tests outlined in the BS EN 443: 1997 (British and European) standards including:

- Shock absorption
- Resistance to sharp objects
- Flame resistance
- Radiant heat resistance

In order to test how well the helmet shells met the European standards for this product, the helmet shells will be tested against existing 'non-plated' French fire fighting helmets in Pacific Helmets Ltd on-sight laboratory. Again, copper plated helmets were used in these tests on the grounds that application of the nickel-plating would only increase the helmets resistance to shock and sharp objects. For the flame test, a nickel-plated sample was tested. The BS EN 443 test methods are outlined in the Appendix.

8.5 ESTABLISHING TARGET SPECIFICATIONS

Table 8.5-1 outlines the marginal and target specifications for the plating quality tests and the product tests for the helmet shells plated in the pilot plant

Table 8.5-1: Pilot plant - plating and product target specifications matrix

Pilot plant plating target specifications				
Test / Metric	Imp.	Unit	Marginal Value	Target Value
Plating Testing				
% Of shell plated	5	%	95%	100%
Plating quality:				
Bend test	5	Subj.	4	5
Sharp object resistance	5	Subj.	4	5
Texture test	5	Subj.	4	5
Shine test	5	Subj.	4	5
Product Testing				
Shock absorption	5	Bin.	Pass	Pass
Sharp object resistance	5	Bin.	Pass	Pass
Flame resistance	5	Bin.	Pass	Pass
Heat resistance	5	Bin.	Pass	Pass

8.6 PILOT PLANT DESIGN AND CONSTRUCTION

8.6.1 Facility Requirements

A minimum floor space of 10 square meters was required with the following features:

- Ventilation - adequate for the use of strong alkaline and acid solutions.
- Washable floor – the plant should be set up on the ground floor. The flooring material should be resistant to strong alkaline and acid solutions, for example, concrete, and should be easily cleaned (hosed down).
- Power source – A number of 220V power sources are required to heat the solutions and run the rectifier.
- Water – both distilled and tap water must be close at hand.
- Compressed air outlet for air agitation system.
- Lighting – sufficient to the pilot plant operator to see safely

Figure 8.6-1 shows the proposed set-up of baths, equipment and work areas of the pilot plant.

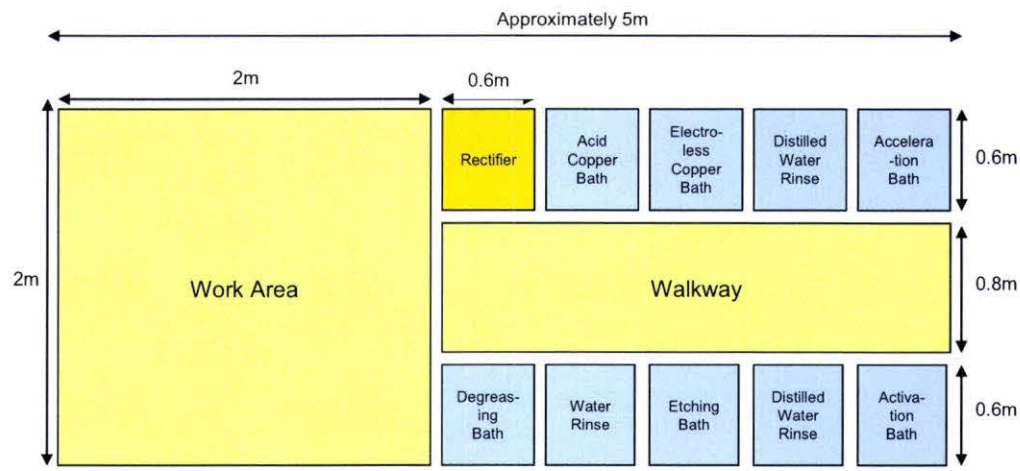


Figure 8-3: Floor plan for the Pilot Plant.

8.6.2 Equipment Requirements

Plating Baths

Eight plating baths were required in total:

- 2 steel baths with heating coils and thermostats up to 80°C for the degreasing and etching solutions.
- 6 fibreglass polyester resin baths for the activator, accelerator, electroless copper, acidic copper, tap water rinse and distilled water rinse.

The baths must be similar in size so that the jig could be transferred between baths efficiently. The bath dimensions were constrained by two factors: (1) The baths must be able to comfortably hold the helmet shell and jig, (2) The bath must not be any bigger than necessary to minimise the amount of solution required to fill the baths.

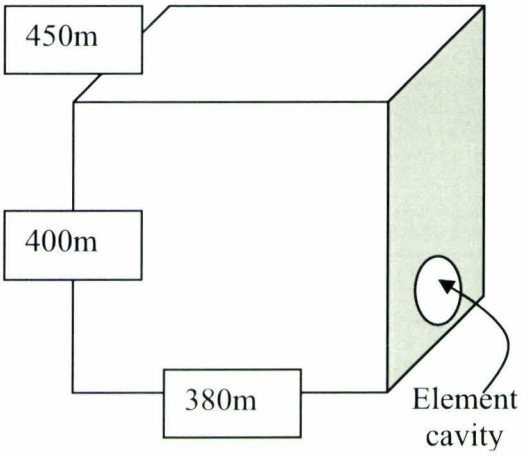


Figure 8.6-2: Plating Bath diagram; dimensions and element hole position

The fibreglass UP resin baths were hand-laminated by PHNZ. Wanganui Steel Engineers constructed the stainless steel baths; the electrical components were wired at PHNZ.

Custom Jig

A custom made jig was required to hold a single helmet shell throughout the plating process. It was necessary that this jig be constructed of steel and coated with a specialty 'jig paint' to protect the jig from being plated. The engineering of the jig was constrained by the size of the baths.

The most efficient shell orientation inside the bath was with the 'back of the head' facing up and the 'neck opening' facing the jig and therefore the side of the bath nearest the electroplating operator's access. This would enable the most surface area of the shell to be directly facing the anodes. It would also allow the helmet shell to be taken in and out of the solutions without trapping air or solution in the troughs of the shell.

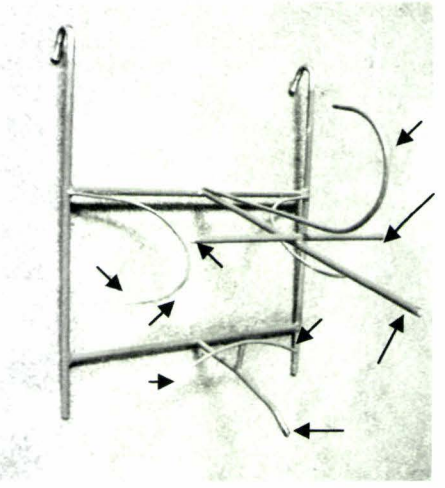


Figure 8.6-3: the helmet shell jig constructed from spring stainless steel. Arrows indicate contact points.

The positioning of the contact points of the jig to the shell is critical to the even distribution of the plating deposition. To ensure a quality appearance on the outside of the shell, the contact points must be inside the object. Positioning the contact points within 30mm of the edge of the shell would aid plating as the current would then be attracted to running across the outside of the convex shell, thereby aiding deposition of copper. For the size of the object a minimum of 6 contact points were desired around the inside rim of the shell.

The engineering of the jig was contracted to Two Wheels Engineering in Palmerston North. Spring stainless steel was used on the 'arms' of the contacts, and ordinary stainless steel used on the rig of the jig. It was then painted with '323 Red' jig paint supplied by Atotech Electroplating supplies. The paint was brushed on in order to protect the jig from corrosion in the plating solutions (except for the points of contact to the helmet shell). Figure 8.6-4 illustrates the jig and the 9 points of contact within 20mm to 30mm inside the rim of the helmet shells.

Electroplating bath, anodes and rectifier

Six copper anodes were made from 100% copper sheeting folded into bars the depth of the bath and distributed across the sides of the bath (excluding the side which would hold the jig). The anodes were wired to a 20A rectifier, which supplied the D.C. power required for the bath.

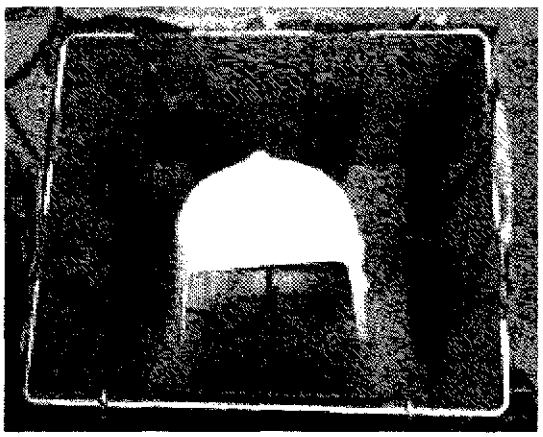


Figure 8-6: view of fibreglass electroplating bath with anodes, jig and shell

Agitation System

Air agitation was used in the degreasing, etching, rinsing, electroless copper and acidic copper baths. The intensity of the aeration was varied according to the requirements of each bath individually.

It was of particular importance that the agitation of the electroless copper solution be an air agitation system in order to aid plating quality. A cheap and simple method of creating air agitation is to use air rocks commonly used to aerate fish tanks. These

porous rocks can be attached to 5mm PVC piping from any controlled air supply to produce air bubbles in a solution. The rocks sink to the bottom of the baths, and the intensity of the air agitation is controlled by the compressed air outlet.

Chemical Requirements

Fifty litres of each solution were required and were ordered through Merck (NZ) Ltd and Scientific Supplies (NZ) Ltd.

8.7 OPERATION OF THE PILOT PLANT

Changes in the ratio of plating surface area to solution size would affect bath times, in particular the etching time, which would have to be re-defined. This section outlines the operating conditions for the new pilot plant, any problems encountered during operation, descriptions of solutions to the problems and ways of avoiding them in the future.

8.7.1 Initial Set-up

The baths and rectifier were positioned as illustrated in Figure 8-7-1. Each solution was made up using the methods selected in chapters 4 through 7. The operating conditions of the baths were initially set as outlined in Table 8.7-1:

Figure 8-7: Pilot Plant set up

Electroplating baths (anticlockwise) – degreasing, etching, water rinse, distilled water rinse, activator, accelerator, electroless copper bath, electroplating bath

Table 8.7-1: Pilot plant bath operating conditions

Bath operating conditions					
Solution	Bath type	Temperature (C)	Time (minutes)	Agitation	pH
Degreasing	Steel	70	5	mild air	n/a
Etching	Steel	70	**To define**	mild air	n/a
Rinsing	Fibreglass	room	<1	mild air	n/a
Activation	Fibreglass	room	15	n/a	n/a
Acceleration	Fibreglass	room	2	n/a	n/a
Electroless	Fibreglass	room	20	mild air	pH 12.5 - 13.0
Electroplating	Fibreglass	room	**Until plated**	mild air	pH <1

NB: room temperature was 23°C ± 1°C

8.7.2 Etching time redefinition

Due to use of a newly made up solution and the change in surface area to solution ration, the etching time had to be redefined. Etch times were tested on both painted and non-painted helmet shells. It was hypothesised that the optimum etching times were between 6 and 21 minutes for both the painted and non-painted shell. The results are outlined in the Table 8.7-2 below:

Table 8.7-2: Pilot plant etching time analysis

Etching Time analysis		
Etch Time (minutes)	Painted Shell	Non-painted Shell
6	Under-etched	Under-etched
9	Good etching	Under-etched
12	Good etching	Under-etched
15	Good etching	Good etching
18	Slightly over-etched	Good etching
21	Over-etched	Slightly over-etched

The outcome was that 9 and 15 minutes was the optimum etching time for the painted shell. That meant that the optimum etch time was 12 minutes, with a 3 minutes buffer either side. The non-painted shells optimum etch time was between 15 and 18 minutes.

8.7.3 Solution Maintenance

Throughout the use of the pilot plant maintenance of the solutions and equipment was carried out as described in Table 8.7-3.

Table 8.7-3: Pilot plant solution maintenance procedures

Solution maintenance procedures	
Solution	**Maintenance procedures**
Degreasing	• Filtered for solids using a fine fish net. • The solution is cheap and easy to replace. The 'droplet test' outlined in chapter 4 can test its effectiveness.
Etching	• Filtered for solids using a fine fish net. • The solution is expensive and corrosive but very stable. Therefore contamination is not a factor. • Heating of the solution causes evaporation of water. Therefore the bath was topped up to 50L as required.
Rinsing	• Both water rinses were replaced regularly, often after every 5 or 6 uses.
Activation	• Filtration required very rarely. • This solution is relatively stable, and therefore contamination is unlikely. • During the pilot plant operation, this solution was not required to be topped up.
Acceleration	• The solution did not require replacing or filtration. • NaOH was added to maintain the solutions concentration.
Electroless plating	• The electroless copper solution was required to be tipped out and remade every time the solution was exhausted. This usually occurred for every trial.
Acid Copper Plating	• Filtration was carried out regularly (once a week) using a fine fish net. • The cathodes, anodes and wiring required cleaning with steel wool to remove copper crystal build-up. • The pH must also be controlled. To maintain a pH of less than 1.0 sulphuric acid is added ml by ml until the pH is satisfactory. • Solution CuSO4 density must also be maintained. During the pilot plants short life it was not necessary to add any CuSO4, but in production the density is maintained by adding CuSO4 and all other components proportionally. Atotech (NZ) recommends a density of 1.0 at 20°C.

8.7.4 Steel Bath Maintenance

One week after the bath had been filled with the etching solution a leak was noticed from where the element was screwed into the back of the bath. Examination of the steel bath identified that the etching solution had eaten through the plumbers 'thread tape'. The solution had also attacked the wiring to the element.

In order to fix the problem Loctite 567, a heavy-duty thread tape was used to re-seal the thread. This seals threaded pipe and fittings instantly, then slowly hard-cures to form an insoluble seal that exceeds the pressure of all sized pipes. Loctite 567 was selected for its excellent chemical resistance in a temperature range of –54°C to 204°C. No further failures occurred.

8.8 PLATING FULL HELMET SHELLS

The chemical budget allowed for five electroless copper solutions to be made during the pilot plant. Therefore plating trials were restricted to five, which are outline below:

1st Helmet Shell

In this trial a painted UP resin shell was used to test the pilot plant using the operating conditions outlined in Table 8.7-1 and an etching time of 12 minutes.

The result was that both an electroless and an acid copper coating were applied. Unfortunately the coating did not adhere well. Touching the surface resulted in the coating rubbing off. This indicated that the surface was not etched for long enough.

However, the unpainted inside of the helmet shell appeared to be coated with a better-adhered copper coating. From this, an assumption was made that a non-painted shell would plate better at these conditions.

2nd Helmet Shell

The second trial used the same methodology as the first in trial 1, with a non-painted shell and an etching time of 15 minutes.

The result was that the helmet shell was again successfully plated with both electroless copper and acidic copper. However, the coating was only adhered in some parts of the outside of the helmet shell. The patchiness of the coating indicated that the degreasing was insufficient.

3rd Helmet Shell

The non-painted shell was degreased for 20 minutes to ensure all grease was removed. Then etching was carried out for 18 minutes (to ensure etching was sufficient). All other variables were maintained as in the 2nd trial.

The result was that this helmet shell was coated with both electroless and acid copper successfully. The coating adhered well. The appearance of the coating was shiny and smooth. However, areas around the base of the helmet were not plated. The activated and plated helmet shells in Figures 8.8-1 and 8.8-2 which show how the same areas of the coated helmet shell have not changed colour with activation or electroless copper. These areas are caused by faults in the moulded helmet itself, and not in the electroless plating process. To fix this problem, changes will have to be made as early on in the

process as the resin-transfer-moulding (RTM) of the UP resin helmet to ensure even plating. The specific mould used to make this shell may need to be replaced.

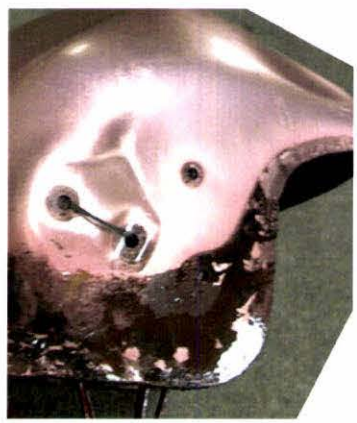
Figure 8-8: Non-painted helmet after acceleration.

Figure 8-9: Non-painted helmet after electroless coppering

4th Helmet Shell

A painted helmet shell was used in the hope of avoiding the problem of a fault with the surface of the part such as with the 3rd helmet shell. This shell was degreased for 20 minutes, etched for 15 minutes, and continued through the process as in trails 1 to 3.

The result was that the helmet shell was plated with a smooth, shiny, well-adhered copper coating. However, approximately 20% of the helmet was not plated. This section was along the base and sides, as illustrated in Figure 8.8-3 below. The areas that are not plated are near the cathode contacts and holes in the helmet shell. The plating appeared to have been 'burned' by the current being too high.



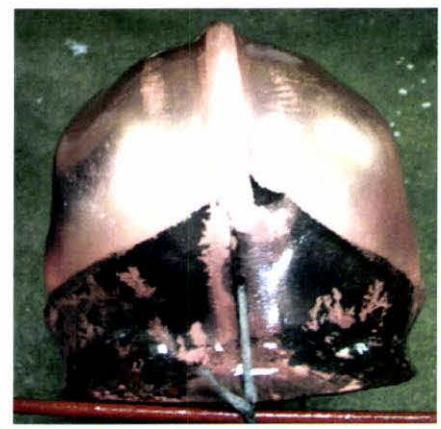


Figure 8-10: 4th Helmet shell copper plated in pilot plant

5th Helmet Shell

This attempt was exactly the same as the 4th helmet shell, but with a lower current run through the acid copper solution. The result was a helmet shell that was over 99% coated in copper (see Figures 8.8-4 and 8.8-5). Apart from a few small random faults, most likely caused by small grease spots, organic matter or faults in the surface of the shell, the surface was relatively smooth and shiny and adhered well. The faults were located at the base of the back of the shell and would be covered by rubber extrusion

Figure 8-11: 5th helmet shell after electroless plating

Figure 8-12: 5th helmet shell after electroplating

8.9 OUTCOME OF PILOT PLANT TRIALS

The 5th helmet shell was successfully plated with copper and was therefore tested against the plating target specifications (see Table 8.9-1).

Table 8.9-1: Pilot plant plating testing target specifications matrix

Pilot plant plating target specifications					
Test / Metric	Imp.	Unit	Marginal Value	Target Value	Plated Helmet
Plating Testing					
% Of shell plated	5	%	95%	100%	99%
Plating quality:					
Bend test	5	Subj.	4	5	4
Sharp object resistance	5	Subj.	4	5	4
Texture test	5	Subj.	4	5	4
Shine test	5	Subj.	4	5	4

The 5th helmet shell passed the plating quality requirements and the process proceeded to the prototyping and product testing stage of the project.

8.10 PROTOTYPING

8.10.1 'Works Like' Prototype

For the purpose of physical testing (outlined in chapter 9) a 'works like' prototype was constructed from a standard F7A helmet, of which the helmet shell had gone through the electroplating process. That is, one of the shells partially electroplated during the pilot plant experiments was used to make up a complete F7A helmet assembled with liner, chinstrap and standard F7A accessories.

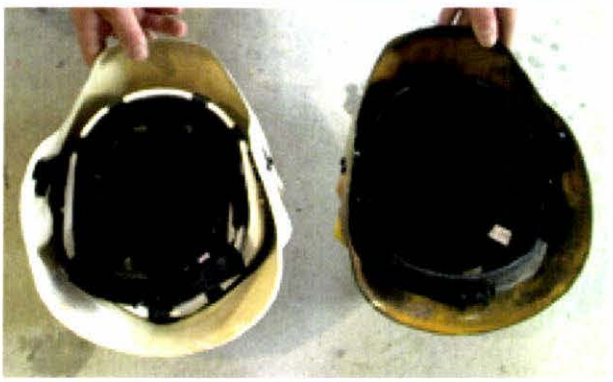


Figure 8-13: Painted and plated helmet shells prior to testing.

Figure 8-14: Inside of helmet with helmet liner, prior to testing.

Figures 8.9-1 and 8.9-2 illustrate the works-like painted F7A and the works-like electroplated F7A prototypes used during product testing against BS EN 443 standards.

8.10.2 'Looks Like' Prototype

To gain an idea of what the final product would look like a standard F7A helmet was assembled using a helmet shell painted with metallic silver enamel. This prototype was for presentation purposes only and was not suitable for physical testing. This prototype will be used in consumer testing carried out at the fire fighting international trade show.

8.11 TESTING PLATED HELMET SHELL

8.11.1 Shock absorption tests

The BS EN 443:1997 (see Appendix) is the British/European standard for helmets for fire fighters. The shock absorption requirements state that 'When the helmet is tested by the method described, the force transmitted to the head-form shall not exceed 15kN'.

In this test, the head-form is rigidly mounted onto a base (bench) and the helmet positioned on it. A striker having a mass of 5.0kg and a hemispherical striking pace of 50mm radius is positioned above the head-form, and released from a height of 2500mm. A low-inertia force transducer firmly attached to the base shall measure the impact force.

Pacific Helmets Ltd has adapted their testing system to use an accelerometer instead of a force transducer. This method is a more commonly used procedure across all international standards. In order to make the tests comparative, PHNZ have used basic physics equations to translate the BS EN 443 requirements from force tests to acceleration tests.

In this example, the 5.0kg striker drop procedure from 2500mm with a maximum impact force of 15kN is translated to a 5.0kg striker drop from 2434mm with a maximum acceleration of 306g.

However, the height of 2434mm is not practical when tested a new or customised product such as the plated French helmet. It was more practical to carry out a comparative test of a plated helmet against a non-plated helmet (which is known to pass the 2434mm tests) at a lower, less destructive height. Therefore, for this project, drop heights of 1000mm and 1675mm (AS 4067: Australian fire fighting helmet standard drop height) were chosen for the comparative tests (see Figures 8.10-1 and 8.10-2). Three consecutive drop tests were carried out at each height on both a plated and a non-plated helmets.

1000mm Drop Test

The first experiment was run to get a general idea of how well the helmet shell would cope with the impact at a shorter drop distance of 1000mm.

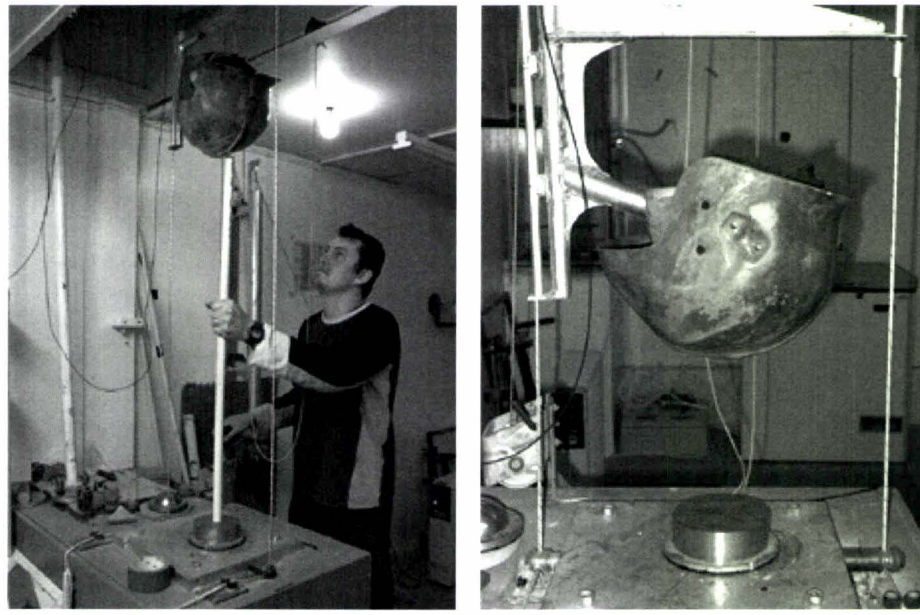


Figure 8-15 Setting up 1000mm drop test measuring equipment

Figure 8-16: Close up of helmet shell of head-form above the striker/target.

The results of the 1000mm drop test are graphed below in Figure 8.10-3:

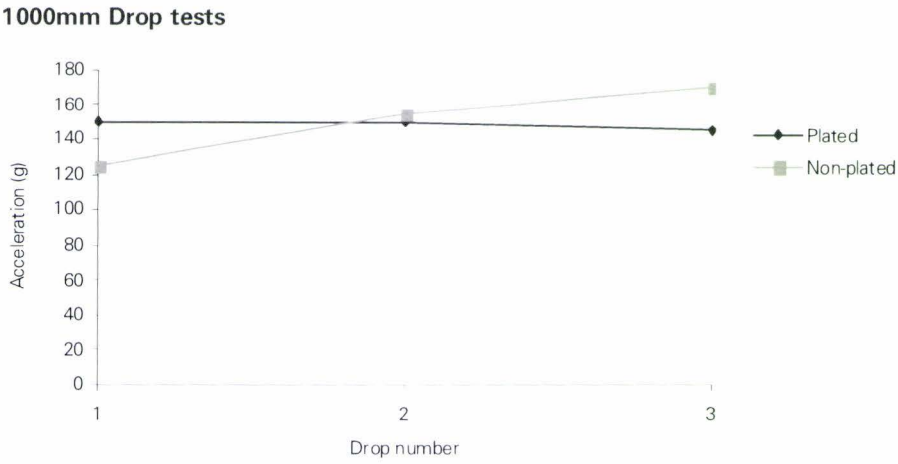


Figure 8-17: 1000mm Drop test results

As the graph illustrates, the acceleration measurements were very similar for both helmets. The non-plated helmet maintained an acceleration output of around 150 (g) for all three drops, whereas the plated helmet showed better shock absorption in the first drop at 125 (g), then decreasing to the same 150 (g) as the plated helmet on the second drop, and to a poorer 170 (g) on the third drop.

1675mm Drop Test

The second experiment used the AS 4067 Standard Drop Test parameters. That is, a drop height of 1675mm. The results are illustrated in Figure 8.10-4 below:

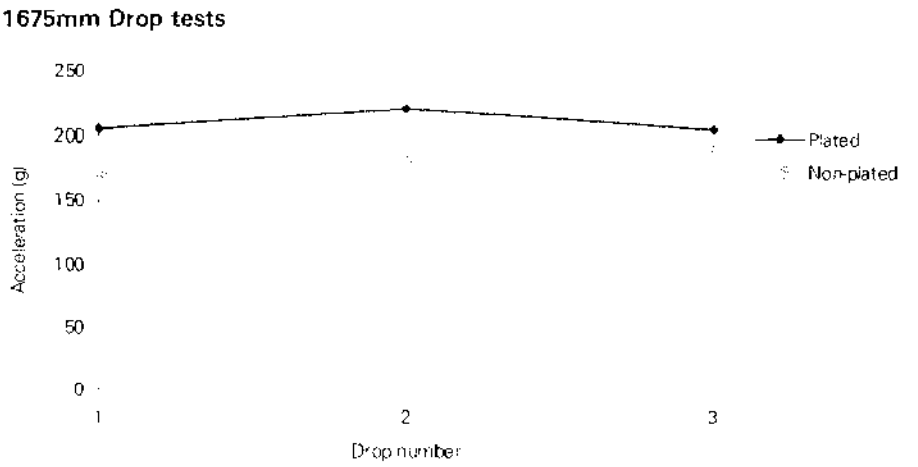


Figure 8-18: 1675mm drop test results

The plated helmet had better shock absorption than the painted helmet at this drop height. The resulting acceleration increases from 170, 180 to 190 on the third drop, whereas the un-plated helmet has higher acceleration values, all over 200g.

The fact that the plated shells output acceleration values slowly increase does not affect how safe the helmet is, as after one, two, or three such impacts the helmet is seen unfit for use, and must be replaced. This is very noticeable when taking into consideration the condition of the helmet shell after three impacts. For both tests, both shells began to break up after the third drop test. The damage to the helmets appeared similar. Photographs of the shells after three drop-tests are shown below:

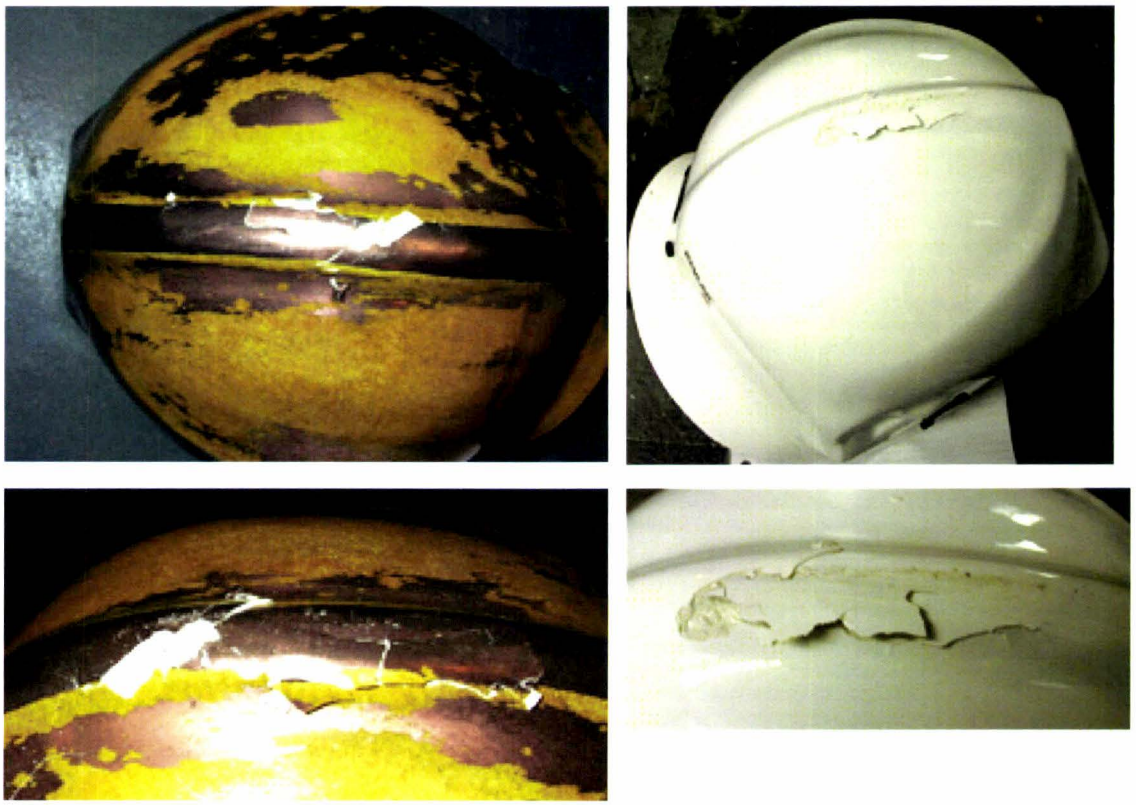


Figure 8-19: Illustrates the damage done to the top of both the plated (left) and painted (right) shells after 3 impacts of 1675mm drops.

In conclusion, the plated helmet shell performed in line with the painted helmet. As the painted helmet shell is known to pass the BS EN 443 shock absorption test, it can be concluded that the plated helmet will also pass this test.

RESISTANCE TO SHARP OBJECTS

EN 443 states that for this test a sharp striker is dropped from 2500mm on to the upper part of the helmet. Any contact of the striker with the head-form is noted.

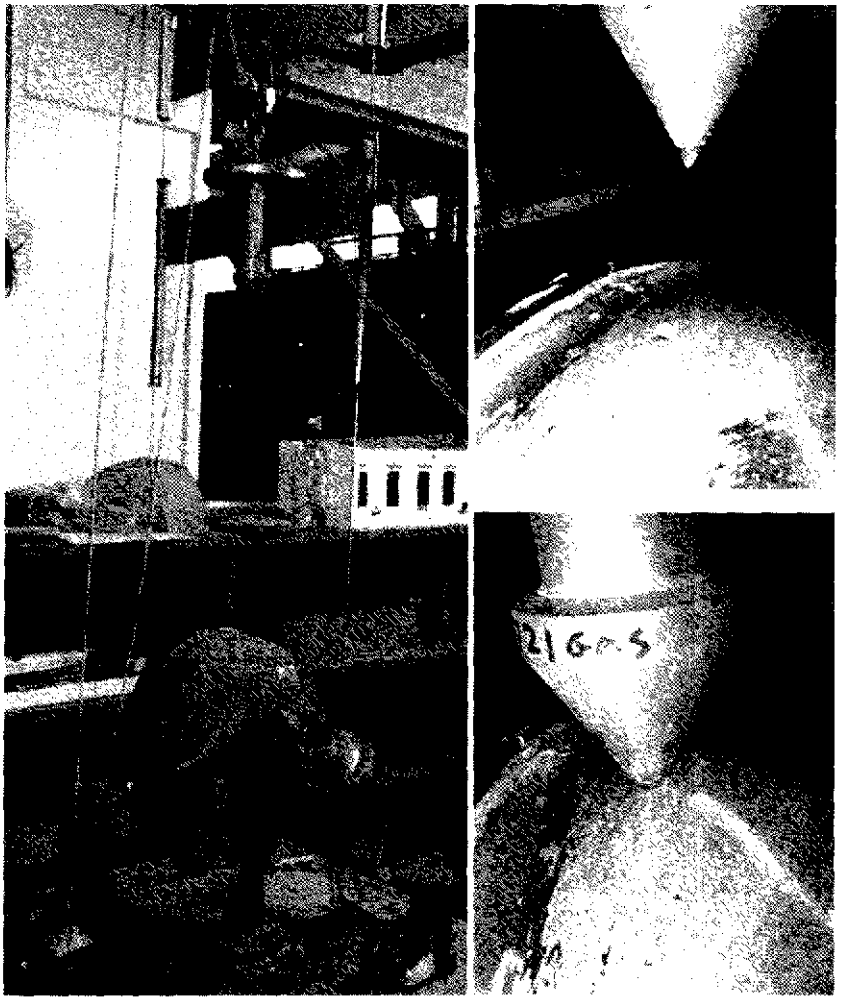


Figure 8-20: left: Resistance to sharp objects testing apparatus (EN 443)
Figure 8-21 Top right: Sharp object penetrating the plated helmet.
Figure 8-22: Bottom right: the damaged plated helmet after penetration.

As with the shock absorption tests, the resistance to sharp objects test heights were adjusted for Pacific Helmets Ltd laboratory to be 976mm. Three such drops were made on each helmet shell to ensure that the helmet was resistant to sharp objects across the helmet shell.

The results were very good. There was no contact between the striker and the head form for either helmet shell, indicating that both helmets were within requirements for this test.

In addition it was noted that the plated helmet shell appeared more resistant to sharp objects, as a smaller hole was made during the tests. The plated helmet had a hole diameter of 7mm whereas the painted helmet had a larger hole diameter of 11mm.

In conclusion, the plated helmet is equal to or better than the painted shell in resisting sharp objects. The plated shell therefore passes the BS EN 443 standard test.

8.7.3 FLAME RESISTANCE

The plated helmet was tested against a painted helmet as outlined in section 5.6 of the BS EN 443 standard. That is, a Bunsen burner blue flame is applied to the helmet shell for 15 seconds (see Figure 8.10-9). The helmet shells were analysed to identify any 'drip' of material during the test, and any visible flame or glow 5 seconds after removal of the flame.

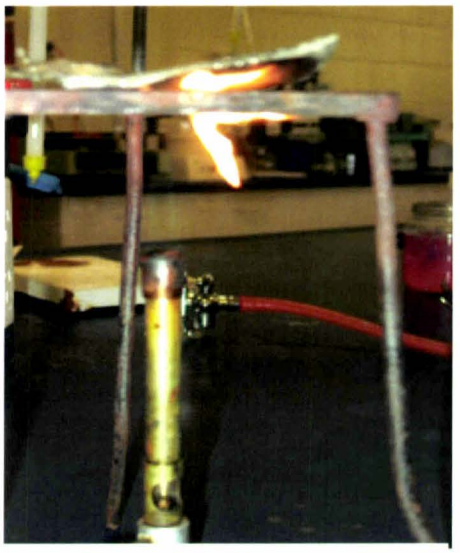


Figure 8-24: Flame test

During testing smaller samples of the plated helmets were used in order to retain the quality of the full helmet shells for prospective consumer testing. The results were that, when tested in accordance with BS EN 443, both the painted and the plated shells showed no sign of 'drip', nor did either of them catch on fire (have a flame), or 'glow' 5 seconds after the flame was removed. The plated coating bubbled up of the UP resin surface. This was expected, and is acceptable after being subjected to such intense heat (see Figure 8.10-10). The painted shell was also damaged, and the flame has began to penetrate the UP resin surface, which was expected and is acceptable (see Figure 8.10-11).

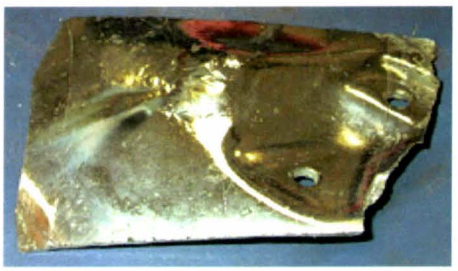


Figure 8-23: Plated sample 5 seconds removed from flame

The test concluded that the both helmet shells met the flame resistance standard.

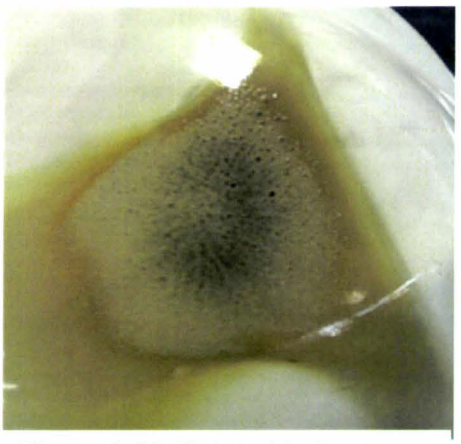


Figure 8-25: Painted helmet surface 5 seconds removed from the flame test.

8.7.4 RADIENT HEAT RESISTANCE

BS EN 443 outlines a procedure where a radiant surface is adjusted until the flux intensity is (7±0.1) kW/m^2. The helmet is then exposed to the radiant heat for (180±2) seconds. The temperature inside the helmet shell (the head-form) should not rise more than 25°C.

Standard heat resistance tests are carried out in an independent lab in Christchurch. These tests are expensive, and time consuming. Therefore responsibility for the radiant heat resistance tests were taken by PHNZ, and the tests were not completed within the scope of this Masters project.

However, given the success of the un-plated F7A test, the ingoing hypothesis was that the plated F7A would also pass the test.

8.12 CONCLUSION

The results of the how the plated helmet performed against the plating and product specifications are tabulated in Table 8.12-1. The table illustrates that the 5th helmet produced in the pilot plant was 99% coated with copper and passed plating quality tests.

The helmet shell was then assembled, and the prototype helmet tested against a painted F7A helmet to ensure that it met BS EN 443 standards. The outcome was that the plated shell was equal to or better than the painted shell, which continually passes all BS EN 443 standard tests.

Table 8.12-1: Plated prototype target specifications results – 5th Helmet

Pilot plant plating target specifications					
Test / Metric	Imp.	Unit	Marginal Value	Target Value	Plated Helmet
Plating Testing					
% Of shell plated	5	%	95%	100%	99%
Plating quality:					
Bend test	5	Subj.	4	5	4
Sharp object resistance	5	Subj.	4	5	4
Texture test	5	Subj.	4	5	4
Shine test	5	Subj.	4	5	4
Product Testing					
Shock absorption	5	Bin.	Pass	Pass	Pass
Sharp object resistance	5	Bin.	Pass	Pass	Pass
Flame resistance	5	Bin.	Pass	Pass	Pass
Heat resistance	5	Bin.	Pass	Pass	?

9 CONCLUSION

9.1 INTRODUCTION

This project began with PHNZ identifying an opportunity in the French fire fighting helmet market. Product, consumer and market research were used to create an initial product specifications list for the helmet product. It was identified early in the project that PHNZ were capable of meeting all except for one of these product specifications using an existing product, the F7A helmet. The only problem was that the F7A was not nickel-plated; a specification identified as being critical in meeting consumer needs and French standards.

PHNZ's inability to plate the F7A helmet shell was the major technical problem in the project. This was due to the helmet shell being made from UP resin. At the beginning of this project, there was no known technology for electroplating UP resin. In addition, literature reviews identified that this technology gap was not for lack of trying. Researchers who made efforts to unlock the secret of plating on UPR and failed to achieve a quality plating finish suitable for this application, included:

- Bauer, Johnson et al. (1971)
- Sopchak and Skovrinski (1984)
- Januschkowetz and Laub (1977)

As explained throughout the thesis, the electroplating UP resin process was found to be made up of four major parts:

1. Etching 'holes' into the UP resin surface
2. Activating the UP resin surface
3. Electroless copper deposition onto the activated UP resin surface.
4. Electroplating onto the conductive electroless coating.

Contrary to industry expert advice that trying to develop such a process would be futile, the project resulted in the development process that met the requirement of the project. With help from Mr Bendary (an electroplating expert in Egypt) and persistent research and development work, a successful process for adhering nickel to samples of UP resin through electro deposition was developed.

Despite the successful application of nickel to samples of UP resin, it was still unclear if the complex shape of the whole UP resin helmet shell could be successfully electroplated. Therefore, a pilot plant was constructed in order to test that the process could successful plate a whole helmet shell.

The final process solutions and operating conditions identified during the pilot plant development are detailed in Table 9.1-1 below. It was this process that was used to plate the helmet shell used to make the works like prototype.

Table 9.1-1: Summary of successful plating solutions and operating conditions

Bath operating conditions					
Solution	**Concept**	**Temperature (°C)**	**Time (minutes)**	**Agitation**	**pH**
Degreasing	standard	70	5	mild air	n/a
Etching	Soln C	70	15	mild air	n/a
Rinsing	standard	room	<1	mild air	n/a
Activation	Silver	room	13	n/a	n/a
Acceleration	standard	room	2	n/a	n/a
Electroless	Copper	room	15	mild air	pH 12.5 - 13.0
Electroplating	Acid Copper	room	15	mild air	pH <1

Works-like and looks-like prototypes of the product were constructed for product testing and consumer testing respectively.

This chapter outlines the results of these tests and how the products design was re-evaluated accordingly. This leads to the presentation of the final product specifications.

Further, a commercialisation plan is outlined, along with a financial assessment that shows significant return on investment and net present values potential.

9.2 EVALUATION OF PRODUCT DESIGN

The product (physical) tests identified that there were no physical problems with the product design. The product passed all the relevant BS EN standard tests.

The preliminary consumer evaluation proves that the aesthetic style and the functionality of the F7A were very pleasing to the consumers. The F7A is very similar in appearance and style to the Gallet F1, which the French currently use. In addition, the similarity in style will allow for a relatively easy integration of the F7A into brigades using existing Gallet F1 helmets. The F7A also meets and exceeds the functionality requirements gathered from consumers.

Therefore it is not necessary to re-design the F7A except to electroplate it with nickel. The product specifications remained the same as those identified in Chapter 2, and are outlined in section 9.3 below.

Figure 9-1: Pacific F7AK/2 Mk 3B (F7A) Structural Fire Helmet - Premiere Model

9.3 FINAL PRODUCT SPECIFICATIONS

Table 9.3-1 outlines the results of the overall product specifications, and how the PHNZ electroplated-F7A prototype compared to the competitor product, the Gallet F1-S.

Table 9.3-1: PHNZ Nickel F7A performance against Gallet F1-

Product specification matrix							
Metric	Need No.	Imp.	Units	Marginal Value	Ideal / Standard Value	Gallet F1-S	PHNZ plated F7A
1. French Standards Tests							
a) Nickel in Colour	11,12	5	Binary	Pass	Pass	Pass	Pass
b) Total Mass	2,6	5	G	<1700	<1400	1200	1300
2. European Standards Tests							
a) Shock absorption	1	5	kN	<15	<14	<15	<15
b) Resistance to Sharp objects	1	5	Binary	Pass	Pass	Pass	Pass
c) Mechanical Rigidity	1	5	mm	<15	<14	<15	<15
d) Flame Resistance	1	5	Binary	Pass	Pass	Pass	Pass
e) Radiant Heat Resistance	1	5	X°	<47	<45	<45	?
f) Electrical Properties	1	5	mA	<1.2	<1.1	<1.2	<1.2
g) Retention system strength	1	5	mm	<15	<14	<15	<15
h) Durability	15,16	4	Years	>3	>5	4	4
i) Sharp edges	3	4	Binary	Pass	Pass	Pass	Pass
j) Irritation to skin	4	3	Binary	Pass	Pass	Pass	Pass
k) Interference with breathing apparatus or eyeglasses.	5	4	Binary	Pass	Pass	Pass	Pass
3. Head Sizes	2	5	cm	54-62	54-64	53-64	54-64
4. Adjustable fit of helmet	7	4	Subj.	>3	>4	4	4
5. Time taken for user to fit helmet	9	3	s	<12	<9	9	9
6. Tools required for fitting adjustment	8	3	List	>2	0	0	0
7. Additional Feature availability	17						
a) Lamp		4	Binary	Pass	Pass	Pass	Pass
b) Neck Protector		4	Binary	Pass	Pass	Pass	Pass
c) Lights and Clips		4	Binary	Pass	Pass	Pass	Pass
d) Custom Badges/Decals etc		4	Binary	Pass	Pass	Pass	Pass
8. Traditional Helmet Form	11	4	Binary	Pass	Pass	Pass	Pass
9. Unit Manufacturing Cost	13	4	$NZD	<230	<200	?	208
10. Manufacturing Flexibility	14,17	4	Subj.	>3	>4	1	5
11. Helmet allows user to hear normally	18	4	Binary	Pass	Pass	Pass	Pass
12. Facilities for fitting optional:	10						
a) Neck protector		4	Binary	Pass	Pass	Pass	Pass
b) Ear protector		4	Binary	Pass	Pass	Pass	Pass
c) Face protection		4	Binary	Pass	Pass	Pass	Pass

The PHNZ electroplated-F7A succeeded in meeting or exceeding, and out-performing the competitor product in all specifications except the radiant heat test, which is yet to be completed.

9.4 COMMERCIALISATION

9.4.1 PRODUCT LAUNCH PLAN

The Nickel plated F7A will be marketed at this years International Fire-fighting trade show. PHNZ's Chief Operating Officer will attend the show, taking with him the final prototype of the Nickel-plated F7A. The product will be put on show and compared to the Gallet F1. Evidence of how well PHNZ's product compared in meeting the BS EN 443 standards will be presented to illustrate PHNZ's products superiority.

After the trade show, PHNZ existing French suppliers will market, supply and liase with French fire brigades to win up coming tenders.

9.4.2 MARKETING PLAN

1. To use the Nickel-plated F7A to penetrate the French market and gain a target market share of 20% over the first 5 years of production.
2. PHNZ wish to use the success of the Nickel-plated F7A to gain a reputation as a quality and competitive helmet manufacturer with the French and European markets.
3. To use its reputation and existing relationships with suppliers to market their range of both plated and non-plated fire fighting helmets as a safer, more functional, and more competitively priced product than the Gallet F1.
4. To increase market share (to 50%) across France over 10 to 20 years while thereby influencing and attempting to penetrate greater Europe.
5. Extend their reputation for making fire-fighting helmets to introduce their extensive range of other rescue helmets to both France and Europe.
6. Gain additional revenue through royalty payments for the licenses of the 'Plating on UP resin process'.

9.5 BUSINESS STRATEGIC FIT

PHNZ are currently in the process of extending their factory to increase productivity. It is hoped that through extending the factory and better production management, PHNZ will be able to increase production by 20% over the next 2 years. Currently 1700 helmets are produced per week. An increase of 20% would result in 2040 helmets per week. This results in an increase of approximately 17,000 helmets per year. If the Nickel-plated F7A is successful in gaining a 25% market share over 5 years then the additional French orders will be 6250 helmets each year (31250 total over 5 years). That counts for

approximately 37% of the total 17,000 helmets PHNZ wish to produce in addition to their annual output of 85,000.

It is hoped that the rest of the 20% increase in production capability will be filled with the production of other products in the product development pipeline, and if all goes well, with additional sales of the nickel-plated F7A in years to come.

9.6 FINANCIAL ASSESSMENT

A financial analysis was carried out in order to forecast the Nickel-plated F7A's expected performance after the product is launched. Details of the analysis, including the calculation of cash flows and sensitivity analysis for net present value (NPV) and internal rate of return (IRR) and payback period are outlined below.

9.6.1 CASH FLOW

9.6.1.1 Initial Investment

The initial investment is dependent upon negotiations with existing electroplating and electroless plating experts within New Zealand. It is hoped that PHNZ will identify an existing electroplater who is interested in forming a relationship with PHNZ in which the electroplating company will pay royalties to PHNZ for the right to use the 'electroplating on UP resin' process, or in exchange for plating the helmet shells for PHNZ at a discounted rate. If such a relationship cannot be formed, then PHNZ may have to contract the work out to an existing electroplater. This may require PHNZ to invest some capital for construction of an UP resin electroless plating line in an existing plant. If this is not possible then the worst-case scenario is that PHNZ may have to construct an electroplating plant in order to plate the helmet shells themselves. This would require significant investment.

In addition, there will also be considerable development cost in scaling up the plating on UP resin process from the 50L pilot plant constructed in this project to a full-scale plant.

Therefore there are three options for plating production:

A. PHNZ build electroplating plant and do plating independently
B. Contract out plating to electroplaters but invest capital in new line.
C. PHNZ form a relationship with electroplaters in which intellectual property (IP) is exchanged for discounted plating rate or royalties.

The plating production method affects both the initial investment and the cost of plating each helmet. This is illustrated in Table 9.6-1 below:

Table 9.6-1: Initial investment and cost analysis

Initial investment and cost analysis				
Plating Production Methodology	Initial Investment (range)	Initial Investment (average)	Cost of plating per helmet (range)	Cost of plating per helmet (average)
A: PHNZ build plant	$500,000 to $2,500,000	$1,500,000	$5 - $10	$7.50
B: Contract out plating	$0 to $250,000	$125,000	$16 - $24	$20
C: Relationship with plater	+$100,000 to -$100,000	$0	$10 - $18	$14

The initial investment ranges in table 9.6-1 are based on discussions with electroplaters, contractors and industry experts. The cost of electroplating for options B and C are based on discussions with electroplaters and option A was calculated using the pilot plant costs as a conservative stretch estimate.

The cost of producing an F7A is $208 (NZD). The total cost of producing a Nickel-plated F7A is therefore $208 plus whatever the cost of plating the helmet is. Therefore depending on which plating production methodology is used, the total cost of the product will be between $213 and $232. This is significantly lower than the initial estimate made in chapters 1 and 2. The change is driven by an increased understanding of the plating technology. Estimates include provisions for logistics costs.

9.6.1.2 Revenue

In addition to the initial investment and the cost of producing helmets, revenue is also affected by the market share (%) and the selling price. It is estimated that a market share of 25% over 5 years. Market share percentages of 5, 10, 15, 20, 25, 30, and 35 were used in the sensitivity analysis to evaluate how profitable the project would be if sales were within this range.

The selling price set by PHNZ for the Nickel-plated F7A is $330 (NZD). However, it is possible that in an effort to better compete with PHNZ, Gallet could lower their F1 price. As a result, PHNZ may need to lower their selling price to better their competition. On the other hand, changes in the market may result in PHNZ being able to increase their selling price. Therefore a range of selling prices from $290 to $350 was evaluated in a sensitivity analysis.

9.6.1.3 Operating Cash Flows

The summaries of the operating cash flows were generated on the basis that there will be an initial investment between $0 and $2.5m (or in the case of receiving royalty

payments in exchange for IP up to $0.1m credit). This will be followed by the first 5 years of expected sales of an expected 25% of the market share. As outlined a number of variables will affect the exact cash flows and therefore the NPV, IRR and payback period. These are evaluated using sensitivity analysis outlined below.

9.6.2 SENSITIVITY ANALYSIS

9.6.2.1 Net Present Value (NPV)

The NPV for each plating production method was calculated using the average initial investment for each (see Figure 9.6-1). A conservative discount rate of 10% has been assumed for the calculations.

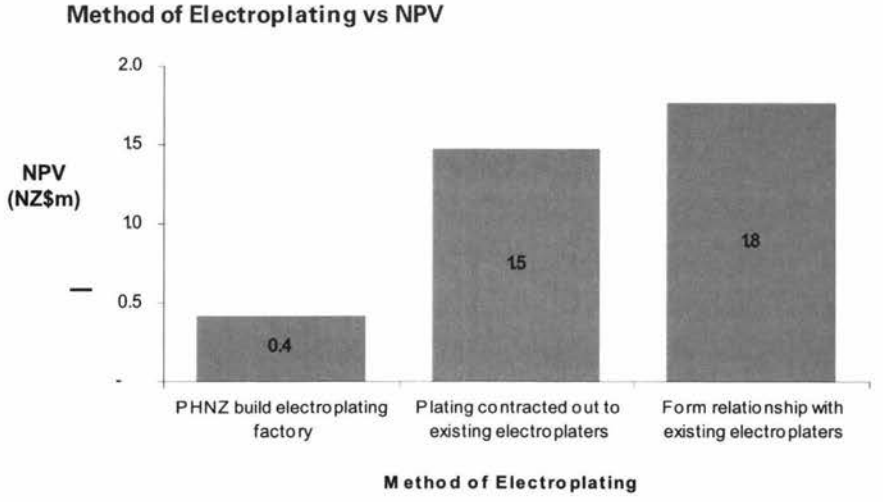


Figure 9-2: Sensitivity analysis – Electroplating method affect on NPV

Figure 9.6-1 shows that all the options are profitable. Option A has an NPV at $0.4m, considerably lower than that of options B and C at $1.5m and $1.8m successively.

To gain a better overall view of how initial investment for each option affects NPV, the graph below illustrates how the initial investment ranges for each method of plating production affects the NPV.

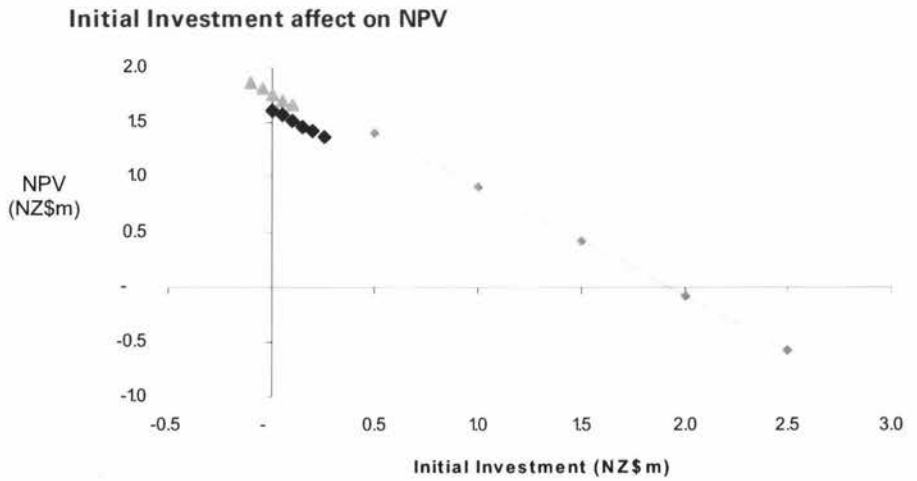


Figure 9-3: Sensitivity analysis – Initial investment affect on NPV

The graph shows that the initial investment for the 'PHNZ doing plating' option has the largest range of potential initial investment. This is dependant upon how smoothly the development and construction of the plating plant is. At worst case scenario it is possible that the construction of the plating plant will cost up to $2.5m. This option has the potential to have a negative NPV should the construction cost over $1.5m (approx.). In addition this option has an overall lower NPV than the contracting out or forming relationship with plater's options. Therefore this option is by far the riskiest and either of the alternatives would be significantly more financially stable.

9.6.2.2 Internal Rate of Return

As with the NPV, average IRR values were calculated for each method of plating the helmet shell. It was found that the IRR for C was not applicable because the average initial investment was nil. The IRR for option A was 20% and the IRR for B was 285%. These differences are mostly due to the variance in initial investment. However, the cost of plating per helmet shell is also a cause.

9.6.2.3 Payback Period

Again this calculation is dependent upon the plating production method used. If all goes well and the market share is 25%, the selling price of each helmet is $330 and the average initial investments for each plating production method are used then the payback periods will be as follows:

A. 1 – 5 years

B. 12 months

C. 6 months or less

9.6.2.4 Effect of Market Share on Financial Performance

The market share gained in the first 5 years of the launch of this product is the most difficult variable to estimate. Therefore a method of estimating a range of NPV between pessimistic to optimistic is appropriate to analyse the effect on the financial performance of the product under these circumstances. In this sensitivity analysis, market shares ranging from 5% to 35% were studied. The results are illustrated in the graph below.

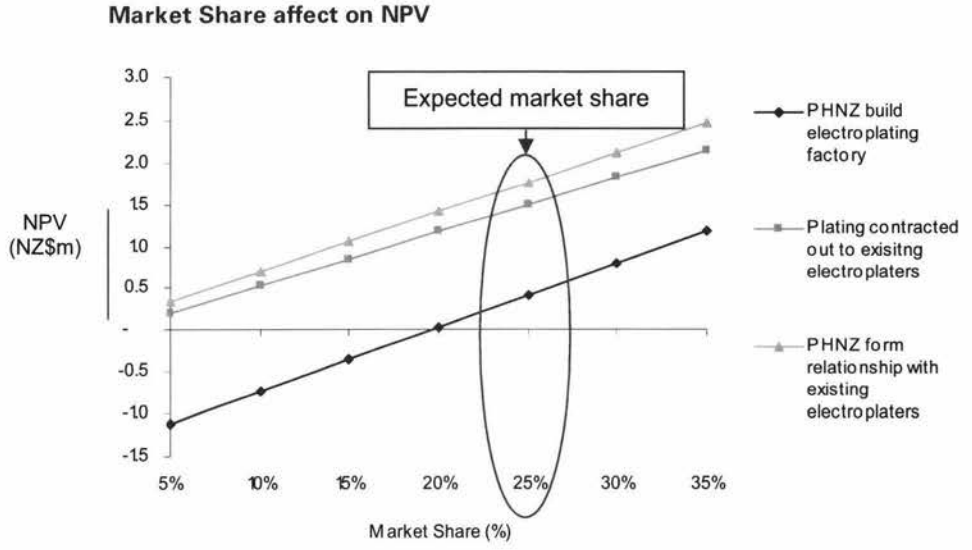


Figure 9-4: Sensitivity analysis - Market share affect on NPV

The graph shows that plating production method (A, B or C) increases in market share greatly increase the NPV. This is due to the relatively low initial investment, and the large return due to a large market size. It also illustrates how plating production methods A and C 's NPV values increase at a higher rate than that of B. This is because method C incurs a higher plating cost per helmet (plating cost is higher). This graph also illustrates how if a lower market share than 15% is achieved, the 'PHNZ build electroplating factory' option is likely to incur a negative NPV, and will therefore not be profitable.

9.6.2.5 Effect of Selling Price on Financial Performance

As with market share, the selling price of the helmet is directly proportional to the NPV. However in this case, the rate of increase is more consistent across the three different plating production methods. This is illustrated in the graph below. The graph also identifies that if the helmet selling price is less than $310 then for the option of 'PHNZ building an electroplating factory', the product will run at a loss.

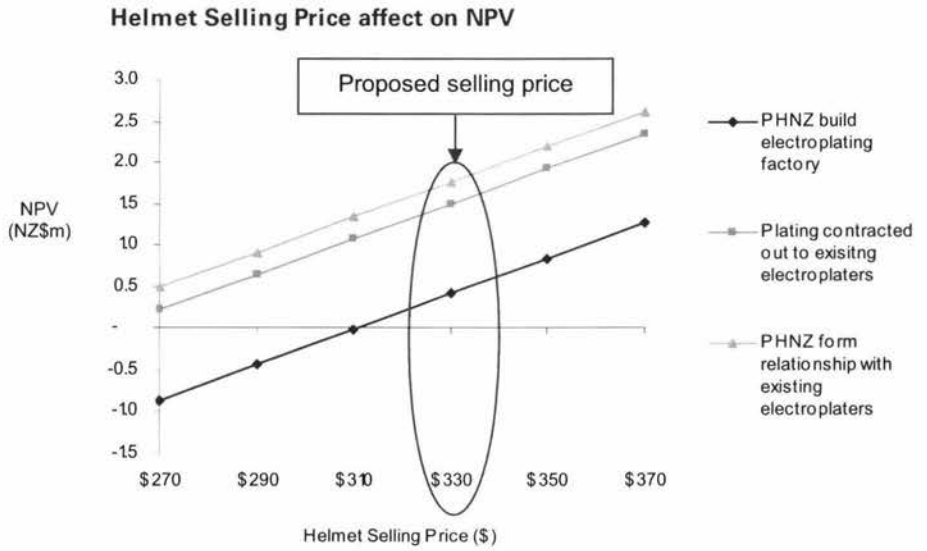


Figure 9-5: Sensitivity analysis – selling price vs. NPV

9.6.3 Overall Financial Performance

Overall the forecasted financial performance of the product is very good if options B or C are used as methods for electroplating the helmet shell with forecasted NPV values of $1.5m and $1.8m consecutively. The payback periods for these options are also very positive, at 12 months and 6 months consecutively.

However, if the 'PHNZ build an electroplating factory' is required, the project has a much higher risk of running at a loss. If the initial investment required is larger than $1.5m then the project runs a very high risk of having a negative NPV value. It is also expected that this option could take as long as 5 years to reach payback period.

Overall the financial analysis shows that very sound financial results will be achieved if options B or C are used to plate the helmet shells. However, if option A is required, the financial risk will be very high, and it is not recommended that PHNZ go through with this method of plating the helmet shells.

9.7 CONCLUSION

The outcomes are in line with the aims and objectives set at the beginning of the project. Overall, each objective and therefore the aim of the project were met, resulting in the successful development of a fire-fighting helmet that met the requirements of the French market. The major technical constraint in achieving this aim was the need for the development of a process to electroplate UP resin. In accordance with the aims and objective, a systematic product development process was carried out. This process gave

rise to sub-processes such as the technical development process and a process development process, as illustrated in Figure 1.8-1 in the introduction.

A final evaluation of the helmet product developed in this project concludes that the final product solution:

- Meets or exceeds the specifications set through preliminary consumer, market and product research.
- Meets or exceeds all technical requirements set by the international standards organisation.
- Can be manufactured using PHNZ existing capabilities with the addition of the plating on UP resin technology, which has been proven viable in the pilot plant constructed during this project.
- Has market potential and is therefore a viable product to commercialise.
- Shows excellent financial performance potential with a reasonably low initial investment.
- Has a sound commercialisation strategy.

9.8 RECOMMENDATIONS

9.8.1 Recommendations for further development of PNHZ's product

The overall recommendation for continuing work on this project is that PHNZ should proceed with this product through to product launch. All aspects of the Nickel-plated F7A fire-fighting helmet should be manufactured as is, at the PHNZ factory in Wanganui, NZ with one exception – the plating of the helmet shells.

PHNZ had originally suggested that they might set up an electroless/electroplating line at their premises in Wanganui. It is recommended that PHNZ do not endeavour to construct and run an electroless plating plant for the purpose of plating the helmet shells. The initial set-up cost and the expertise required to run the plant outweigh the returns of the French fire-fighting helmet. In addition, the operation would be much more complex and restricted by very tight standards and OSH regulations that PHNZ initially considered.

If such a plant were to be constructed in New Zealand by PHNZ or anyone else, such as an existing plating company, the plant would require independent facilities especially for plating purposes – that is, it should not be incorporated into an existing non-plating facility.

It is unknown at this stage whether there is an existing demand for a specialist electroless copper plating onto UP resin facility either in New Zealand of globally . It is possible that given the development of the plating on UP resin technology, an existing electroless or electroplating company may be interested in expanding their facilities to include such a line.

It is recommended that PHNZ share their knowledge of this technology with an existing electroplater and perhaps go into business with such a company in order to share set-up costs, reduce production costs and fully leverage existing plating expertise. In this case, an electroplating plant set-up specialist will be required to ensure all aspects of the plant are set up correctly.

Alternatively, it is possible that Mr Bendary's plant in Egypt could be adapted to produce plating that is suitable for PHNZ's application to fire-fighting helmets. One disadvantage of this option is the additional logistics to Egypt, which, given the increase in oil prices would be significant.

9.8.2 Recommendations for further research

Recommendations for further research and development of the plating on UP resin process:

- Cost – the solutions used in this process are expensive. In order to reduce costs research in exact methods of maintaining the baths in an optimum manner such that as little waste as possible occurs will result in cost savings.
- Environmental issues – although the toxicity of the solutions has been decreased in some areas such as the removal for the need for chromic and sulphuric acid etchants, there are still many toxic and dangerous chemicals used in the process solutions. Any research that would result in the reduction of the use of such chemicals, or changing to less toxic chemicals would benefit both those in the work environment and the earth itself.
- Decrease bath instability – the benefits of changing from Palladium to Silver activators has been documented, and discussed through this thesis. One of the major advantages of the Silver activator is increased bath stability. This results in extended solution life along with improved ease of plating. Any such improvement to the other solutions in the process would render beneficial to the industry.

10 APPENDICES

1) N.I.T.No.311 FRENCH STANDARD FOR FIRE SERVICE AND RESCUE PERSONNEL

2) BS EN443 (1997) BRITISH/EUROPEAN STANDARD: HELMETS FOR FIRE FIGHTERS

TRANSLATION FROM FRENCH

DRAFT TRANSLATION – FOR INFORMATION ONLY

TECHNICAL INFORMATION SHEET N.I.T.No. 311 2002

TECHNICAL RULES FOR PERSONAL EQUIPMENT FOR FIRE SERVICE AND RESCUE PERSONNEL

TYPE "F1" PROTECTION HELMET FOR FIREMEN

Technical information sheet approved by Decision of the Director of Civil Defence and Security of .....

ANALYSIS

This technical information sheet has been drawn by the Civil Defence and Security Directorate of the Ministry of the Interior, to implement the provisions of the Regulations of 6 May 2000 and to supplement the various standards applicable in this area. The purpose of the document is to standardise and optimise personal equipment for fire service personnel. It provides general and detailed specifications of the equipment item, and in particular lays down the requirements regarding basic materials, design criteria and decorative materials.

Compliance with the provisions of this technical information sheet will be the basis for an application for the application to the Ministry of the Interior for the classification of the equipment item and its recommendation for use.

REGULATIONS:

- European Directive 89/686 EEC of 21 December 1989, amended, on personal protective equipment
- Regulations of 6 May 2000 on uniforms, insignia and badges for the fire service

MODIFICATIONS:

- Cancels and replaces the C.C.T.P document of June 1995

NOTE D'INFORMATION TECHNIQUE

CASQUE DE PROTECTION DE TYPE "F1" POUR SAPEURS - POMPIERS

Dépôt légal le 19 avril 2002
I.S.B.N. : 2-11-090739-8

NB:

The protective helmet is an item of category 3 item of Personal Protective Equipment, in accordance with the EC Commission categorisation guide published on 8 January 1996.

The helmet is required to meet the general requirements laid down in European Directive No. 89/686 on personal protective equipment and the standard NF EN 443: May 1998, and the requirements set out in this technical information sheet.

1. GENERAL DESCRIPTION:

The helmet for fire service and rescue staff shall be "nickel" in colour, to enhance its thermal reflection properties.

The helmet shall be of the enclosing type, designed to protect the following areas:

- the entire top of the skull
- the back of the neck
- the temples and ears
- the front of the forehead

➢ mass of complete helmet, with screens (face and eye screens), without accessories and options:
- 1400g max, for size 56
- 1700g max for size 64

➢ retention system

➢ lining with shock absorption system

➢ 2 fold-away screens (1 transparent eye protection screen, 1 thermal facial protection screen)

➢ attachment points for fitting a insulating respiratory mask with straps

➢ 1 special panel, coated in gold with the words "SAPEURS-POMPIERS" [fire service] and/or emblems of the unit

➢ reflective strips in different colours according to rank.

NB: There may be additional options over and above this general specification (lamp, neck apron, communication equipment, etc.).

2. MATERIALS:

2.1 Main helmet elements :
- cap and under-shell: thermoplast or duroplast

- screens: the transparent eye screen shall protect the eyes against splashing, and the gold-colour facial screen shall protect the face against radiant heat

- retention system: straps, self-adhesive bands, leather, plastic buckles

2.2 Leather elements :
- as per identification card No. 22 (01/94) of brochure 5500 of GPEM/TC.

2.3 Chin strap and lining:
- thermostable materials

2.4 Self-adhesive bands:
- as per identification card RA 20 and RA 25 (05/89) of brochure 5508 of GPEM/TC, and class B flame retardant materials as per standard NF G 08-184 (12/95).

2.5 Hairnet:
- pre-oxidised para-aramid/carbon

2.6 Wires:
- high tensile strength, UV and abrasion resistant, in accordance with brochure 5505 (12/91) of GPEM/TC

2.7 Shock absorption and comfort materials:
- non-flammable and/or fire retardant materials.

2.8 Buckles:
- materials resistant to saline mist, with no rusting after 96 hours conditioning as per standard NF X 41-002

2.9 Reflective strips:

2.9.1 Characteristics of silver-grey strip (officers):
- reflective material, meeting single characteristic requirement for class 2,
- silver-grey material with white-coloured reflection,
- meets requirements of standard NF EN 471,
- resistant to temperature of 200°C, in ambient air, for 5 minutes.

2.9.2 Characteristics of yellow and orange-red colour strips (under-officers and ordinary firemen):
- combined characteristic materials
- resistant to temperature of de 200°C, in ambient air, for 5 minutes
- meets requirements of standard NF EN 471, except for reflection coefficient of the 2 products and chromatic coordinates for orange-red product as set out below.

Table 1

minimum reflection values, in cd / (lx.m²), new

Lighting angle	5°	20°	30°	40°
Observation angle 0.33° (20')	65	45	13	4

Table 2

colour of orange-red product

colour		chromatic coordinates				minimum luminance factor b min.
		1	2	3	4	
Red	X	0.49	0.62	0.562	0.694	0.25
Orange	Y	0.38	0.38	0.269	0.306	

2.9.3 Characteristics of silver-grey and blue strip (auxiliary firemen):
- The silver-grey colour is identical to the officers' identification colour, and the blue colour is to comply with "PANTONE Process blue C". **(see diagram)**

2.9.4 Characteristics of the silver-grey and green strip (medical service) :
- The silver-grey colour is identical to the officers' identification colour, and the green colour is to comply with "PANTONE 7490 green". **(see diagram)**

3. DETAILED DESCRIPTION:

3.1 Cap:
- the helmet consists of an external cap structure, of the enclosing type;

- this cap consists of a front half-mould on the upper helmet body up the level of the ears, displaced with respect to the rear half-mould;
- the helmet has a longitudinal stiffening rib, forming a crest, starting from the back of the neck and widening through to the front edge;
- a badge panel is placed on the front section, as an extension of the crest;
- the half-mould of the upper body accommodates two retractable screens. One is an eye protection screen, the other a facial protective screen;
- an under-shell used to secure the lining and providing the receptacle for the screens;
- the cap has attachment means for the two screens such as to ensure they remain stable;
- two essentially vertical oblong receptacles integrated with or attached to the cap, used to secure the straps attaching the mask of the respiratory unit on the helmet are placed in the lateral parts of the helmet;
- the inside of the helmet is formed so as to accommodate accessories such as neck aprons and communication systems.

3.2 Head cover:
- the stuffing between the shell and the lining is made from special materials, designed in particular to absorb the energy of an impact.

3.3 Complete lining:
- the lining, adjustable to all sizes, is attached at the level of the maximum head circumference [#] of the wearer. It must allow the use of the mask of the respiratory unit, with or without straps;
- the lining must be appropriately adjusted to maintain the stability of the helmet and comfort for the wearer without excessive pressure on the head. It performs the following functions:
  1- surrounds the upper part of the head, with a height adjustment system;
  2- keeps the back of the neck section in place, by means of an adjustment system;
  3- has an adjustment system for adjustment to the correct head circumference.

3.4 Screens:
The screens, situated in the visual field, are spherical and concentric;
- the eye screen must meet the general requirements set down in standard NF EN 166; it has a rounded edge at the point of contact with the face;
- the facial screen is lowered in front of the eyes with a simple action of a hand wearing a glove as per technical information sheet 306, over the section of the cap of the helmet remaining accessible on the outside. It must provide protection against radiant heat;
- in the lowered position, comes down to the bottom lip, in the sizes covered by the lining;
- the distance between the respiratory area of the face and the facial screen must be sufficient to prevent the screen from fogging up;
- the two screens must be operated independently.

3.5 Retention system:
- the retention system comprises a supple chin-strap attached at 2 or 3 points, with chin piece and opening buckle operated with one hand wearing a glove as per technical information sheet No. 306, with a width of 20 ± 2mm; it is tied to the cap to secure the structure on the head at all times, even when exposed to sudden movements;
- the fee end of the chin strap must not be able to come away suddenly when the chin strap is open;
- the closing system of the chin strap, with helmet placed on the head and the chin strap unfastened, must never in any circumstances make it inconvenient to wear the mask of the insulating respiratory unit.

3.6 Options:
Any adaptations for options as per §1 and their fastening systems must be approved by the helmet manufacturer.

4. ADDITIONAL SPECIFICATIONS OVER AND ABOVE STANDARD NF EN 443:1998

4.1 Cap

4.1.1 Resistance to splashes of molten zinc:
- 300g liquid zinc heated to 440°C poured onto the top of the helmet from a height of 50 to 100 mm;
- at the end of the test the cap must not have been penetrated by the molten zinc.

4.1.2 Resistance to combustion gases and smoke:
- cap to be exposed for 5 minutes to polystyrene smoke, then vinyl polychloride smoke, at a temperature of 150°C;
- at the end of the outside coating must still be resistant.

4.1.3 Resistance to chemicals:
- the following products to be applied to the outside surface of the cap for 30 seconds: 33% hydrochloric acid, ammonia, acetone, trichloroethylene;
- at the end of the tests the surface must not be significantly impaired.

4.1.4 Electrical insulation:
Before the test, the cap of the helmet is to be placed for 24h ± ½ h in a solution of 3g/l ± 0.2g/l sodium chloride at a temperature of 20°C ± 2°C. The cap of the helmet must then be removed from the bath, dried, then placed, head down, in a sufficiently large receptacle. This receptacle and the cap of the helmet shall then be filled with the same sodium chloride solution, up to 10mm below the bottom edge of the cap.

A nominal alternating voltage [sic – no voltage specified – Translator] of 60 Hz, must be applied between two electrodes, one immersed in the solution contained in the cap of the helmet and the other in the solution contained in the receptacle outside the cap of the helmet.

The voltage must then be increased to 1200V ± 25 V a.c. and held at that level for 15s. The leak current must then be recorded, along with any sign of voltage drop. During the test, the leak current must not exceed 1.2mA.

NOTE 1: If possible, the helmet should undergo the test before any holes have been made in the cap.

NOTE 2: The position of the cap of the helmet in the sodium chloride solution for this test must be adjusted if necessary as follows:
- no orifice in the cap is above the level of the water, and
- adjustment of any cap units whose bottom edges are not straight.

4.2 Screens

4.2.1 Impact resistance:
- a steel ball of 46mm in diameter with a mass of 0.4kg is allowed to fall from a height of 2.50m.;
- after the test the screens there must be no contact between the screens and the dummy head, there must be no fracture of the screens or detachment of material on the eye side.

4.2.2 Perforation resistance:
- the screen perforation tests are to be carried out in the following conditions: ambient temperature for 4 hours and –20°C for 4 hours;
- place a conical punch, with angle of 60° and mass of 0.3kg, in contact with the screen. Release a mass of 3kg from a height of 0.25m for the eye screen and 0.50m for the facial screen.
- at the end of the test the screens must not be perforated, and there must be no fracture of the screens or detachment of material on the eye side.

4.2.3 Combustion resistance:
- place a Bunsen burner (propane) with a nozzle of 10mm in diameter in contact with the screen, and remove as soon as the screen catches fire; measure the flame propagation time between two points 10mm apart;
- at the end of the test the flame propagation time must be more than 10 seconds.

4.2.4 Face screen resistance to radiant heat:
- place the screens at 150mm from two infrared tubes of 750W, with the IR tubes 100mm apart, a source temperature of 450°C, and expose screens for 12 minutes;
- at the end of the tests there must be no significant changes to the screens (colour, mechanical strength).

4.2.5 Combustion gas and smoke resistance:
- expose screens for 5 minutes to polystyrene smoke, then vinyl polychloride smoke, at a temperature of 150°C;
- at the end of the test there must be no significant changes to the screens (colour, mechanical strength).

4.2.6 Resistance of screens to chemicals:
- apply the following chemicals to the outside surface of the screens for 30 seconds: 33% hydrochloric acid, ammonia, acetone, trichloroethylene;
- the screens must still be resistant at the end of the tests.

5. REFLECTIVE ELEMENTS:

- the reflective elements are to be rectangular, with a width of 35 ± 1mm along a generatrix starting from the oblong orifices and ending at the rear part of the crest (see diagram);
- the contact surface between the cap and the attachment straps must not have any reflective elements.

Colour of straps according to rank

Officer:	**silver-grey**
Under-officer:	**yellow**
Ordinary fireman:	**orange-red**
Auxiliary personnel:	**blue, bordered with silver-grey**
Medical service:	**green bordered with silver-grey**

6. COMPLIANCE VERIFICATION:

- CE type test: by an organisation as notified.
- Specific requirements: by a laboratory designated by the civil security equipment committee.

7. MARKINGS:

7.1 CE mark:
- as per Directive 89/686 EC and standard NF EN 443 1998.

7.2 Other marks:.
- label showing recommended status from the Directorate of Civil Defence and Security;
- a unique serial number for product identification.

8. INFORMATION NOTICE:

Each helmet must be accompanied by a notice in accordance with Directive 89/686 EEC, as amended (Annex II § 1.4), clearly stating the following:
- periodic visual checks, and checks to be carried out after any specific operational event from which a deterioration in equipment performance characteristics has been observed.

9. PACKING:

The helmets are to be packed individually, with the information notice.

BRITISH STANDARD

BS EN
443 : 1997

Helmets for firefighters

The European Standard EN 443 : 1997 has the status of a British Standard

ICS 13.220.10, 13.340.20

National foreword

This British Standard is the English language version of EN 443 : 1997 published by the European Committee for Standardization (CEN). It supersedes BS 3864 : 1989, which is withdrawn.

The UK participation in its preparation was entrusted by Technical Committee PH/6, Head protection, to subcommittee PH/6/3, Helmets for firefighters, which has the responsibility to:

- aid enquirers to understand the text;
- present to the responsible European committee any enquiries on the interpretation, or proposals for change, and keep the UK interests informed;
- monitor related international and European developments and promulgate them in the UK.

A list of organizations represented on this subcommittee can be obtained on request to its secretary.

Cross-references

The British Standards which implement international or European publications referred to in this document may be found in the BSI Standards Catalogue under the section entitled 'International Standards Correspondence Index', or by using the 'Find' facility of the BSI Standards Electronic Catalogue.

Compliance with a British Standard does not of itself confer immunity from legal obligations.

Summary of pages

This document comprises a front cover, an inside front cover, the EN title page, pages 2 to 20, an inside back cover and a back cover.

This British Standard, having been prepared under the direction of the Health and Environment Sector Board, was published under the authority of the Standards Board and comes into effect on 15 December 1997

ISBN 0 580 28802 1

Amendments issued since publication

Amd. No.	Date	Text affected

EUROPEAN STANDARD
NORME EUROPÉENNE
EUROPÄISCHE NORM

EN 443

September 1997

ICS 13.220.10; 13.340.20

Descriptors: Fire fighting, accident prevention, helmets, definitions, characteristics, specifications, tests, mechanical strength, thermal resistance, marking, instructions

English version

Helmets for firefighters

Casques de sapeurs pompiers

Feuerwehrhelme

This European Standard was approved by CEN on 1997-09-04. CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration.

Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Central Secretariat or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Central Secretariat has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and United Kingdom.

CEN

European Committee for Standardization
Comité Européen de Normalisation
Europäisches Komitee für Normung

Central Secretariat: rue de Stassart 36, B-1050 Brussels

Ref. No. EN 443 : 1997 E

Foreword

This European Standard has been prepared by Technical Committee CEN/TC 158, Head protection, the secretariat of which is held by BSI.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by March 1998, and conflicting national standards shall be withdrawn at the latest by March 1998.

This European Standard has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association and supports essential requirements of EU Directive(s).

For relationship with EU Directive(s), see informative Annex ZA, which is an integral part of this standard.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

Contents

1 Scope

This European Standard specifies the principal characteristics required for a helmet for firefighters with regard to the level of protection, comfort and durability.

It allows options to take account of particular national requirements.

Helmets complying with this standard are not necessarily intended for special applications (for example: oil fires, forest fires).

Annex A and figures 1 to 9 are integral parts of this standard.

2 Normative references

This European Standard incorporates by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies.

ISO 1817 : 1985	*Rubber, vulcanized — Determination of the effect of liquids*
ISO 4892-1 : 1994	*Plastics — Methods of exposure to laboratory light sources — Part 1: General guidance*
ISO 4892-2 : 1994	*Plastics — Methods of exposure to laboratory light sources — Part 2: Xenon-arc sources*
ISO 6487 : 1987	*Road vehicles — Measurement techniques in impact tests — Instrumentation*
EN 960	*Headforms for use in the testing of protective helmets*

3 Definitions

For the purposes of this European Standard, the following definitions apply:

3.1 firefighter's helmet (hereafter referred to as helmet)

Headgear intended to ensure protection of the wearer's head against hazards which might occur during operations carried out by firefighters.

3.2 headform

A shape replacing the head which is used for testing certain helmet characteristics.

NOTE. The headform is designed in accordance with EN 960.

3.3 basic plane

3.3.1 basic plane of the human head

A plane at the level of the opening of the external auditory meatus (external ear opening) and the lower edge of the orbits (lower edge of the eye sockets).

3.3.2 basic plane of the headform

The plane which corresponds to the basic plane of the human head.

3.4 reference plane

A construction plane parallel to the basic plane of the headform at a distance from it which is a function of the size of the headform.

3.5 longitudinal vertical median plane

The vertical plane of symmetry of the headform.

3.6 sagittal plane of the helmet

The plane corresponding with the longitudinal vertical median plane of the headform when the helmet is correctly adjusted on it.

3.7 central vertical axis

The line relative to the headform that lies in the plane of symmetry, that is normal to the basic plane at a point equidistant from the front and the back of the headform at the level of the reference plane.

3.8 vertical axis of the helmet

The axis corresponding with the central vertical axis of the headform when the helmet is correctly adjusted on it.

3.9 basic shape

The outer shape which the helmet would have if it had neither comb nor brim nor any of the fairings or radiusing associated with these.

3.10 helmet shell

The component which gives the helmet its general shape and on which may be fixed various accessories.

3.11 brim

A ridge protruding outwards from the basic shape of the shell forming the lower edge of the shell and including its associated fairings and radiusing.

3.12 integral part

A part which is not removable from the helmet without use of tools.

3.13 accessory

An optional part which is removable from the helmet without need of tools.

3.14 padding

3.14.1 protective padding

Material which serves to dampen shock impact energy.

3.14.2 comfort padding

Material which serves to improve comfort for the wearer.

3.15 retention system

Those parts which are responsible for securing the helmet in position on the head, including items which enable adjustment or improved comfort.

3.16 chinstrap

Part of a retention system, including a strap which passes underneath the wearer's chin and which helps to ensure that the helmet is correctly maintained in place.

3.17 neck-guard

Integral part or accessory which protects the back of the neck from water or other liquids, from hot materials and from radiant heat.

3.18 eyes and/or face shield

Integral part or accessory placed in front of the eyes and covering part or the whole of the face.

3.19 ear flaps

Integral part or accessory of the helmet which protects the ears of the wearer.

3.20 facepiece fixing

System enabling a facepiece of a respiratory protective device to be fixed to the helmet in such a way that correct sealing around the face is achievable.

3.21 dripping

Softening with material movement and consequent detachment.

4 General characteristics

4.1 The fit of the helmet shall be adjustable, in order to improve the wearing comfort and the helmet efficiency. This adjustment shall be easily feasible by the wearer without the use of tools. When this adjustment covers several sizes of head circumference, the relevant instructions shall be given in the information supplied by the manufacturer.

4.2 There shall be no sharp edges, roughness or projection on any part of the helmet which is in contact or potential contact with the head when it is worn, such as is likely to cause discomfort or injury to the wearer.

4.3 For those parts of the helmet that come into contact with the skin, materials which are known to be likely to cause skin irritation or any adverse effect on health shall not be used. For a material not in general use, advice as to its suitability shall be sought before its introduction.

4.4 The materials should be of durable quality. Their characteristics shall not undergo appreciable alteration under the influence of ageing or of circumstances of use to which the helmet is normally subjected (exposure to sun, rain, cold, contact with the skin, effects of sweat).

4.5 Substances recommended for cleaning, maintenance or disinfection shall have no adverse effect on the helmet and shall be known not to be likely to have any adverse effect upon the wearer, when applied in accordance with the manufacturer's instructions.

4.6 After the fitting of any interchangeable integral part or accessory the helmet shall comply with this standard. The replacement of these parts shall be described in the instructions of the manufacturer.

4.7 The helmet shall allow the wearer to hear under normal circumstances of use.

4.8 The helmet shall have the facility for the fitting of optional neck, ear and face protection unless these form integral parts of the helmet.

4.9 Care shall be taken in order to avoid helmet interference with the wearing of self-contained breathing apparatus or corrective or protective glasses.

4.10 The components defined in **3.11**, **3.12**, **3.13**, **3.16**, **3.17**, **3.18**, **3.19** and **3.20** are optional.

5 Requirements

5.1 Protected area

When adjusted on the headform as in **6.1.2**, the helmet shall at least cover all the area 12,7 mm above the reference plane (see line AA' in figure 1).

5.2 Field of vision

When a helmet is adjusted on the headform as in **6.1.2**, the wearer's field of vision shall correspond to the following angles:

a) a dihedral angle of at least 105° measured horizontally between L and K on each side of the sagittal plane which passes through the point L (see figures 3 and 5);

b) an upper dihedral angle greater than 7° above the reference plane and which is defined by the straight line passing through L_1 L_2 (see figures 4 and 5);

c) a lower dihedral angle greater than 45° under the basic plane and which is defined by the straight line passing through K_1 K_2 situated on the surface of the headform at 31 mm on each side of point K (see figures 4 and 5).

5.3 Shock absorption

When a helmet is tested by the method described in **6.3**, the force transmitted to the headform shall not exceed 15 kN.

5.4 Resistance to sharp objects

When the helmet is tested in accordance with **6.4**, there shall be no contact between the striker and the headform.

5.5 Mechanical rigidity

When the helmet is tested in accordance with **6.5**, the maximum transverse and longitudinal deformations of the helmet shall not exceed 40 mm. The residual deformations shall not exceed 15 mm.

5.6 Flame resistance

When the helmet is tested in accordance with **6.6** the material shall not show:

- any drip during the whole test;
- any visible flame or glow 5 s after removal of flame.

If the external surface of the shell is made of more than one material, each material shall be tested.

5.7 Radiant heat resistance

When the helmet is tested in accordance with **6.7**, the temperature measured at the surface of the artificial head shall not rise more than 25 °C above the standard laboratory temperature, (20 ± 2) °C.

No part of the helmet shall melt to such a degree as to cause dripping of material.

Any damage or distortion exhibited by the helmet shall not adversely affect its operational compatibility or protection during impact test.

5.8 Electrical properties

5.8.1 When the helmet is tested in accordance with **6.8.1**, no evidence of breakdown shall be visible and the leakage current shall not exceed 1,2 mA.

5.8.2 When the helmet is, in addition, optionally tested in accordance with **6.8.2**, no evidence of breakdown shall be visible and the leakage current shall not exceed 1,2 mA.

5.8.3 When the helmet is, in addition, optionally tested to **5.8.1** and if needed to **5.8.2**, in accordance with **6.8.3**, no evidence of breakdown shall be visible and the leakage current shall not exceed 1,2 mA.

NOTE 1. These requirements are intended to provide protection to the wearer against short term accidental contact with live electrical conductors at voltages up to 440 V a.c.

NOTE 2. The test in **6.8.1** is intended to simulate closely the situation in use, that is the leakage current to the wearer via a live conductor touching the shell.

NOTE 3. The test in **6.8.2** is dependent only upon the transverse resistance of the shell (thickness). This effectively precludes the use of a metal shell and of metal fasteners passing through the shell.

NOTE 4. The test in **6.8.3** is also dependent upon the surface resistance of the shell and effectively precludes the use of shells which have a conductive surface (metal electro-plating). This test is intended to obviate danger if the wearer touches a helmet whose shell is in contact with a live conductor.

5.9 Retention system strength

For retention systems including a chinstrap the helmet shall be tested by the method described in **6.9**.

The maximum elongation of the whole system shall not exceed 15 mm for a load of 250 N.

The minimum width of the chinstrap shall be at least 15 mm for a load of 250 N, and the breaking strength shall be between 500 N and 1 000 N.

NOTE. No test method has been adopted as yet for a retention system not including a chinstrap. Such a retention system has to comply with the relevant essential requirements of the EEC Directive 89/686.

6 Test procedures

6.1 Samples and helmet adjustment

6.1.1 *Samples*

For every type of helmet, helmet samples shall be submitted for testing in the condition in which they are offered for sale, including any requisite holes in the shell and any means of attachment for accessories specified by the manufacturer.

No helmet sample that has been subjected to testing shall be offered for sale.

The minimum number of samples required for one set of tests is as follows:

- 1 helmet for shock absorption test (high temperature);
- 1 helmet for shock absorption test (low temperature);
- 1 helmet for shock absorption test (wet conditioning);
- 1 helmet for resistance to sharp objects test (high temperature);
- 1 helmet for resistance to sharp objects test (low temperature);
- 1 helmet for flame resistance test;
- 1 helmet for radiant heat test;
- 1 helmet for electrical properties test;
- 1 helmet for strength of the retention system test;
- 1 helmet for mechanical rigidity test.

Additional helmets shall be required if needed for optional testing.

6.1.2 *Helmet adjustment*

Before any testing on a headform, the helmet shall be adjusted in accordance with the manufacturer's instructions. If the wearing adjustment covers several sizes of headform then the size of headform representing the most unfavourable case shall be used.

6.2 Conditioning

6.2.1 *General*

Before any testing the helmet shall be conditioned in accordance with the conditioning sequences defined in table 1 and the relevant specifications defined in **6.2.2** to **6.2.8**.

6.2.2 *Stabilizing procedure*

The helmet shall be preconditioned for at least 72 h at standard temperature (20 ± 2) °C and standard relative humidity (65 ± 5) %.

6.2.3 *UV ageing*

6.2.3.1 *Apparatus*

A high pressure xenon 450 watt lamp with quartz casing, operated in accordance with the lamp manufacturer's instructions.

A means to support the helmet so that it is exposed to the radiation.

6.2.3.2 *Procedure*

Secure the helmet so that the vertical axis through the crown of the helmet (as worn) is perpendicular to the axis of the lamp and the distance between the crown of the helmet and the axis of the lamp is (150 ± 5) mm. Expose the helmet to the radiation for (400 ± 4) h. It shall then be removed and allowed to return to laboratory ambient conditions.

NOTE. The method described in annex A may be used as an alternative.

6.2.4 *Thermal shock*

Expose the helmet successively to the following conditions:

a) 1 h at a temperature of (−10 ± 2) °C;
b) 1 h at a temperature of (60 ± 2) °C;
c) 15 min totally immersed in distilled water at a temperature of (10 ± 2) °C;
d) 1 h at a temperature of (60 ± 2) °C;
e) 20 h to 24 h at standard temperature (20 ± 2) °C and standard relative humidity (65 ± 5)%.

The time interval between sequences a) to b), b) to c) and c) to d) shall be within 5 s.

During sequences d) and e), the helmet shall be in a position that allows it to drain.

Optional temperatures in sequence a) are (−20 ± 2)°C, (−30 ± 2)°C or (−40 ± 2)°C.

6.2.5 *Solvent conditioning*

Take a cotton cloth approximately 150 mm square and approximately 25 ml of a solvent consisting of test liquid B in accordance with ISO 1817 : 1985, table 1. Using the cloth soaked in the solvent, apply the solvent to all those regions of the outside surface of the helmet shell within 50 mm of the retention system fixing, and keep these regions wet with the solvent for (7,5 ± 2,5) s. Repeat the procedure on the remainder of the external surface, keeping these regions wet for (12,5 ± 2,5) s. Do not carry out further conditioning or testing during the following 30 min.

6.2.6 *Wet conditioning*

The helmet shall be totally immersed in distilled water at (20 ± 2) °C for between 4 h and 24 h.

6.2.7 *'Thermal plus' conditioning*

The helmet shall be exposed to a temperature of (50 ± 2) °C for between 4 h and 24 h.

6.2.8 *'Thermal minus' conditioning*

The helmet shall be exposed to a temperature of (−10 ± 2) °C for between 4 h and 24 h. If any optional temperature is used in accordance with **6.2.4**, that temperature shall be used for 'thermal minus' conditioning.

Table 1. Conditioning

	Stabilizing procedure	UV ageing	Thermal shock	Solvent B	Thermal plus	Thermal minus	Wet	Specific test
Sequence	1	2	3	4	5	5	5	6
Protected area	X							X
Field of vision	X							X
Shock absorption	X	X	X	X	X			X
	X	X	X	X		X		X
	X	X	X	X			X	X
Resistance to sharp objects	X	X	X	X	X			X
	X	X	X	X		X		X
Flame resistance	X	X	X		X			X
Radiant heat	X	X	X					X
Electrical properties	X	X	X					X
Strength of the retention system	X	X	X					X
Mechanical rigidity	X	X	X					X

6.3 Shock absorption

6.3.1 *Principle*

Shock absorption is measured by the direct measurement of the maximum force transmitted to a rigidly mounted helmeted headform.

6.3.2 *Apparatus*

The base of the apparatus shall be monolithic and sufficiently large to offer full resistance to the effect of the blow. It shall have a mass of at least 500 kg and shall be suitably installed to obviate the return compression wave.

A headform shall be rigidly mounted on the base, either in a vertical position or in an inclined position, in order to permit testing to **6.3.3**.

A striker, having a mass of $\left(5{,}0\ {}^{+0.1}_{0}\right)$ kg and a hemispherical striking face of (50 ± 1) mm radius, shall be positioned above the headform so that its axis passes through the impact point and so that it may be dropped in either free or guided fall. If guided fall is employed, the velocity of the striker, measured at a distance not exceeding 60 mm prior to impact, shall be within 5 % of that which would be obtained with free fall.

The impact force shall be measured by a low-inertia force transducer firmly attached to the base. It shall be positioned so that its axis is co-axial with the path of the striker. The force transducer shall be able to withstand forces up to 40 kN without damage.

The measuring system, including the headform and its mounting, shall have a frequency response in accordance with channel frequency class CFC 600 of ISO 6487 : 1987.

6.3.3 *Procedure*

a) Adjust each of the sample helmets in accordance with **6.1.2** and condition in accordance with **6.2**.

b) Mount the sample on the headform in the manner in which it is intended to be worn on the head.

c) Allow the striker to fall on to each of the 5 impact points shown in figures 1 and 2.

d) Carry out the first impact within (60 ± 10) s of removal from conditioning. Within (60 ± 10) s of the first impact, return the helmet to the requested thermal conditions for a period of (15 ± 2) min. Remove the helmet and carry out the next impact within (60 ± 10) s. Repeat this procedure for the subsequent impacts.

e) The drop height shall be ($2\,500 \pm 5$) mm, measured from the underside of the striker to the target point on the helmet.

NOTE. This corresponds to a nominal impact energy of 123 J.

f) For each impact, a record shall be made of the transmitted force and the maximum shall be noted.

6.4 Resistance to sharp objects

6.4.1 *Principle*

A sharp striker (simulating the corner of a roof slate) is dropped on to the upper part of the helmet. Any contact of the striker with the headform shall be noted.

6.4.2 *Apparatus*

A test headform is mounted on a rigid base. A sharp striker is mounted, point downwards, so that it can be dropped in substantially frictionless guided fall onto the upper part of the helmet, avoiding any local reinforcement.

The striker is shown in figure 6 and consists essentially of a carriage, which may be of any suitable type, carrying below it a flat steel blade with parallel faces. The lower section of the blade tapers in width, but not in thickness, to an edge which has a small flat at right angles to its axis. The upper section of the blade has a constant cross-section and is long enough to enable the tip of the blade to reach the test headform without any part of the striker other than the blade touching the helmet.

Details of the striker are as follows.

Mass:	(400 ± 10) g
Thickness:	($6{,}0 \pm 0{,}25$) mm
Width of upper section:	($38{,}0 \pm 0{,}25$) mm
Included angle of taper of lower section:	(40 ± 2)°
Width of flat tip:	($0{,}25 \pm 0{,}05$) mm
Hardness of tip:	50 to 45 HRC

A suitable device shall be provided in order to detect any contact between the striker and the headform.

6.4.3 *Procedure*

a) Adjust each of the sample helmets in accordance with **6.1.2** and condition as in **6.2**.

b) Mount the sample helmet on the headform in the manner in which it is intended to be worn on the head.

c) Allow the striker to fall with the vertical axis perpendicular to the surface of the helmet, on to each of 3 sites separated by at least 70 mm, measured with a chord and within the area defined by a circle of 100 mm diameter centred on the central vertical axis of the helmet.

d) Carry out the first impact within (60 ± 10) s of removal from conditioning. Within (60 ± 10) s after first impact, return the helmet to the requested thermal conditions for a period of (15 ± 2) min. Remove the helmet and carry out the next impact within (60 ± 10) s. Repeat this procedure for the subsequent impact.

e) The drop height shall be ($2\,500 \pm 5$) mm, measured from the tip of the striker to the target point on the helmet.

6.5 Mechanical rigidity

6.5.1 *Principle*

The helmet is subjected to transverse compressive force, then to longitudinal compressive force. The maximum and the residual deformations are measured.

6.5.2 *Procedure*

a) Condition the helmet as specified in **6.2**.

b) Place the helmet between two guided rigid parallel plates of size 300 mm × 250 mm nominal, having their lower 300 mm long inner edges radiused to ($10 \pm 0{,}5$) mm.

c) Position the lower edges of the plates at the level of the AA' plane.

d) Apply an initial force of 30 N perpendicular to the plates, so that the helmet is subjected to a compressive force. After 30 s measure the distance between the plates.

e) Increase the forces by 100 N/min up to 630 N and hold for 30 s. Measure the distance between the plates and calculate the maximum deformation.

f) Decrease the force to 25 N and then immediately increase to 30 N, and hold for 30 s. Measure the distance between the plates and calculate the residual deformation.

g) Make measurements to the nearest millimetre, and note the extent of damage, if any.

6.6 Flame resistance

6.6.1 *Principle*

A standard flame is applied to the outside of the helmet and any tendency to drip, glow or to continue burning after removal of the flame is observed.

6.6.2 *Apparatus*

The apparatus consists of a supply of gas, a gas burner, a pressure control device and pressure gauge.

The gas shall be propane with a minimum purity of 95 %.

The gas burner shall have a bore diameter of 10 mm and an adjustable air vent.

6.6.3 *Procedure*

a) Adjust the gas pressure to ($3\,450 \pm 50$) Pa and the air vent so that the blue cone is clearly defined, although turbulent, and is (45 ± 5) mm long. The outer flame shall be entirely free of visible yellow area.

b) Condition the helmet as specified in **6.2**.

c) Support the burner at an angle of (45 ± 10) ° to the vertical, so that the flame points upward.

d) Support the complete helmet, so that at the point to be tested the plane tangential to the surface is horizontal (see figure 7). Maintaining these angles, apply the outer part of the flame to the point of test for (15 ± 2) s.

e) The test point (see figure 8) shall be any suitable point inside the areas defined by the intersection of the surface of the shell with:

- a 100 mm diameter cylinder centred on the vertical axis of the helmet;
- a 200 mm diameter cylinder centred on the vertical axis of the helmet;
- planes parallel to the sagittal plane of the helmet and 25 mm distant from this plane.

6.7 Resistance to radiant heat

6.7.1 *Principle*

Heat radiation of a known intensity from an infrared source is allowed to fall onto the outer surface of a helmet mounted on an instrumented headform. The temperature of the headform surface is measured.

When this part of the test is completed the helmet is impacted once only on the site which has been exposed to the heat.

6.7.2 *Apparatus*

6.7.2.1 *Components*

The principle of a suitable apparatus is shown in figure 9. The apparatus consists of:

- a bank of heaters (**6.7.2.2**);
- a calibrated radiometer/calorimeter (**6.7.2.3**);
- a wooden headform (**6.7.2.4**);
- a set of temperature sensing elements (**6.7.2.5**).

6.7.2.2 *Bank of heaters*

A heater or a bank of heaters is mounted with its radiating surface horizontal and facing downwards. The radiating surface shall be flat and its dimensions (250 ± 5) mm × (250 ± 5) mm.

The peak wavelength of the emitted heat radiation shall be between 2 µm and 3 µm. The intensity of radiation shall be uniform and shall be adjustable.

6.7.2.3 *Calibrated calorimeter/radiometer*

A calibrated (see notes) calorimeter/radiometer is mounted on a movable and adjustable device with its sensing surface parallel to the bank of heaters and facing upwards. The centre of its sensing surface shall be adjusted on the vertical axis of the heater.

6.7.2.4 *Headform*

A headform, constructed of hardwood or of any material with an equivalent thermal conductivity and complying with EN 960, shall be mounted on a movable and adjustable device.

The test site shall be one of the two points, L4 - L5, defined in figure 2, corresponding to a 30° lateral inclination of the headform relative to the vertical.

6.7.2.5 *Temperature sensing elements*

Three calibrated (see notes) temperature sensing elements [preferably consisting of thermocouples mounted on circular copper discs of (7 ± 1) mm diameter] are secured by electrically insulating adhesive to the headform surface on the side to be exposed to the heat.

Their centres shall be within 5 mm of a transverse vertical plane passing through the test site, at the following positions:

a) on the central vertical axis;

b) on the AA' plane;

c) mid-way between position a) and b) measured along the headform surface.

NOTE 1. Suitable ISO or CEN standards should be selected, when available, for these calibration requirements.

NOTE 2. Surfaces adjacent to this test equipment should not reflect the radiant heat falling on them or allow passage of measurable quantities of heat into the test equipment area.

NOTE 3. The effects of draughts should be minimized.

NOTE 4. All supports for headform and radiometer/calorimeter should be of low heat conductivity and reflectivity.

6.7.3 ***Procedure***

a) Condition the helmet as specified in **6.2**.

b) Mount the helmet on the headform, in accordance with **6.1.2** and in the manner it is intended to be worn on the head, with the test site lying on the vertical axis of the heater bank and measure the distance from the radiating surface.

c) Move the helmeted headform aside to allow setting of the radiant heat intensity.

d) Move the radiometer/calorimeter under the heater bank until their vertical axes are coincident and adjust the distance from the radiating surface in compliance with the distance measured in **6.7.3**.b. Adjust the heater controls until the flux intensity measured is $(7 \pm 0,1)$ kW/m^2, or $(14 \pm 0,1)$ kW/m^2 optionally. Remove the radiometer/calorimeter.

e) Replace the helmeted headform in the position determined in **6.7.3**.b and expose the helmet to the radiant heat for (180 ± 2) s. Record the temperatures.

f) After removal, allow the helmet to cool to ambient temperature for at least 4 h. After inspection, impact the helmet once on the exposed lateral point, using the procedure defined in **6.3** except the conditioning. The test result shall comply with the requirement of **5.3**.

6.8 Electrical properties

6.8.1 ***Conductive headform test***

6.8.1.1 *Principle*

The leakage current between the outside and inside of the complete helmet (as supplied by the manufacturer) is measured at a specified voltage, when the helmet is mounted on a metal headform in compliance with EN 960.

6.8.1.2 *Procedure*

a) Condition the helmet as specified in **6.2**.

b) Immerse the complete helmet in fresh tap water at room temperature for a period of (15 ± 2) minutes. Remove the helmet from the water and allow to drain for not longer than 2 min.

c) Mount the helmet crown uppermost on an appropriately sized aluminium headform with the retention system firmly secured.

d) Apply an alternating test voltage at nominally 50 or 60 Hz between the aluminium headform and a suitably insulated hand-held metal probe of 4 mm diameter and with a hemispherical radiused end.

e) Apply the probe at any point on the external surface of the helmet shell situated at, or above, its lower edge. Repeat the test in order to investigate a number of test points.

f) At each test point, increase the voltage at a steady rate within 1 min to (1200 ± 25) V a.c., and maintain at this value for 15 s. Record the leakage current at this voltage together with any evidence of breakdown.

6.8.2 ***Wet helmet insulation test (optional)***

6.8.2.1 *Principle*

The leakage current between the outside and inside of the helmet shell is measured at a specified voltage.

6.8.2.2 *Procedure*

a) Condition the helmet as specified in **6.2**.

b) Before the test, place the helmet shell for $(24 \pm 0,5)$ h in a $(3 \pm 0,2)$ g/l solution of sodium chloride at a temperature of (20 ± 2) °C. Remove the helmet shell, wipe and place upside down in a container of appropriate size. Fill the container and the helmet shell with the sodium chloride solution up to 10 mm below the lower edge of the shell.

c) Apply an alternating test voltage at nominally 50 or 60 Hz between an electrode immersed in the solution inside the helmet shell and another electrode in the container, outside of the helmet shell.

d) Increase the voltage at a steady rate within one min to (1200 ± 25) V a.c. and maintain at this value for 15 s. The leakage current at this voltage shall be recorded, together with any evidence of breakdown.

NOTE 1. For the purposes of this test it is permissible to plug any holes in the shell.

NOTE 2. The orientation of the helmet shell in the sodium chloride solution for the test should be adjusted where necessary in order to accomodate shells whose lower edge is not straight.

6.8.3 ***Surface insulation test (optional)***

6.8.3.1 *Principle*

The leakage current between any 2 points on the surface of the complete helmet is measured at a specified voltage.

6.8.3.2 *Procedure*

a) Condition the helmet as specified in **6.2**.

b) Ensure that the shell of the helmet is dry before the test.

c) Apply an alternating test voltage at nominally 50 or 60 Hz between two suitably insulated hand-held metal probes of 4 mm diameter and with hemispherical radiused ends.

d) Apply the probes at any two points on the surface of the helmet shell (inside and/or outside) located not closer than 20 mm to each other.

e) Repeat the test in order to investigate a number of pairs of test points.

f) At each test point, increase the voltage at a steady rate within one min to (1200 ± 25) V a.c., and maintain at this value for 15 s. Record the leakage current at this voltage together with any evidence of breakdown.

6.9 Retention system strength

6.9.1 ***Principle***

The helmet is supported on a headform. The width of the chinstrap, the elongation and the ultimate tensile strength of the system are measured.

6.9.2 ***Apparatus***

The apparatus consists of a headform, suitably supported, and an artificial jaw comprising two cylindrical rollers of diameter $(12,5 \pm 5)$ mm, with their longitudinal axes separated by (75 ± 2) mm. A means of applying a known variable force to the artificial jaw is also required.

6.9.3 ***Procedure***

a) Condition the helmet in accordance with **6.2** and mount it on the headform with the chinstrap passed around the artificial jaw.

b) Apply an initial load of 30 N to ensure that the fastening device is correctly tightened. Note the position, P_0, of the load-bearing spindle.

c) Increase the load linearly over a period of 30 s up to 250 N. Maintain this value for 2 min. Then note the position, P_1, of the load-bearing spindle and measure the width of the strap. The distance, P_0 to P_1, is considered as the elongation of the system.

d) Increase the load linearly at a rate of 500 N per min, until rupture or opening of the system. Note the corresponding value.

7 Marking

7.1 Every helmet claimed to comply with the requirements of this European Standard shall carry durable marking on the shell giving the following information.

a) Number of this European Standard.

b) Name or identification mark of the manufacturer.

c) Year of manufacture.

d) Type of helmet (manufacturer's designation).

e) Its size or size range (in cm).

7.2 All the replaceable parts shall be clearly identifiable.

7.3 Every helmet claimed to comply with the optional requirements of this European Standard shall carry durable marking on the shell giving the following information:

- radiant heat classification (see **5.7**);
- electrical properties classification (see **5.8**);
- low temperature classification (see **6.2.4** and **6.2.8**).

The options and the corresponding markings are shown in table 2.

Table 2. Optional performance requirements — Markings

Option	Marking
Radiant heat classification: 14 kW/m	[14] ******
Electrical properties classification:	
- according to **6.8.2**	E2
- according to **6.8.3**	E3
Low temperature classification:	
−20°C	**
−30°C	***
−40°C	****

Marking of any optional requirements shall be adjacent to each other

EXAMPLES: [14]E3****** E2E3**

8 Information to be supplied by the manufacturer

The following information shall be clearly and fully provided with each helmet in one of the official languages of the country of destination.

a) Name and address of the manufacturer or agent and type(s) of helmet.

b) Instructions or recommendations regarding storage, use, size-adjustment, cleaning, maintenance, servicing and disinfection.

c) Details of any optional requirements of this standard which apply to the helmet, e.g. by reference to the marking system (see **7.3**).

d) Details of accessories approved by the manufacturer and appropriate spare parts, including reference to sizes where necessary.

e) Details of the type of packaging suitable for transportation of the helmet.

f) Warning that the safety intended to be provided by the helmet can only be ensured when it is properly assembled and correctly fitted, and that removable parts shall not be worn separately.

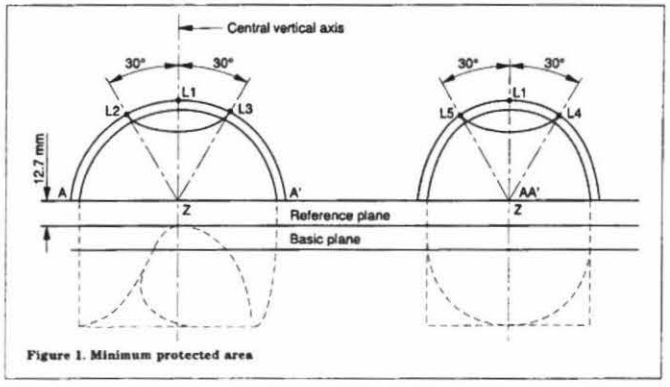


Figure 1. Minimum protected area

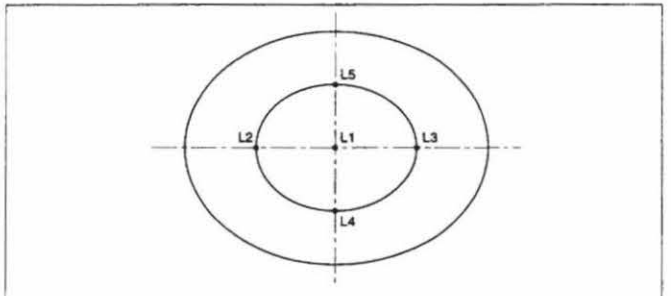


Figure 2. Impact points on the helmet

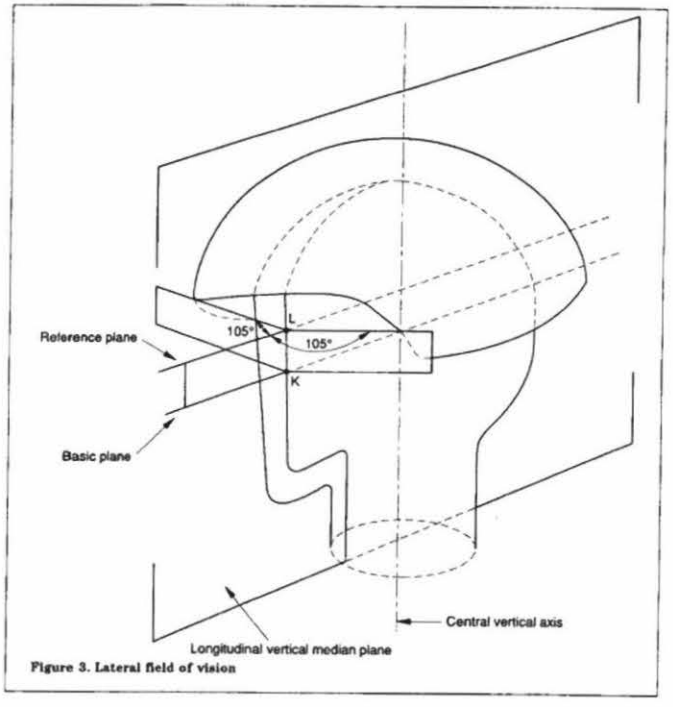


Figure 3. Lateral field of vision

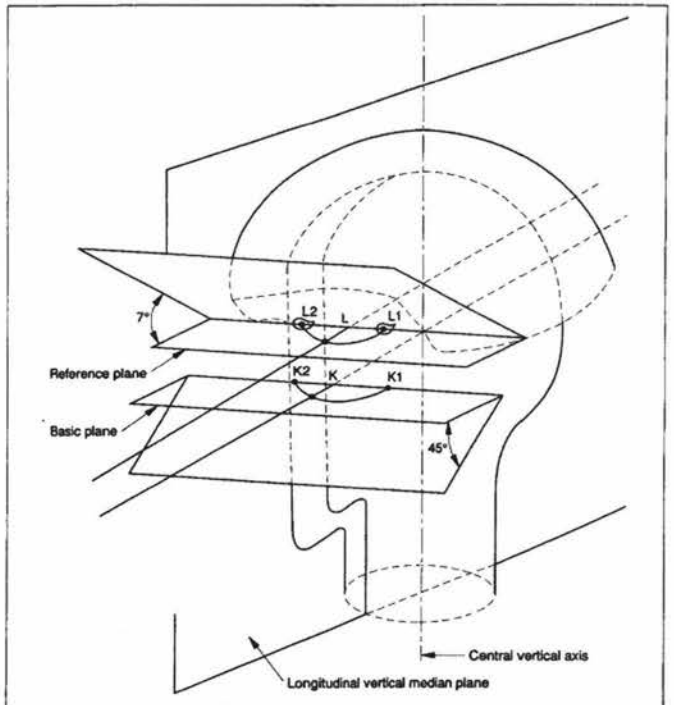


Figure 4. Vertical field of vision

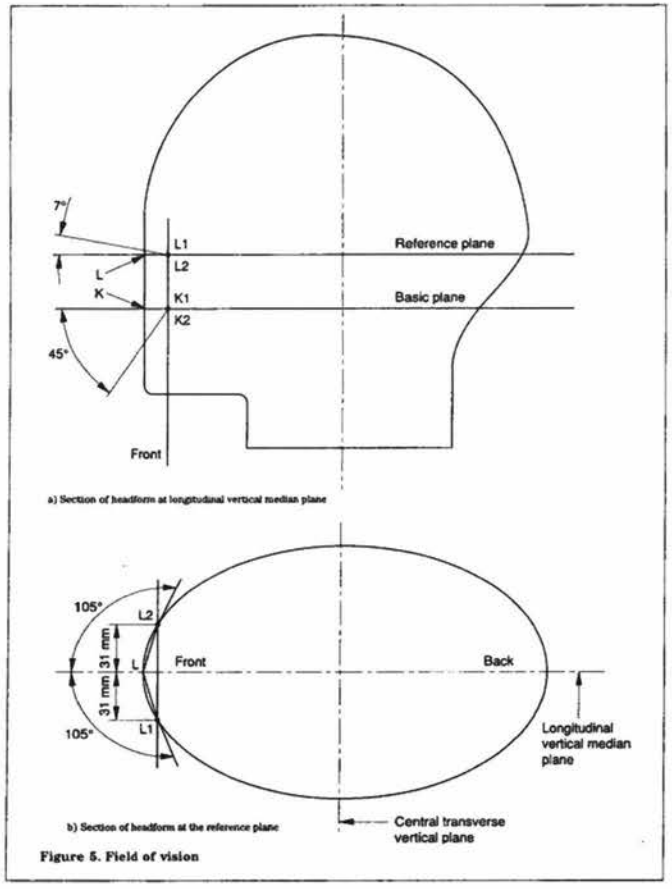


Figure 5. Field of vision

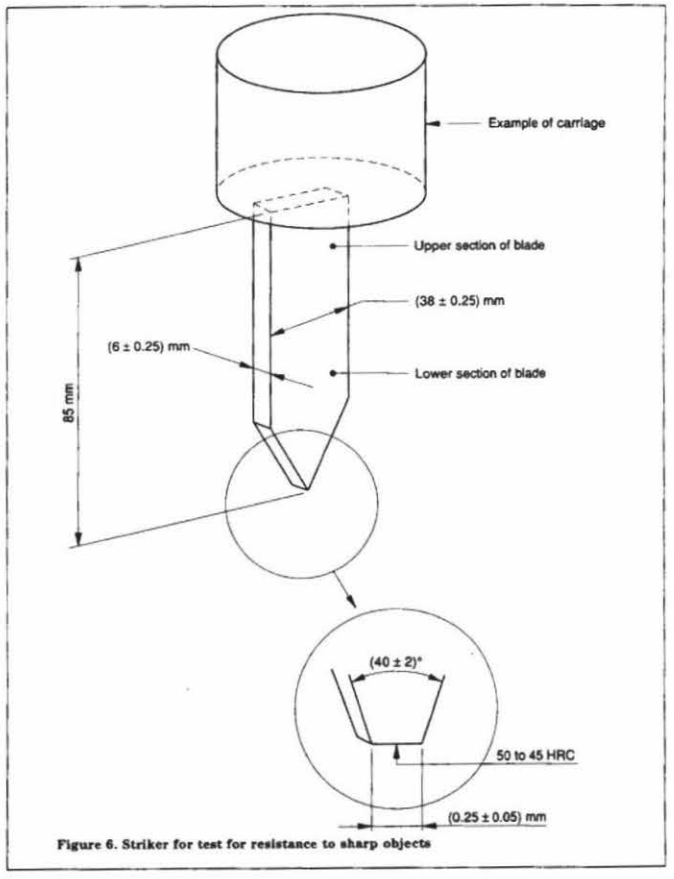


Figure 6. Striker for test for resistance to sharp objects

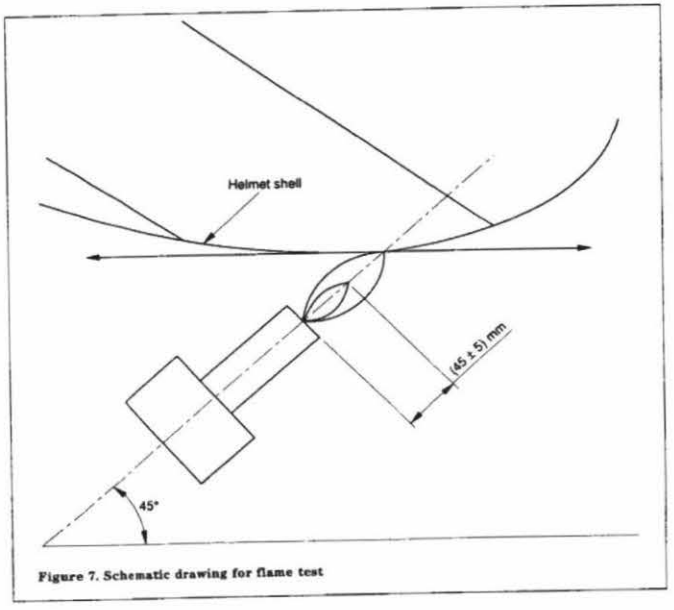


Figure 7. Schematic drawing for flame test

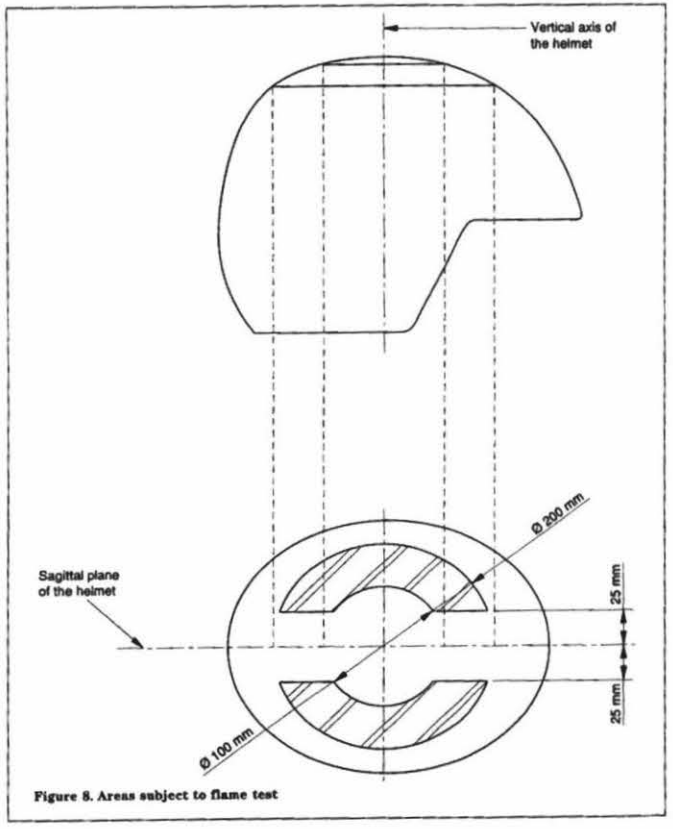


Figure 8. Areas subject to flame test

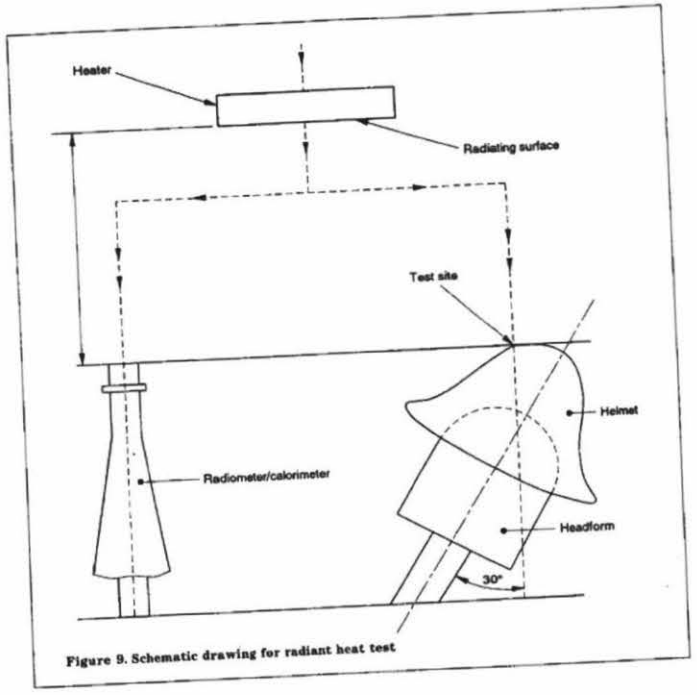


Figure 9. Schematic drawing for radiant heat test

Annex A (informative)

UV ageing — Alternative test method

The helmet submitted to artificial ageing should be exposed to the radiation of a Xenon arc lamp. The radiant energy of the lamp should be filtered to provide a spectral power distribution that closely approximates that of terrestrial daylight.

The helmet should be fixed on a cylindrical holder concentric to the lamp and which rotates at a speed of 1 to 5 rev/min around its axis.

Each helmet which will subsequently be tested for shock absorption or for penetration should be orientated so that the area of test is directed towards the lamp. The plane tangential to the shell at this point should be normal to a radius of the cylindrical holder.

The radiant energy incident in the plane of the test areas should be either measured or calculated from information provided by the manufacturer of the test apparatus. The exposure interval should be adjusted so that the exposed samples should receive a total energy of 1 GJ/m^2 over the wavelength range 280 nm to 800 nm.

The sample should be sprayed with distilled or demineralized water (having a conductivity below 5 μS/cm) intermittently with a cycle of 18 min of spraying and 102 min without spraying. During the latter periods the measured relative humidity should be (50 ± 5) %.

The temperature within the test chamber should be measured with a black standard thermometer placed at the same distance from the lamp as the exposed test areas of the helmets. The temperature should be maintained at (70 ± 3) °C.

All other test and calibration conditions for the apparatus should be in accordance with ISO 4892-1 and ISO 4892-2, Method A.

NOTE 1. Not all available test apparatus, otherwise meeting the requirements of ISO 4892, will incorporate sample holder frames of diameter sufficient to accomodate complete helmets.

NOTE 2. The position of the water sprays may require adjustment in order to avoid interference with the test samples.

NOTE 3. The energy output of the Xenon arcs should be capable of being reduced below normal operational levels, so as to maintain acceptable intensities in the sample surface plane required by this procedure.

Annex ZA (informative)

Clauses of this European Standard addressing essential requirements or other provisions of EU Directives

This European Standard has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association and supports essential requirements of EU Directive 89/686/EEC.

WARNING. Other requirements and other EU Directives may be applicable to the product(s) falling within the scope of this standard.

The following clauses of this standard are likely to support requirements of Directive 89/686/EEC, Annex II:

EU Directive 89/686/EEC, Annex II	Clauses of this standard
1.1 Design principles	**4.1** to **4.9**, **5** and **6**, **7**, **8**
1.2 Innocuousness of PPE	**4.2**, **4.3**, **4.7**, **4.9**
1.3 Comfort and efficiency	**4.1**, **4.4**, **4.6**, **4.8**, **4.9**
1.4 Information supplied by the manufacturer	**4.5**, **4.6**, **7**, **8**
2.4 PPE subject to ageing	**6.2.1**, **6.2.3** and **5.3/6.3**, **5.4/6.4**, **5.6/6.6**, **5.7/6.7**, **5.8/6.8**, **5.9/6.9**, **5.5/6.5**
2.9 PPE incorporating components which can be adjusted or removed by the user	**4.1**, **4.8**
2.12 PPE bearing one or more identification or recognition marks directly or indirectly relating to health and safety	**7**, **8**
3.1 Protection against mechanical impact	**5.3/6.3**
3.8 Protection against electric shock	**5.8/6.8**

Compliance with the clauses of this standard provides one means of conforming with the specific essential requirements of the Directives concerned and associated EFTA regulations.

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