HEAVYWEIGHT PHOSPHATING OF RUBBER-TO-METAL BONDED PRODUCTS

A THESIS SUBMITTED FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

By

Peter Johnson June 1981

THE UNIVERSITY
OF ASTON
IN BIRMINGHAM

THE UNIVERSITY OF ASTON IN BIRMINGHAM

Peter Johnson
Submitted for the Degree of Ph.D 1981

Heavyweight phosphating of rubber-to-metal bonded products.

SUMMARY

The initial objective set for this project was to identify a range of anti-corrosion finishes for rubber-to-metal bonded products, that would withstand the periods of exposure to the salt spray test required by the sponsoring manufacturer's customers. Preliminary research showed that the range of finishes used were capable of meeting the customers requirements but the phosphate and sealant finishes used for over 45% (volume) of production were failing to meet the requirements imposed on them. Having determined that the phosphate and sealant finishes could not easily be replaced the objective became to ensure that these finishes achieved their potential resistance to the salt spray test.

A literature survey is presented, covering the salt spray test and the heavyweight phosphating of mild steel. The work then concentrates on three areas, the preparation of the metal surfaces for phosphating, the phosphating solution used and the phosphating plant used.

Preparation of the metal surfaces for phosphating was found to be inadequate. The work of identifying and installing a machine capable of the required cleaning action is described.

Organic materials leached from the rubber sections of the products were detected in the phosphating solution. It is suggested that these materials interfered with the phosphating reactions. The work of identifying and introducing a more suitable phosphating solution is described.

These changes resulted in the phosphate and sealant finishes meeting the customers salt spray resistance requirements, and the performance of the finishes in an atmospheric corrosion test also show a corresponding improvement. To ensure the consistent production of the required quality of phosphate and sealant finishes the purchase of a fully automatic phosphating plant is recommended.

The sponsors attitude to anti-corrosion finishing is discussed with reference to the business environment in which the company operates.

Key Words: Phosphating; Rubber; Corrosion; Finishing; Automotive.

DEDICATION

This work is dedicated to my mother.

ACKNOWLEDGEMENTS

I would like to take this opportunity to thank Dr. G.Beaumont, Mr. D.Hickson and in particular Dr. A.Amass of the University of Aston in Birmingham for the many useful discussions that have taken place during this work. In Dunlop I was fortunate to be supervised by Mr. G.Hopkins. To these people and the many others I am unable to include here, I wish to extend my thanks for the help and attention they freely gave.

CONTENTS

Page Number

Chapter 1 - Introduction

Page Number

Chapter 2 - Literature Survey

Chapter 3 - Experimental Method

Page Number

Page Number

Chapter 4 - Preparation of the metal surface for phosphating

Page Numbers

Page Number

Page number

Page Number

LIST OF TABLES

Page Number

Chapter 1

Chapter 2

Chapter 3

Chapter 4

Chapter 5

Page Number

Chapter 6

LIST OF FIGURES

Page Number

Chapter 1

Chapter 2

Chapter 3

Chapter 4

Chapter 5

Page Number

Page Number

Chapter 6

Chapter 7

CHAPTER 1

INTRODUCTION

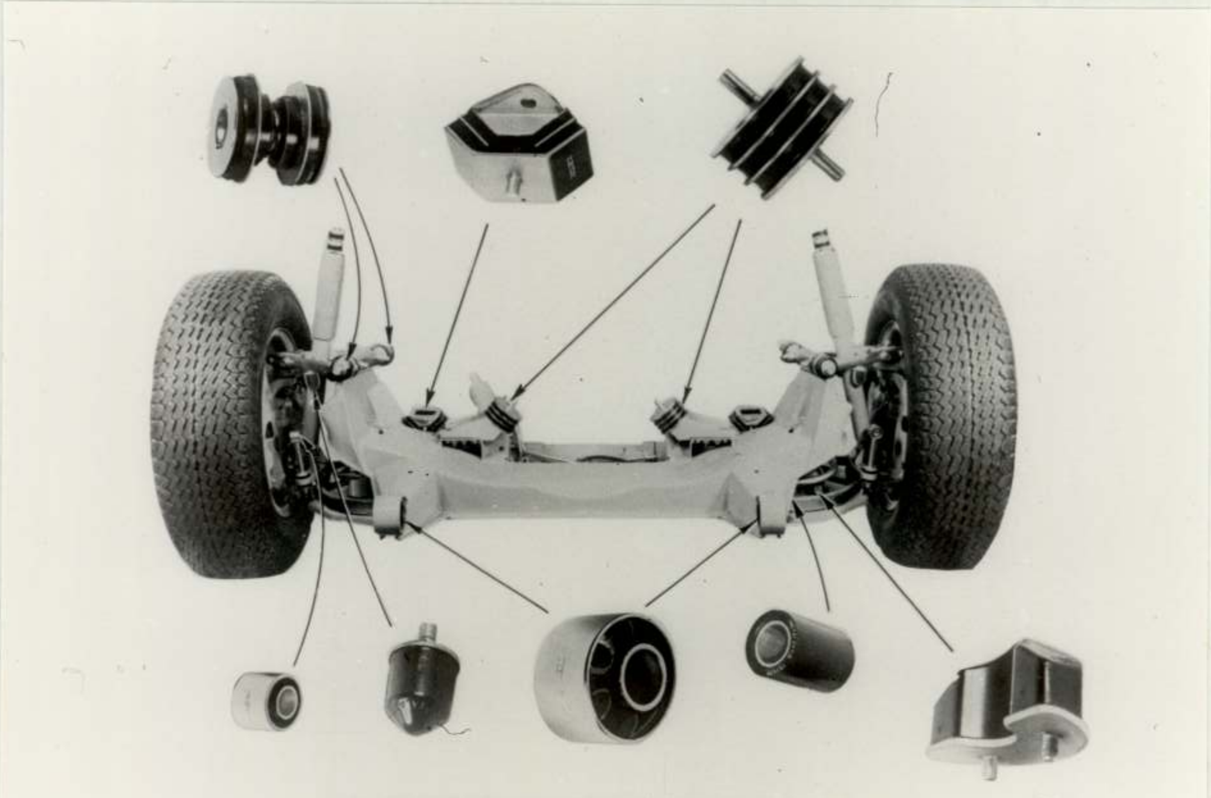
1.1. Products and markets

The work presented in this thesis is concerned with the anti-corrosion finishing of the ferrous metals in the rubber-to-metal bonded products made by Metalastik, a product group of Dunlop Polymer Engineering Division, Leicester. These rubber-to-metal bonded products are used to combat the effects of noise vibration and wear in every branch of engineering. Three sales departments service this market, and in a typical year each department accounts for the following percentage of Metalastik's total sales volume.

Department	% of total sales(volume)
Automotive	56
Rail and Marine	15
Industrial	29

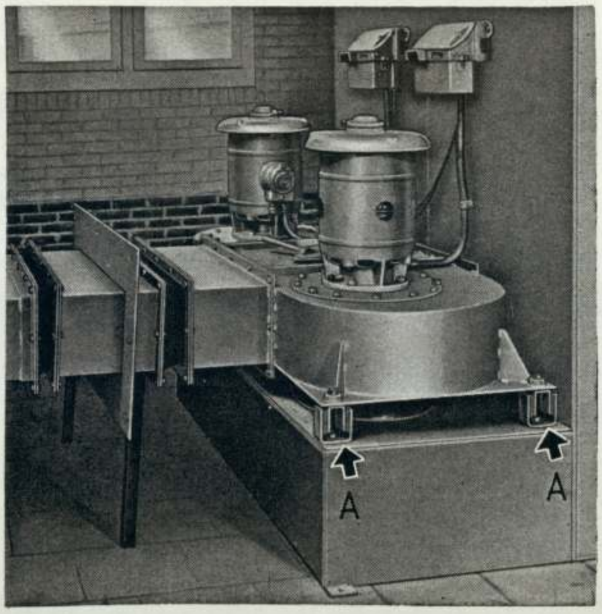
A few typical products are presented in figures 1.1 to 1.3 to give an indication of their variety, in both physical size and use. For a more comprehensive view of the uses of these products, Allen, Lindley and Payne's book, Use of Rubber in Engineering (1) should be consulted.

The large percentage of automotive sales combined with the environmentally exposed mounting positions of the products used in that market indicates one of the major inputs into this project was to be the finishing requirements of the automotive customers.



FRONT SUSPENSION OF JAGUAR XJ6
SHOWING METALASTIK COMPONENTS FITTED

Figure 1.1 Examples of rubber-to-metal bonded products supplied to the automotive market

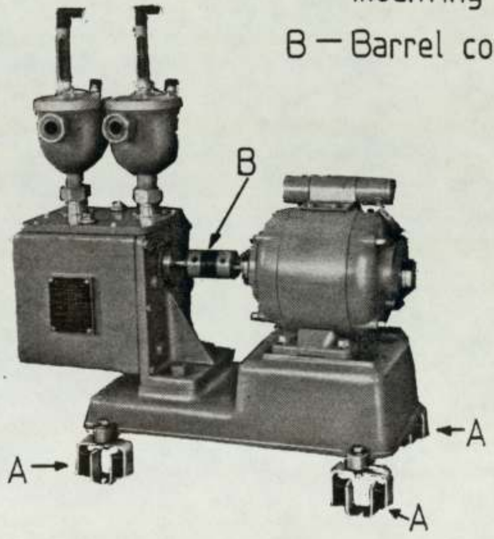


Extractor fans

Key

A — Double-U-shear mounting

B — Barrel coupling



Compressor

Figure 1.2 Examples of rubber-to-metal bonded products supplied to the industrial market

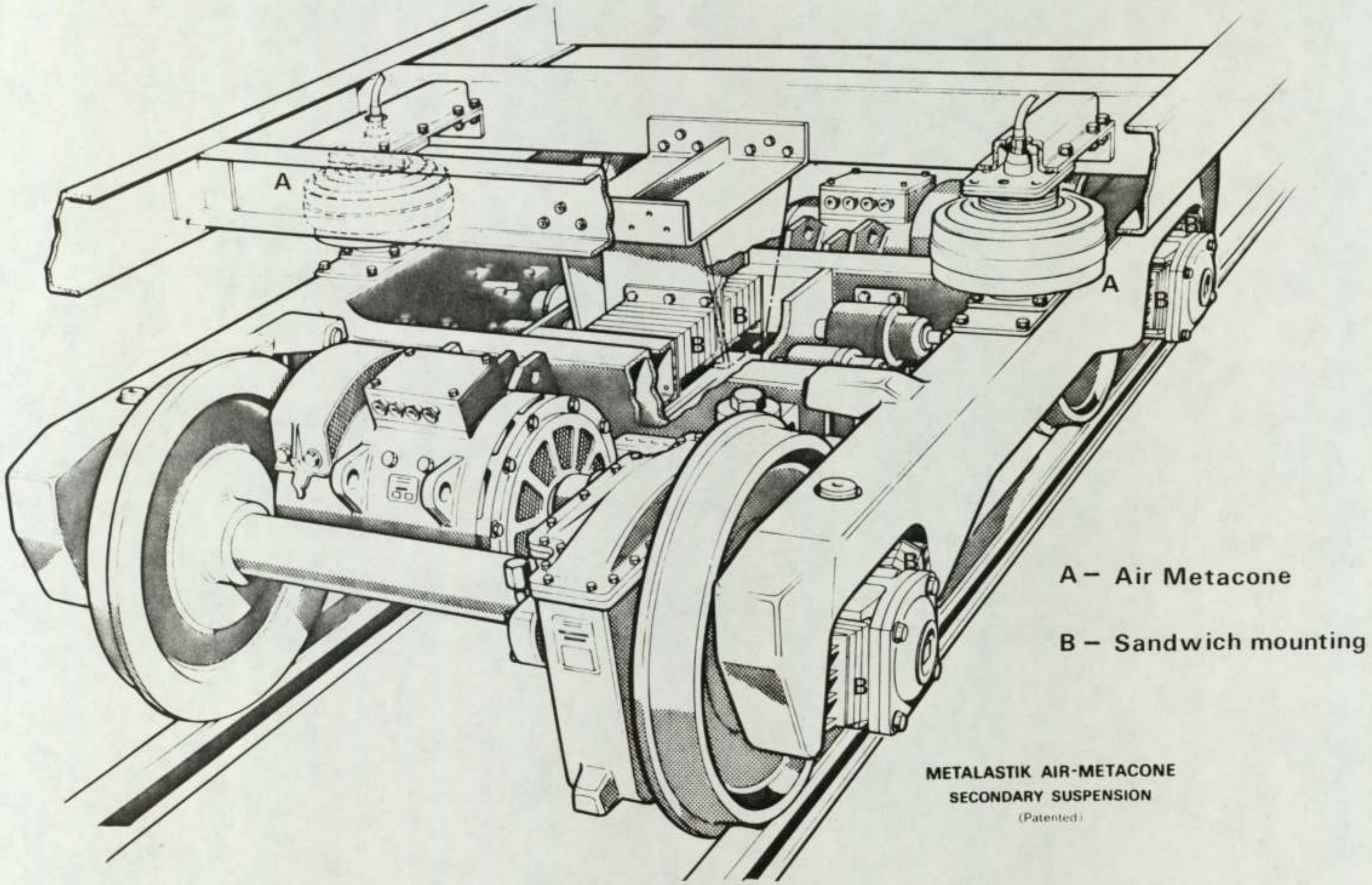


Figure 1.3 Examples of rubber-to-metal bonded products supplied to the rail market

1.2 Manufacture

In this section a brief overview of the manufacturing processes, at Metalastik, relevant to the project is presented, with emphasis on the areas of direct relevance to the anti-corrosion finishing of these products. The processes are presented in a schematic flow diagram in figure 1.4 under three headings:-

(i) Material preparation

The production of the rubber compound and preparation of the metal sections.

(ii) Bonding and curing

Assemblage of the metal sections and the rubber compound to form the product.

(iii) Finishing operations

The cleaning, mechanical and anti-corrosion finishing operations carried out after bonding and curing.

1.2.1 Material preparation

There are two clearly discernable routes in materials preparation, the production of the rubber compound and the preparation of the metal sections.

1.2.1.1 Rubber compound

Rubber compounds are manufactured on site. The ingredients used vary according to which compound is being made but would typically include:-

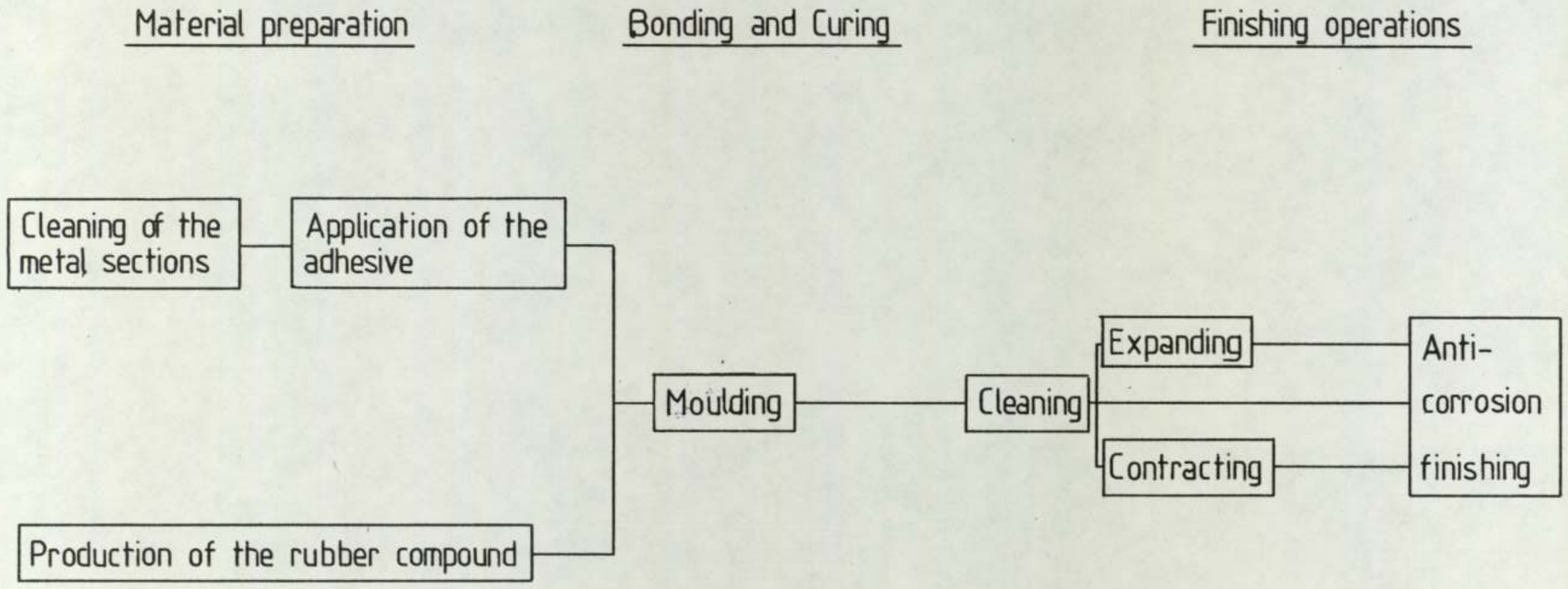


Figure 1.4 A schematic representation of production routes

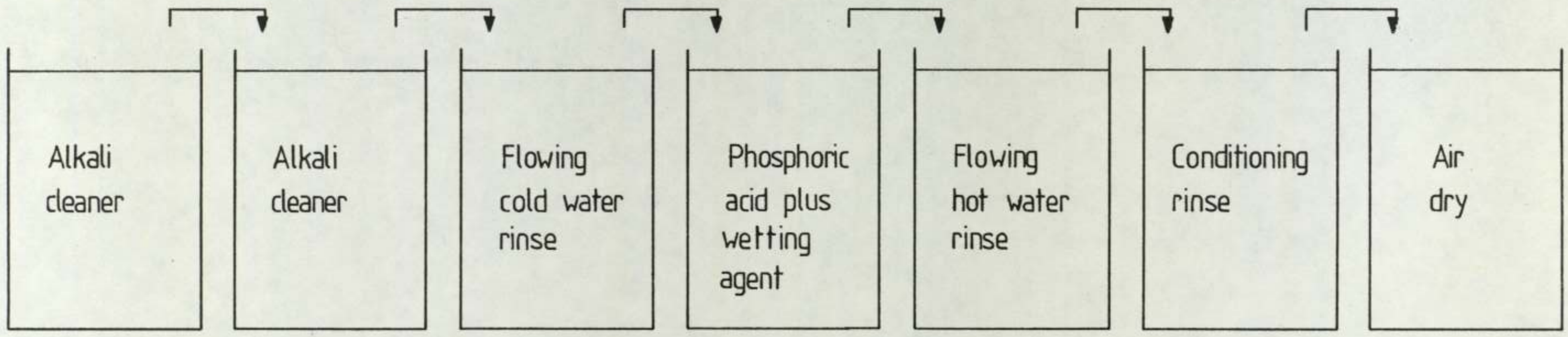
Material	Parts by weight
Rubber	100
Sulphur	2.5
Zinc Oxide	5
An accelerator	0.5
A filler	50
An antidegradant	1

1.2.1.2 Metal preparation and adhesive application

This stage has important ramifications for the surface condition of the products, at the later anti-corrosion finishing stage. The metals, which are bought in, are cleaned either chemically or by a combination of trichloroethylene degreasing and abrasive cleaning prior to application of an adhesive coating. The adhesives are proprietary materials, similar in appearance to paints, specifically formulated for bonding rubber to metal. The application methods used result in adhesive being applied either selectively when only the metal surfaces to be bonded are coated, or non selectively when all the metal surfaces are coated.

(i) Chemical cleaning

The metal sections, loaded on jigs or in baskets, are carried by an overhead conveyor and immersed in the solutions showed schematically in figure 1.5 . The first two tanks contain alkali cleaning solutions to remove the soils from the metals. A water rinse then prevents drag over of alkali into the fourth tank containing an acid pickle for removing any light oxide contamination. The metals then pass through a rinse, followed by a solution containing chromic



<u>Figure 1.5</u> A schematic representation of chemical cleaning

and phosphoric acid for conditioning the metal surfaces. This method of cleaning is usually followed by non selective application of the adhesive, by dipping the metal sections in vats of adhesive.

(ii) Trichloroethylene degreasing and wheelabrating

The metal sections are degreased by immersion in a tank of trichloroethylene vapour, then mechanically cleaned by blasting with G12 chilled iron grit (wheelabrating) and finally the degreasing dip in the trichloroethylene vapour is repeated. This method of cleaning is usually followed by selective application of the adhesive by hand brushing or spraying.

1.2.2 Bonding and curing

Shaping, curing and bonding, of the rubber to the metal sections is achieved by the heat and pressure of a moulding operation. Three moulding methods are used at Metalastik. Firstly, compression moulding in which the rubber & metal sections are placed in the cavity of a mould which is then closed and loaded onto a heated press. Secondly, transfer moulding in which the metal sections and a pre-shaped rubber blank are placed in cavities connected by transfer holes in the mould. When loaded into a heated press, the closing action of the press causes the uncured rubber to be extruded through the transfer holes to fill the areas between the metal sections. Thirdly, injection moulding in which the metal sections are loaded into the cavity of a mould contained in a press. When the mould and press are closed preheated rubber is extruded into the cavity.

Curing and bonding is quickest by injection moulding as preheating the rubber reduces the time required to achieve the moulding temperature.

1.2.3 Finishing operations

1.2.3.1 Removal of excess rubber

Any excess rubber, such as spew pips or flash, is removed by hand trimming or buffing. The amount of flash varies with the moulding method, injection moulding usually producing the least. At Metalastik a large proportion of the products are manufactured by either compression or transfer moulding. These require a substantial amount of wire brushing to remove the flash, particularly products that were non selectively coated with adhesive, as the flash bonds to the metal.

1.2.3.2 Metal manipulation

As the rubber cools, after moulding, it contracts. In parts whose metal sections are constrained from relative movement to accommodate this contraction, as in bushes such as that shown in figure 1.6 , the rubber-to-metal bond comes under tension. To relieve this tension and put the bond under compression the outer metal can be contracted by a swaging operation, and/or the inner metal expanded by a drifting operation. Both operations require the use of lubricants which are removed as soon as practicable to prevent deterioration of the rubber. The lubricants are removed by loading the parts into wire baskets and immersing them in a solution of alkali cleaner, then a solution of rust inhibitor on a plant known as the Revel Degreaser.

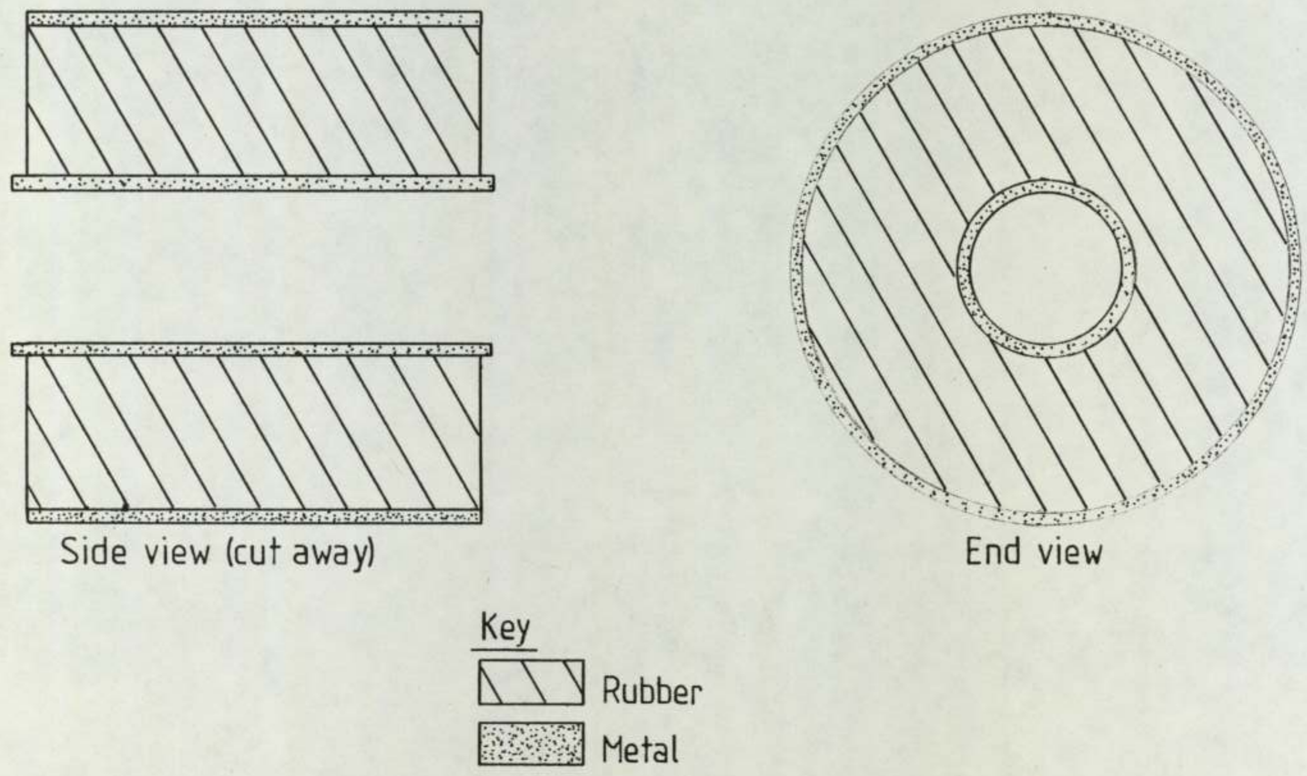


Figure 1.6 A schematic representation of a bush.

1.2.3.3 Anti-corrosion finishing

The anti-corrosion finishing facility at Metalastik produces the following range of standard finishes:

Temporary protective oil finish
Thin coat of paint($\approx 12\ \mu m$)
Thick coat of paint($\approx 25\ \mu m$)
Phosphate only
Phosphate and oil
Phosphate and stain
Phosphate and a thin coat of paint
Phosphate and a thick coat of paint

The individual processes by which the finishes are applied, are discussed in the following sections.

(i) Phosphating

Metalastik has two phosphating plants, one manual and one automatic tipping basket. Each immerse the parts in a solution of alkali cleaner, then after rinsing in water and conditioning in a dilute solution of oxalic acid the parts are immersed in a heavyweight zinc phosphating solution. The parts are then rinsed and immersed in a phosphate sealing rinse prior to drying in warm air.

(ii) Oil

An oil finish is applied both as a temporary protective finish to the bare metal and also as a sealant over phosphate coatings. The parts are loaded into a wire basket and then immersed in a tank of oil.

(iii) Stain

A resin based black finish is used to seal phosphate coatings. The parts are loaded into wire baskets and immersed in a tank of stain.

(iv) Painting

Parts are painted with an Etch Primer Finish (E.P.F.) by three methods. Firstly, there is a dipping process where the components are loaded onto the hooks of a conveyor which dips them in a tank of paint, then carries them through a warm air oven to an unloading station. A single pass through this process produces a thin ($\approx 12\ \mu m$) paint film on the component. Secondly, there is hand spraying where the components are placed on rotatable tables in spray booths. Paint is sprayed using pressure pot fed guns until the required coating thickness of paint is achieved. Thirdly, there is automatic spraying where the parts are placed on rotating turrets, and pass through an oven heated to $90^{\circ}C$ before being presented to a pair of fixed spray nozzles, which apply a thick coat of paint in one pass. ($\approx 25\ \mu m$).

1.3 Interface between the project and company

In addition to the normal IHD supervisory group (2,3) the author had a guidance group at the Division consisting of Mr. Brentegani, General Manager, Mr. Reed, Technical Manager, and Mr. Hopkins, Technical Laboratory Manager. This group met every six weeks to discuss progress and is an indicator of the level of interest shown in the project by the Division.

During the course of the work numerous changes occurred to the managerial infrastructure at Metalastik. The chain of command

changed, several people changed position and several new people became managers. This affected the project in two ways:-
The chain of command and the people through whom the author had to implement work changed, several times in some instances, and in addition Mr. Brentegani's replacement, Mr. Thompson, took over the Divisional guidance group. In view of these changes, where memoranda are referred to in the text, the position of the sender will be indicated.

1.4 The original aim of the project

Metalastik's original objective for the project was:-

> "To identify a range of anti-corrosion finishes for ferrous metals in rubber-to-metal bonded products that will meet customers specifications and other requirements".

1.4.1 The history of anti-corrosion finishing at Metalastik

When Metalastik started trading in 1937 bonding of the rubber and metal was achieved by electroplating a thin layer of brass onto the metal section and subsequently moulding the rubber in contact with the brass plate. Under the influence of heat and pressure the rubber cured and bonded to the brass plate. This use of plating meant that the exposed (unbonded) metal surfaces of the product were plated with brass which, provided subsequent manufacturing operations on the metals did not severely damage the plating, offered a degree of corrosion protection. Products that required better protection had a coat of petroleum jelly applied.

No other anti-corrosion finish was required on a large scale until 1947 when a part for the Austin A40 required a phosphate and stain finish. To meet this requirement a manually operated phosphating plant was installed and proprietary chemicals were bought from Pyrene Chemical Services Ltd. The surfaces to be phosphated were debrassed, processed through the plant then dipped in a black resin based stain finish and air dried.

No further changes occurred until 1962 when the first specification covering anti-corrosion finishing was imposed on products for the new Morris 1100 car. The specification required a phosphate and paint finish, so a Stein Atkinson dip plant was installed for the application of the paint film. Some hand spraying equipment was also purchased to supplement capacity and Goodlass Wall's Black Universal Primer paint was purchased for application by both methods.

The most dramatic change to anti-corrosion finishing was in 1965 when Metalastik changed from using plating to adhesives for bonding. Metalastik had been using adhesives on a small scale since 1953 following advances in adhesive technology in 1950 that produced a range of adhesives at least as good for bonding rubber and metal as brass plating (4). In 1965 brass plating was discontinued and adhesives were used instead. A new plant, which became known as 'C' plant was purchased for applying the adhesives. It consisted of a chemical cleaning line followed by up to three dip tanks for applying multicoats of adhesive. Equipment for the application of adhesives by spray was also purchased.

This change to adhesives had a major affect on the anti-corrosion finishes offered by Metalastik as the products no longer had at least a coating of brass on exposed metal surfaces. Products entered the metal finishing department with the exposed metal surfaces in one of two surface conditions:-

(i) An adhesive coating damaged by the production methods to expose large areas of metal (see 1.2.3.1).

(ii) Bare mild steel contaminated with handling soils.

However, the only change made to metal finishing was to use a Goodlass Wall paint more compatible with the adhesive it covered. No attempt was made to clean adhesive residues off products prior to phosphating metal surfaces, as it was felt that the adhesive residues provided a measure of protection and the phosphate coating would develop to protect the areas where damage had exposed metal.

Two further machines were purchased for use in the metal finishing department. In 1967 an automatic phosphating plant was purchased to replace the manual phosphating plant. However, when the plant was installed it was found incapable of processing relatively large or small products and the manual plant had to be kept in operation. To supplement the capacity of the paint shop a Binks Bullows spray application machine was purchased, on which parts loaded on rotating turrets passed through a preheating oven and then in front of two spray guns. Except for some changes in the materials and combinations of finishes used no other changes were made prior to the commencement of the project in 1977.

1.4.2 Synthesis of the project's aim

Introduction of anti-corrosion finishes in response to customer requirements led to the lack of an overall finishing policy. Over the years, the number of specifications customers imposed on finishes increased, and difficulties began to arise in meeting these specifications. The combination of these factors led to Metalastik proposing this project.

The first stage of the project was to determine whether Metalastik had interpreted its problem correctly. The anti-corrosion finishing requirements of the customers were discussed with the Managers of Metalastik's sales departments. This led to the following categorisation of customers:-

(i) Industrial

With one exception these customers do not impose specifications on the finishing of Metalastik products. Either Metalastik provides a finish from the standard range or supplies the products with a temporary anti-corrosion treatment.

(ii) Rail and Marine

Generally the same applies for these customers as for the industrial customers. Occasionally special requirements arise but these are small orders for large products that are treated in a special manner for metal finishing.

(iii) Automotive

The automotive customers stipulate the finish to be applied to Metalastik products and impose specifications that each finish must satisfy. These specifications take the form of a general description of the finish and the quality assurance tests it must pass.

This broad categorisation was confirmed by discussions with the Manager of the Product Design and Development Department, and also by examining all the customer specifications, relating to metal finishing, held by Metalastik. Other than one specification from Massey Ferguson and one from the Ministry of Defence, all were from automotive customers.

Although these specifications, particularly those covering paint finishes, require a number of quality assurance tests, Metalastik only uses the time to the appearance of corrosion in the ASTM B117 salt spray (fog) test to assess its finishes. This was because the ASTM B117 salt spray (fog) test is required by almost all the specifications imposed on Metalastik finishes and it was felt to be the most difficult and important quality assurance test to meet. The salt spray resistance claimed for each of Metalastik finishes is presented in Table 1.1 with the resistances required by the customers specifications covering that finish on Metalastik products.

TABLE 1.1 The salt spray resistances required of Metalastik finishes

FINISH		Claimed by Metalastik	Hours resistance to the salt spray (fog) test ASTM B117 - 73* Required by Automotive customers			
			BRITISH LEYLAND	VAUXHALL	FORD	TALBOT (CHRYSLER)
Temporary protective		16	-	-	-	-
Phosphate only ***		-	-	-	-	-
Phosphate and oil ***		24	48	20 - 48	-	72
Phosphate and stain ***		16	56	20 - 48	24	72
PAINT FINISHES	Thin coat of paint	16				
	Thick coat of paint	36				
	Phosphate and a thin coat of paint	48	48			
	Phosphate and a thick coat of paint	96	72 - 100	96 -144**	96	96

* Where more than one specification is imposed on a finish the highest and lowest salt spray resistances required are quoted.

** This specification covers one product only, therefore the lowest and highest salt spray resistances required on the other products supplied to this customer are also quoted.

*** All the specifications covering these finishes require a minimum true phosphate coating weight of 7.5 gm^{-2} (B.S. 3189 Class 1A).

From Table 1.1 it can be seen that there are two groups of finishes that do not meet all the imposed specifications. The first group, paint finishes, contains only one specification for Vauxhall. This requires a salt spray resistance of 144 hours for a paint finish, when Metalastik only claims 96 hours for its top paint finish, however only 1 product was being supplied to this specification.

The second group contains the specifications which cover the finish phosphate and stain or oil. While Metalastik only claims 16 and 24 hours resistance to ASTM B117 respectively for these finishes, the customers require between 20 and 72 hours. A survey of the finishes supplied on the products manufactured at Metalastik revealed that approximately 45% by volume of Metalastik's products are supplied to the automotive market with either a phosphate and oil or phosphate and stain finish, and that 60 to 70% by volume are supplied to various markets with a finish based on a phosphate coating.

To ascertain whether this situation was likely to alter substantially, the automotive customers were visited to discuss whether any changes were likely to the finishes or salt spray requirements imposed on the finishes required for rubber-to-metal bonded products. The automotive customers all indicated that there were no plans for changes to these products.

1.4.2.1 The alternatives to phosphating

The first solution to be considered was the possibility of a replacement for the phosphate finish. To assess the feasibility of this, phosphating and its possible replacements were compared using the questions shown in Table 1.2. A yes answer to each question has a poor rating of -1 and a No answer a good rating of +1. Considering each question in turn the reasons for rating a yes answer as poor are given after the table.

TABLE 1.2 Evaluation of the alternative finishes for the rubber-to-metal products produced by Metalastik

* If the answer to the criteria is YES the finish is rated poorly at -1, if NO the finish is rated well at +1

CRITERIA / FINISH	A	B	C	D	E	F	G	Total Rating
Zinc(sheradizing)	-1	+1	-1	-1	-1	+1	+1	-1
Zinc(galvanizing)	-1	+1	-1	-1	-1	+1	+1	-1
Zinc(electro-plating)applied prior to bonding	-1	+1	-1	-1	+1	-1	+1	-1
Zinc(electroplating) applied after bonding	+1	-1	-1	-1	+1	-1	+1	-1
Zinc(mechanical plating)	+1	+1	-1	-1	+1	+1	+1	+3
Zinc(spray)	+1	+1	-1	-1	-1	-1	-1	-3
Phosphate and Oil or Stain	+1	+1	+1	+1	+1	+1	+1	+7
High temperature stoving paint	-1	+1	-1	-1	+1	-1	+1	-1
Paint	+1	+1	-1	-1	+1	-1	-1	-1
Powder coating	-1	+1	-1	-1	+1	-1	+1	-1

KEY *

A - Would the finish require application prior to bonding ?

B - Is the finish likely to attack the rubber-to-metal bond ?

C - Would the finish fail to impart the required surface characteristics ?

D - Would the finish require changes to to product drawings ?

E - Would the finish require the dimension of the product to be changed ?

F - Would the finish fail to cope with the inner bores of bushes and other recesses ?

G - Would the finish rely on the skills of the operator ?

A. Would the finish require application prior to bonding ?

Any finish that requires processing temperatures in excess of 120°C is rated poor as it would have to be applied to the metal sections prior to bonding to prevent damaging the rubber. This would require expensive long term changes to the moulding and finishing facilities to avoid damaging the anti-corrosion finish on the products.

B. Is the finish likely to attack the rubber-to-metal bond ?

Any finish that might attack the rubber-to-metal bond is rated as poor. Where a finish can be reformulated to avoid this problem (for example changing the solvents used as thinners for a paint) it is considered in its optimum condition.

C. Would the finish fail to impart the required surface characteristics ?

For parts such as bushes, which push fit into a housing, the automotive customers prefer the surface properties imparted by a phosphate coating plus stain or oil. All single application finishes other than phosphating have to be rated as poor against this criterion.

D. Would the finish require changes to product documentation ?

To replace phosphating would require Metalastik and its customers altering the documentation on a large number of products supplied both as original equipment and to the spares market. As the automotive customers estimate each alteration costs in excess of £500 any finish other than phosphating has to be rated as poor against this criterion.

E. Would the finish require the dimensions of the product to be changed ?

There is an allowance of 25 microns on surfaces to be phosphated which have to meet tolerances. Any finish producing a coating thicker than 25 microns is rated as poor due to the changes to components that would be required to meet these tolerances and also the alterations that would be required to ensure that the threads of fasteners were not blocked.

F. Would the finish fail to cope with the inner bores of bushes or other recesses ?

Finishes that cannot easily coat recessed areas such as the inner bores of bushes are rated as poor.

G. Would the finish rely on the skills of the operator ?

Finishes that would be applied at Metalastik but which could not be easily automated are rated as poor due to the difficulty of ensuring the quality of the finish under shop floor conditions.

The difficulty of replacing phosphating can be seen by considering the total rating achieved by each finish in Table 1.2. Phosphating has the best rating and a good margin exists between it and the next best rated finish. To ensure the product mix manufactured by Metalastik was not likely to move away from the products requiring a phosphate coating a list of the products that accounted for 80% of the volume of work phosphated, which were all for the automotive market, was sent to the Marketing Department and a sales forecast requested. The department was unable to provide individual forecasts, but stated "Providing Metalastik maintains its competitiveness, sales of these products will continue at approximately their current levels".

1.4.3 Redefinition of the project's aim

The original aim of the project to identify a new range of finishes to meet present and future customer specifications was not completely correct. Work was in fact required to improve the existing middle range finishes to meet existing specifications, otherwise the project would be working towards meeting a relatively small number of future orders requiring high levels of anti-corrosion protection from the weak base of a system that could not meet the large number of orders requiring medium levels of corrosion protection.

Therefore in the following work the phosphating of rubber-to-metal bonded products is investigated with a view to meeting the salt spray resistance requirements of the specifications covering the phosphate and stain or oil finishes. The specifications covering these two finishes only require that the phosphate coating weight is above the minimum value for a heavyweight phosphate coating, exhibits no visual defects and when sealed achieves the required number of hours resistance to the salt spray test.

CHAPTER 2

LITERATURE SURVEY

2.1 Phosphating

Phosphating is the reaction of phosphoric acid solutions containing metal phosphates and usually modifying agents plus an accelerator with metal surfaces converting them to an insoluble integral layer of inorganic metal phosphate crystals. The resulting coatings are classified according to their weight per unit surface area. The British Standard covering phosphating, BS 3189, gives the following classification.

Class	Coating Weight gm^{-2}	
	Minimum	Maximum
1A and 1B	7.5	-
2	4.5	7.5
3	1.5	4.5
4	0.2	1.5

A comprehensive coverage of the subject phosphating can be found in Guy Lorins book (5) Phosphating of Metals, which has been extensively drawn on in this work. However, as all the specifications covering the finishes phosphate and oil or stain, that are referred to in Table 1.2 require a 1A class of coating this review will be limited to the development on mild steel surfaces of a class 1A phosphate coating by immersion in a phosphating solution.

2.1.1 Equilibration equation for a zinc phosphating solution

Zinc phosphating solutions are based on orthophosphoric acid, formula H_3PO_4, a tribasic acid for which the series of salts for a divalent metal M would be:-

$M(H_2PO_4)_2$	$MHPO_4$	$M_3(PO_4)_2$
primary phosphate	secondary phosphate	tertiary phosphate

For zinc Salmon and Terry (6) describe 5 zinc phosphates, two primary, two secondary and one tertiary:-

(i) The diacid primary phosphate $Zn(H_2PO_4)_2\ 2H_3PO_4$

(ii) The primary phosphate dihydrate $Zn(H_2PO_4)_2 2H_2O$

(iii) The secondary phosphate monohydrate $Zn\ HPO_4\ H_2O$

(iv) The secondary phosphate trihydrate $Zn\ HPO_4\ 3H_2O$

(v) The tertiary phosphate tetrahydrate $Zn_3(PO_4)_2 4H_2O$

Of these only (ii) and (v) are stable, the tertiary phosphate tetrahydrate occurring in nature as the mineral hopeite. Under the influence principally of temperature or a rise in pH a solution of the primary zinc phosphate will dissociate to form the secondary and tertiary salts and free phosphoric acid. The overall equilibrium reaction and two intermediate equilibrium steps are given by equations 2.1, 2.2 and 2.3 respectively.

$$3Zn(H_2PO_4)_2 \rightleftharpoons Zn_3(PO_4)_2\downarrow + 4H_3PO_4 \qquad 2.1$$

$$Zn(H_2PO_4)_2 \rightleftharpoons ZnHPO_4 + H_3PO_4 \qquad 2.2$$

$$3ZnHPO_4 \rightleftharpoons Zn_3(PO_4)_2\downarrow + H_3PO_4 \qquad 2.3$$

The deposition of phosphate crystals on a metal surface is based on the principle that if a metal M is placed in contact with a primary phosphate solution it will react with the free phosphoric acid present as shown in equation 2.4.

$$M + 2H_3PO_4 \rightarrow M(H_2PO_4)_2 + H_2\uparrow \qquad 2.4$$

The consumption of free phosphoric acid increases the pH of the solution and shifts the equilibratium in equation 2.1 to the right causing the precipitation of insoluble tertiary phosphate at the metal/solution interface.

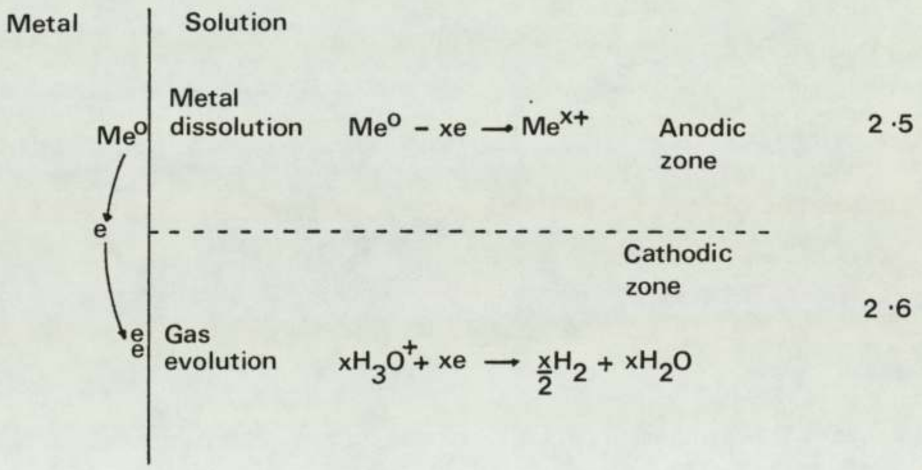
To prevent hydrolysis causing the precipitation of tertiary phosphate throughout the bath a certain amount of free phosphoric acid must always be present. The amount required increases with increase in the solution temperature. However, the more phosphoric acid that is present in the solution the longer is the time required to shift the equilibrium in equation 2.1 at the metal surface which results in more metal being consumed as shown in equation 2.4. Therefore phosphating solutions are designed to contain just sufficient phosphoric acid to maintain the hydrolysis equilibrium at the working temperature.

Although this describes the basic principle of a phosphating solution an explanation of why the phosphate crystals precipitated at the metal/solution interface should bond to and cover the metal surface requires closer examination of the processes occurring at the metal surface. For this the role of an accelerator will be considered simply as an oxidising agent, and the processes will be considered in two stages acid attack then nucleation and growth.

2.1.2 Acid attack

The first stage is the acid attacking the metal. U.R.Evans (7) describes the essential features of acid attack, but of importance here are the processes occurring at individual points on the metal surface. The anodic and cathodic reactions which characterise acid attack on the metal can be regarded as localised and corresponding to differently polarised zones, with metal dissolution taking place at anodic sites and hydrogen evolution at cathodic sites. The process can be considered schematically as shown in figure 2.1.

Figure 2.1 Acid attack on the metal



In the ideal situation a metal would etch uniformly over its surface and the zones would be continuously alternating between being anodic and cathodic.

2.1.3 Nucleation and growth

Until 1965 there were two separate theories regarding the nucleation and growth of phosphate coatings. One involved nucleation and growth principally at cathodic zones and the other principally at anodic zones. Both theories relied on the alternation of the polarity of the zones to explain the deposition of a phosphate coating over the entire metal surface.

2.1.3.1 Cathodic theory

W. Machu (8) suggested that crystal nucleation localised principally at microcathodic regions. At these regions a fall in the acidity of the solution at the solution/metal interface results from the acid attacking the metal. This causes the solution to approach a pH at which precipitation of phosphates will occur. L.O.Gilbert (9) reported this process could occur at pH values 4.05 to 4.90. Combining the equation for phosphoric acid attacking iron 2.7 with equation 2.1 gives equation 2.8 .

$$2Fe + 4H_3PO_4 \rightarrow 2Fe(H_2PO_4)_2 + 2H_2\uparrow \qquad 2.7$$

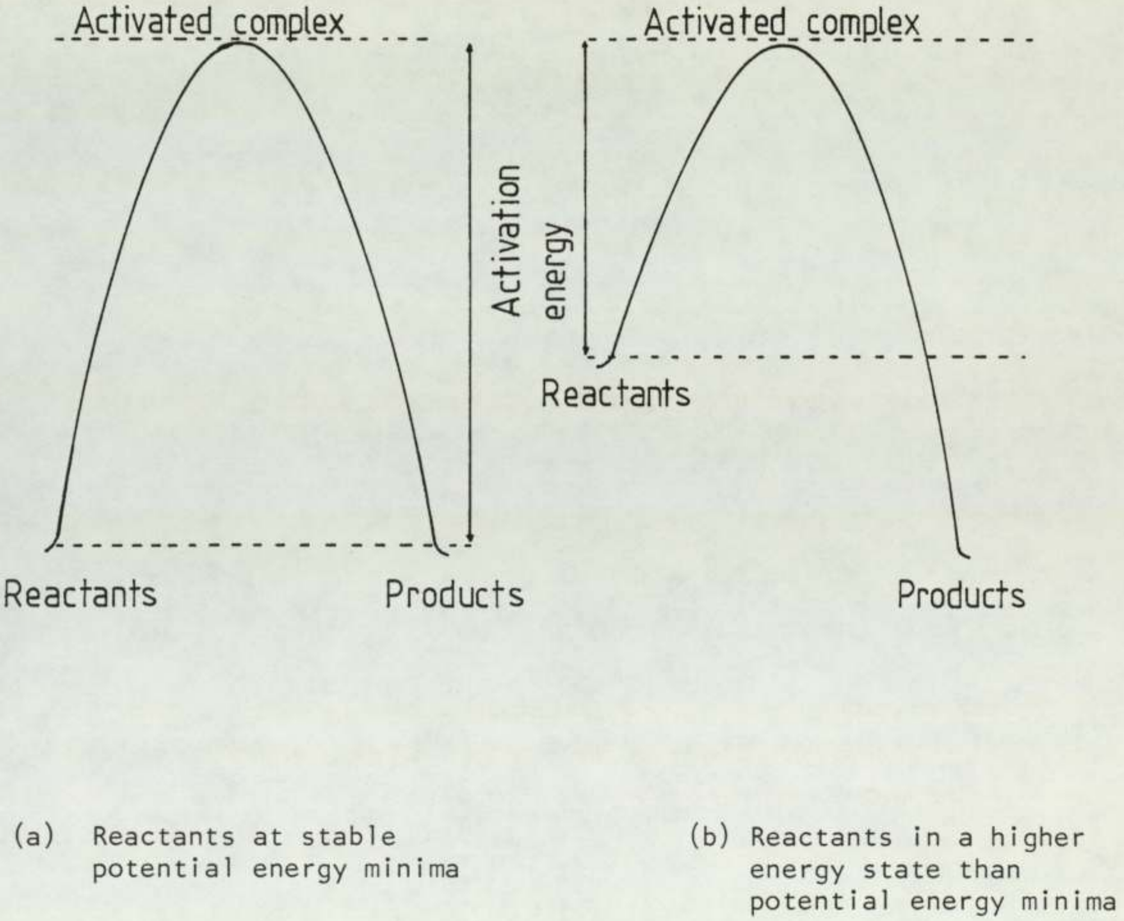
$$3Zn(H_2PO_4)_2 + 2Fe \rightarrow Zn_3(PO_4)_2\downarrow + 2Fe(H_2PO_4)_2 + 2H_2\uparrow \qquad 2.8$$

Machu (10) had to subsequently supplement this theory as it could not explain the existence of a phosphate layer rich in iron between the phosphate coating and the iron substrate, first suggested by Tyvaert (11) and then confirmed by Saison (12). Machu supplemented his theory by suggesting the existence of "active centres" on the surface of the metal which:

> "were formed by points or projections of microcrystals of the metal surface where unsaturated and very powerful atomic bonding forces can come into operation. Thus the microscopic seed formed initially at the cathode would be iron rich".

The author's interpretation of this is as follows: Before a chemical reaction can take place the reactants involved must be raised to a state of higher potential energy. They are then said to be activated or to form an activated complex. This process is shown in schematic form in figure 2.2a. Reactants and products are both at stable potential energy minima; the activated complex is the state at the top of the potential energy barrier.

Figure 2.2 Energy barrier surmounted by a system in a chemical Reaction



(a) Reactants at stable potential energy minima

(b) Reactants in a higher energy state than potential energy minima

If the energy level of one or all the reactants is increased the activation energy required to raise them to the state of higher potential energy is reduced, as shown schematically in figure 2.2b. Therefore if there are sites on the surface of a metal immersed in a phosphating solution where metal atoms are in a higher energy state than the surrounding metal atoms, the activation energy for the phosphating reactions will be lower and the reactions will preferentially occur at these sites. These "active centres" will occur at grain boundaries where there will be atoms at energy levels above their ground state as a result of having unfilled electron shells. "Active centres" will also occur as a result of deformation of the metal causing twinning and dislocations, both of which will be areas of metal surface in a higher energy level than the surrounding metal surface.

According to Machu, as these areas will be nucleation sites for the phosphate crystals, he suggests the first phosphate crystals will be phosphates of the base metal, iron. Then his proposed reactions would deposit zinc phosphate crystals over this iron rich layer. The number and distribution of these active centres would govern the distribution of crystal nucleii. A large number of well distributed nucleii would produce a good fine phosphate coating and conversely a small number of poorly distributed nucleii would produce a poor coarse phosphate coating. Therefore the surface condition of the metal is of prime importance. Consequently the surface treatments applied to the metal prior to phosphating affect the phosphate coating produced, for example:-

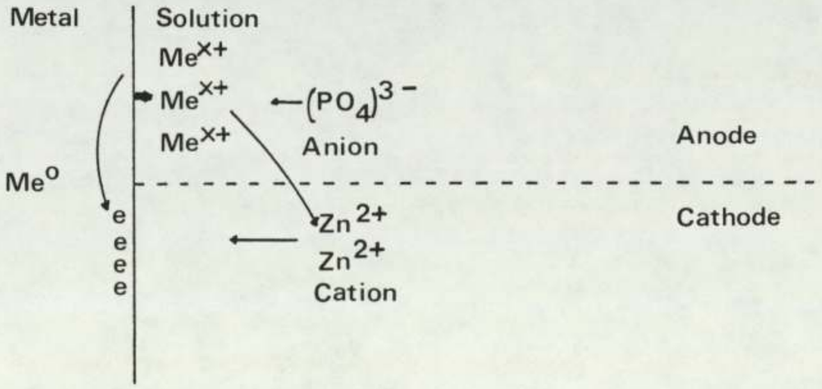
(i) Deformation operations on the metal - would produce dislocations and twins on the metal surface, all nucleation sites of high energy.

(ii) Cleaning of the metal surface - would remove oxidised layers and soils, improving access to the potential nucleation sites.

2.1.3.2 Anodic theory

Wulfson is cited by Cupr and Pelikan (13) as being the first to suggest that crystal nucleation and growth is principally an anodic phenomenon. If an element of surface is under acid attack as shown in figure 2.1 the addition of the constituents of the solution would give the situation presented schematically in figure 2.3.

Figure 2.3 Acid attack in the presence of the constituents of the phosphating solution



Anions PO_4^{3-} from the solution approach the anode where ions from the metal have been released into the solution as a result of the acid attack. The solubility product $(M^{2+})_3(PO_4^{3-})_2$ is rapidly exceeded thus resulting in the formation of insoluble tertiary metal phosphate. As the metal ions involved could be either dissolved iron or zinc from the solution this theory allowed for the presence of an iron rich phosphate layer under the phosphate coating.

2.1.4 Rationalisation of anodic and cathodic theories

V. Cupr and J.B.Pelikan (13,14) undertook work to evaluate the two theories of anodic and cathodic nucleation and growth. They immersed steel test panels in a phosphating solution and withdrew specimens at regular intervals between 15 seconds and 15 minutes and noted the structure of the surface. The following observations were made:-

(i) From the moment of immersion in the solution the surface becomes covered with a passivation layer ranging in colour from clear irridescent yellow to deep violet. At this stage some areas remain unaffected but formations of a nodular type appear.

(ii) As the time of contact with the liquid increases the nodular masses become more numerous and very rapidly become nucleii for crystallisation.

(iii) Later crystals appear initially grouped in zones between which passivation of the metal is at its maximum.

(iv) Finally the crystals spread and coalesce, enclosing passivated microsurfaces between crystalline zones.

From these observations a theory was evolved involving the ion $ZnPO_4^-$ at the anodic and cathodic areas on the metal surface. The ions resulting from the equilibrium equation 2.1 are

$$Zn(H_2PO_4)_2 \rightleftharpoons ZnPO_4^- + H_2PO_4^- + 2H^+ \qquad 2.9$$

2.1.4.1 Anodic zone

The $ZnPO_4^-$ ion reacts with iron atoms to produce mixed Fe - Zn phosphates.

$$Fe + 2ZnPO_4^- \rightarrow Zn_2Fe(PO_4)_2 + 2e \qquad 2.10$$

The dissolution of iron from the anodic zone produces soluble ferrous phosphate.

$$Fe^{2+} + H_2PO_4^- \rightarrow FePO_4^- + 2H^+ \qquad 2.11$$

The accelerator in the solution(oxidising agent) converts this to insoluble ferric phosphate which is precipitated from the solution to form a sludge.

$$FePO_4^- - e \rightarrow FePO_4\downarrow \qquad 2.12$$

2.1.4.2 Cathodic zone

At microcathodic surfaces the decrease in acidity associated with the increase in concentration of $ZnPO_4^-$ ions allows the solubility product of $Zn_3(PO_4)_2$ to be exceeded, causing its precipitation.

$$Zn^{2+} + 2ZnPO_4^- \rightarrow Zn_3(PO_4)_2\downarrow \qquad 2.13$$

However, in this reaction the accelerator has an essential role to play. Considering the acid attack stage shown in Figure 2.1, charge transfer between the zones polarises the metallic surface which leads to the movement of ions at the metal solution interface. At the cathodic surface a high concentration of Zn^{2+} and Fe^{2+} cations develop forming a dielectric layer at the interface. However this zone will be permeable to H^+ ions which will prevent the metal ions from closely approaching the metal surface. The role of the accelerators (oxidising agents) is to react with the H^+ ions and hence allow the metal cations to approach the metal surface, thus allowing reaction 2.13 to occur causing deposition of phosphate crystals.

In addition the $H_2PO_4^-$ ion from equation 2.9 can react with the Zn^{2+} ion to regenerate $ZnPO_4^-$ ions

$$Zn^{2+} + H_2PO_4^- \rightarrow ZnPO_4^- + 2H^+ \qquad 2.14$$

2.1.4.3 Initial reactions at the metal/liquid interface

M.J.Bigeon (15) extended Machu's theory of active centres by assuming that a metal surface activated by the presence of such centres would be oxidised on immersion in the acid medium, leading to the formation of ferrous oxide. This oxide would be rapidly attacked by the free phosphoric acid.

$$2H_3PO_4 + FeO \rightarrow Fe(H_2PO_4)_2 + H_2O \qquad 2.15$$

$$2H_3PO_4 + 3FeO \rightarrow Fe_3(PO_4)_2 + 3H_2O \qquad 2.16$$

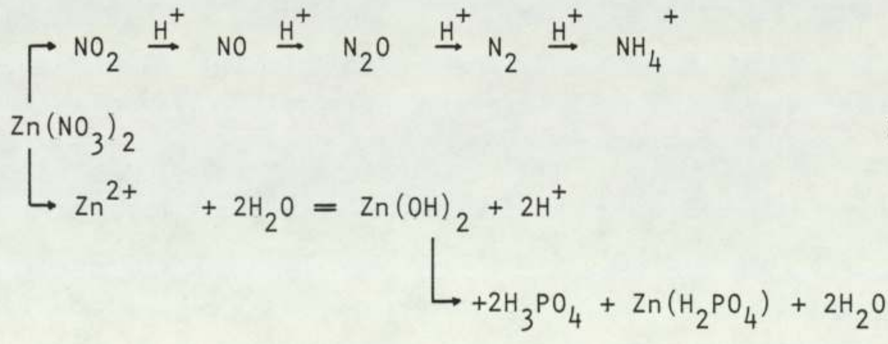
This would favour the formation of an iron rich phosphate layer underneath the phosphate coating itself. Additionally the formation of an oxide layer would prevent acid attack of the metal causing a decrease in hydrogen evolution. This effect combined with the previously discussed role of accelerators (2.1.4.2) would explain the observed decrease in gas evolution with increase in immersion time in a phosphating solution.

2.1.5 Accelerators and modifying agents

D.James and D.B.Freeman (16) indicate the principal difference between various zinc phosphate processes lies in the selection of the accelerator system and to some extent the use of coating modifying agents. Although the paper quoted refers to lightweight zinc phosphating processes, it is suggested that the statement also holds true for the heavyweight zinc phosphating processes.

2.1.5.1 Accelerators

The nitrate/nitrite accelerator system used in the phosphating solutions in this work is the most widely used system for zinc phosphating processes (16). The nitrate has to be added to the solution and is present in the form of salts with metals such as sodium, zinc, nickel, manganese, calcium and ammonium. Zinc nitrate operating as an accelerator in the solution undergoes the following transformation (5).



$$\begin{aligned} Zn(NO_3)_2 &\to NO_2 \xrightarrow{H^+} NO \xrightarrow{H^+} N_2O \xrightarrow{H^+} N_2 \xrightarrow{H^+} NH_4^+ \\ Zn(NO_3)_2 &\to Zn^{2+} + 2H_2O = Zn(OH)_2 + 2H^+ \\ Zn(OH)_2 &\to +2H_3PO_4 + Zn(H_2PO_4) + 2H_2O \end{aligned} \qquad 2.17$$

Apart from its reactions as an oxidising agent it can be seen that zinc nitrate provides a reserve of zinc ions which can reconstitute primary zinc phosphate by reaction with free phosphoric acid. Although the nitrate ion is transformed rapidly during processing its progressive disappearance from the solution is less rapid than that of phosphate because at low values of pH (between 0 and 3) the nitrite ion will disproportionate and regenerate nitrate ions.

$$3NO_2^- \overset{2H^+}{\rightleftharpoons} NO_3^- + 2NO\uparrow + H_2O \qquad 2.18$$

It is often necessary therefore to use two solutions with quite different nitrate contents for the initial make up (IMU) of a phosphating solution, and for replacement (R) of chemicals in the solution during use of the phosphating solution. The roles of the accelerator at cathodic and anodic surfaces are:-

At anodic zones iron is dissolved in the ferrous state with a reaction rate V1.

$$Fe^o - 2e \rightleftharpoons Fe^{2+} \quad VI \qquad 2.19$$

this becomes soluble ferrous phosphate as shown in equation 2.19. At microcathodic zones nitrate is reduced to nitrite with reaction rate V2.

$$NO_3^- + 2e \overset{2H^+}{\rightleftharpoons} NO_2^- + H_2O \quad V2 \qquad 2.20$$

The ferrous ion will react immediately with the nitrite to form a ferric ion, which will be precipitated as insoluble phosphate and form a sludge.

$$FePO_4^- - e \longrightarrow FePO_4\downarrow \qquad 2.21$$

The microanodic and microcathodic reactions are characterised by different rates, which depend on the conditions of equilibrium and temperature of the bath. Two cases may arise -

(i) V1 greater than V2 (iron side)

Ferrous ions are produced in such amount that there is insufficient to effect complete oxidation. A phosphating solution in this condition becomes increasingly enriched in ferrous ions at a rate proportional to V1 - V2 and is said to be "working on the iron side".

(ii) V2 greater than V1 (nitrite side)

Due to an excess of nitrite, ferrous ion is absent from the solution, as it is immediately oxidised and precipitated as sediment. In this condition a phosphating solution is said to be "working on the nitrite side". If it is necessary to work a phosphating solution on the nitrite side where V2 does not exceed V1 continuous additions of nitrite in the form of sodium nitrite can be made. This can be achieved by continuous dropwise addition of a solution, or by regular addition of the salt.

However the amount of nitrite present must be optimised otherwise in baths of high total acidity the sodium nitrite can rapidly decompose.

$$NaNO_2 + 3H^+ \rightarrow \left\{\begin{matrix} NO_3^- \\ H_2O \\ 3Na^+ \end{matrix}\right. + H^+ + 2NO\uparrow \qquad 2.22$$

The nitric oxide will be converted to nitrous fumes on contact with air.

2.1.5.2 Modifying agents

The only modifying agents relevant to this work are nickel and amino polyacids.

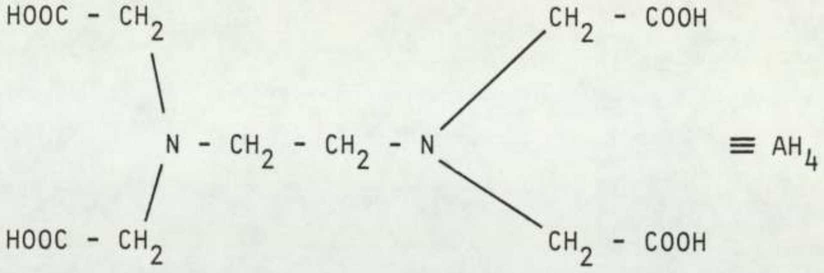
(i) Nickel

Nickel was first added to a phosphating solution to reduce the processing time required to achieve a phosphate coating and produce a smoother crystalline coating. Chamberlain(17) reported that the presence of nickel caused a 20% increase in the weight of phosphate coating deposited. The mechanism by which nickel achieves this is not clearly understood. Guy Lorin (5) suggests that nickel plays a part in the formation of the sub layer to the phosphate coating, however microprobe analysis (5) has cast doubt on this theory as nickel has been detected in the actual phosphate crystals.

(ii) Amino poly-acids

These compounds began to be used as modifying agents for phosphating solutions shortly before 1955. M.J.Bigeon (15) suggested the use of nitrilotriacetates and ethylenediamino-tetraacetates while W.Machu (18) emphasised the effectiveness of ethylene diamine tetraacetic acidThe addition of these complexes improves the functioning of a phosphating solution in respect of reduced formation of sediment and increased coating weight. It may be assumed that the action of amino-polyacids is related to their complexing effect.

Ethylene diamine tetraacetic acid (EDTA)



At pH 2 AH_4 exists in equilibrium with ionised forms in the molar ratio.

$$AH_4 \; : \; AH_3^- \; : \; = 0.55 : 0.40 : 0.05$$

for a pH slightly above 2.5 this ratio becomes

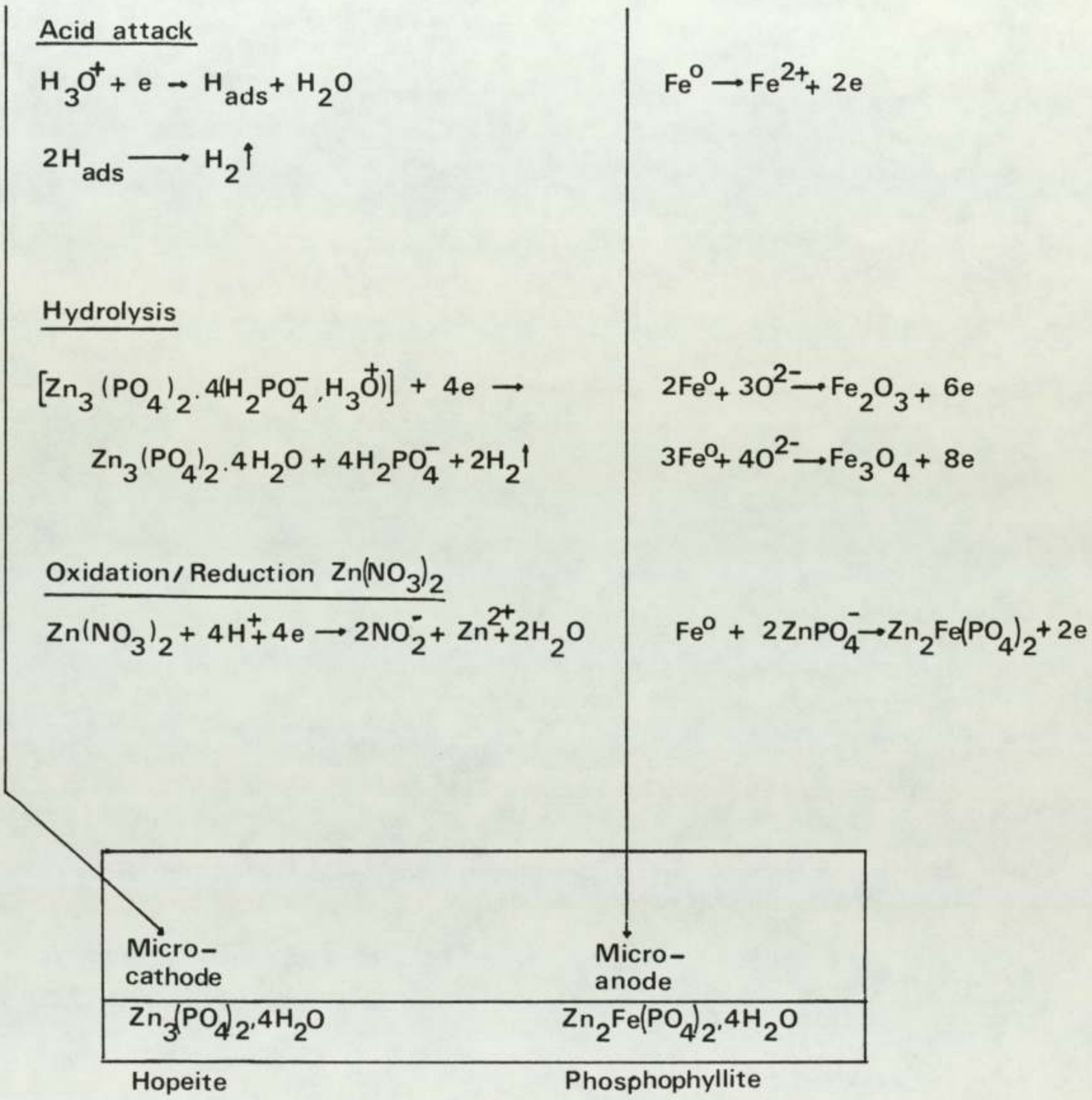
$$AH_4 \; : \; AH_3^- \; : \; AH_2^{2-} = 0.27 : 0.45 : 0.28$$

Since the changes in pH at the solution/metal interface are considerable the metal complexes formed are variable.

2.1.6 Summary of phosphating reactions

J.Cournot and Guy Lorin (19) summarise the basic reactions in a phosphating solution in the manner shown in figure 2.4. Electron-microprobe analysis of coatings (5) has shown that phosphophyllite can be a plate like crystal and hopeite a needle like crystal that generally lies in the plane of the substrate metal. Hopeite is precipitated preferentially in highly accelerated phosphating solutions, while coatings consisting mainly of phosphophyllite crystals result from solutions containing a low concentration of accelerator.

Figure 2.4 Summary of phosphating reactions



2.1.7 Preparation of the metal surface for phosphating

2.1.7.1 Cleaning the metal surface

The metal surface must be in a condition that facilitates both the first stage of the phosphating process of acid attack, and the development of nucleii at the areas of high energy suggested by Machu (2.1.3.1). The cleaning methods available (20) are acid pickling, alkali degreasing, solvent degreasing and abrasive cleaning. The actual combination used is chosen to counteract any negative effects imparted by operations on the metal surface such as heat treatment or mechanical deformation.

2.1.7.2 Conditioning the metal surface

After cleaning the parts are usually rinsed prior to phosphating to minimise the amount and effect of contaminants carried over into the phosphating solution. To aid the rinses in this function and also to control the coating weight of phosphate deposited, additions can be made to the rinses.

G.W.Jernstedt (21) suggests the use of a collodial suspension of insoluble titanium salts and describes such a suspension as:

Disodium phosphate	1 - 20 gl^{-1}
Titanium	.01 - 1 gl^{-1}
pH	8 -8.5

An alternative is the use of oxalic acid (5).

2.1.8 Treatments applied to the phosphate coating

2.1.8.1 Conditioning of the coating

The phosphate coating produced consists of crystals separated by pores. According to Machu (22) these pores represent

0.5 to 1.5% of the phosphated surface area. These pores, which are potential corrosion sites can be blocked off by treating the phosphate coating with a conditioning solution. One such solution contains chromic and phosphoric acid. The chromic acid is believed to react with the metal to seal the base of the pore, and with the phosphate crystals to fill in the pore to some extent, as shown schematically in figure 2.5.

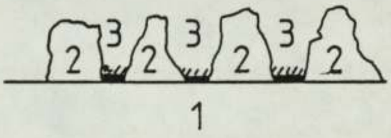
Figure 2.5 Conditioning of a phosphate coating with chromic acid

Key

1. Base metal
2. Phosphate crystal
3. Pore

■ Passivated metal surface

▨ Blocking off of pore



The health risks associated with chromic acid, covered by Burges (23), have led to the development of solutions for blocking the pores that do not contain chromic acid. One such solution based on tannin is Parcolene 85 supplied by Pyrene Chemical Services Ltd.

2.1.8.2 Further reaction with the coating

The coating can be improved (24,25) by treatment with such processes as Endurion, a final dip in a boiling solution of stannous chloride and other ingredients which impregnates the pores of the coating with a tin complex. This seals the pores and improves the corrosion resistance of the coating both on its own and when used with a supplementary finish. However, Endurion is little used in this country due to the expense and difficulties associated with its use.

2.1.8.3 Drying of the coating

It has been suggested (5) that an improvement in the protective value of a phosphate coating, that has been conditioned in chromic acid (2.1.8.1) can be achieved by heating it above $100^{\circ}C$ for several minutes.

2.1.9 Supplementary finishes over phosphate coatings

L.F.Spencer (26) classifies the use for phosphate coatings according to their coating weights as described in Table 2.1.

Table 2.1 Classification by coating weight of the uses of phosphate coatings

Coating Weight g/m^2	Description	Use
1.5	Light phosphating	pretreatment for painting
1 to 7	Medium phosphating	pretreatment for painting or in conjunction with a lubricant for use in cold deformation of metals.
10 to 40	Heavy phosphating	for use with sealants as an anti-corrosion treatment.

According to R.F.Drysdale (27) medium and heavyweight phosphate coatings are not normally used as a pretreatment for painting for three reasons. Firstly, the heavier phosphate coatings are thicker (5), and due to the porosity of the coating a greater amount of paint is required to completely cover the surface than would be required with a lightweight coating on the same surface. Secondly, the thicker coating causes sinkage of the applied paint film, leading to difficulties in gloss retention. Thirdly, a paint coating over a lightweight phosphate coating has better adhesion properties than if applied over a heavyweight coating. This is of importance if the finished article is likely to be damaged in service, or has to be fabricated further after painting.

However if these considerations are not important Drysdale (27) indicates a heavyweight coating to be an acceptable pretreatment to painting.

2.1.10 Corrosion resistance of phosphate coatings

The protective value of a bare phosphate coating is very limited and corrosion tests are normally carried out on the phosphate coating and a supplementary finish. Commonly employed accelerated corrosion tests include the salt spray test, humidity test and water soak test. The most commonly employed salt spray test is that used in this work, continuous exposure to 5% salt solution at 35^oC according to ASTM B117-73. With painted panels the usual practice is to make a scratch down to the substrate before exposure and the results are in terms of the spread of rust from the scratch. Additionally for painted panels and also for panels dipped in an oil or stain sealant, breakdown is measured in terms of surface rusting. While there is much argument over the relevance of the salt spray test to actual service exposure, it is the test most specified by manufacturers (5).

Although the author found references to the salt spray resistance of paint finishes over lightweight phosphate coatings, little definitive work was found on the salt spray resistance of

UNIVERSITY LIBRARY

the phosphate and oil or stain finish. The author suggests the relative amounts of work published on the corrosion resistance of these types of finish reflects the importance attached to their uses. Taking the car as an example the phosphate and paint finish is used on car bodies and is easily visible to the potential purchaser. Therefore a lot of work has been done and published on improving the corrosion resistance of this finish. The phosphate and oil or stain finish is used on components which are generally not easily visible to the potential purchaser, therefore less importance is attached to the finish and less work has been published on the corrosion resistance of this type of finish.

Nevertheless improvement in the protective properties of the phosphate and oil finish is evident from figures given by W.R.Cavanagh (28) according to which phosphated steel with oil protection showed a salt spray resistance of 24-36 hours in 1940, 48 hours in 1950 and 72-96 hours in 1960.

Pyrene Chemical Services Ltd., indicated that a phosphate and stain sealant finish would now be expected to achieve 72 to 96 hours. According to Spencer (26)a zinc phosphate coating of 2-5 gm^2 coated with an air drying paint could be expected to achieve between 100 and 150 hours salt spray resistance. Therefore the finishes used by Metalastik could reasonably be expected to meet the salt spray resistance requirements indicated in Table 1.2.

2.1.11 Coating weight curves

A phosphate coating has not achieved its full protective properties until the phosphate crystals have coalesced, when the coating is said to have completed. The immersion time required to achieve this can be determined by plotting a coating weight curve, i.e. the dependence of the weight of phosphate coating deposited on a metal on time. There are three coating weights of importance, the true and addition phosphate coating weight and the weight of metal lost. The addition coating weight is the difference in weight of the sample before and after phosphating. The true coating weight is the difference in weight of the sample before and after stripping the phosphate coating off. The weight of metal lost from the sample during phosphating is given by subtracting the addition coating weight from the true coating weight. The weights in grammes are then divided by the surface area of the sample in metres to standardise the coating weights to grammes per square metre.

The ideal curve for the true coating weight is presented in figure 2.6 where the time to completion is defined as the time taken for the curve to reach a constant coating weight. After completion the graph fluctuates due to alternate dissolution and deposition of the coating. The variability in the characteristics (29) of the mild steel specimens can also lead to different phosphate coating weights on nominally identical specimens. This has led to some workers (30) presenting coating weight curves in the form shown in figure 2.7.

In figure 2.8 the addition coating weight and weight of metal lost curve are superimposed on the ideal true coating weight curve from figure 2.6. The metal loss curve reaches a constant when the phosphate coating has completed to the extent that no bare metal is available for acid attack. As this constant will therefore occur at approximately the same time for both the weight of metal

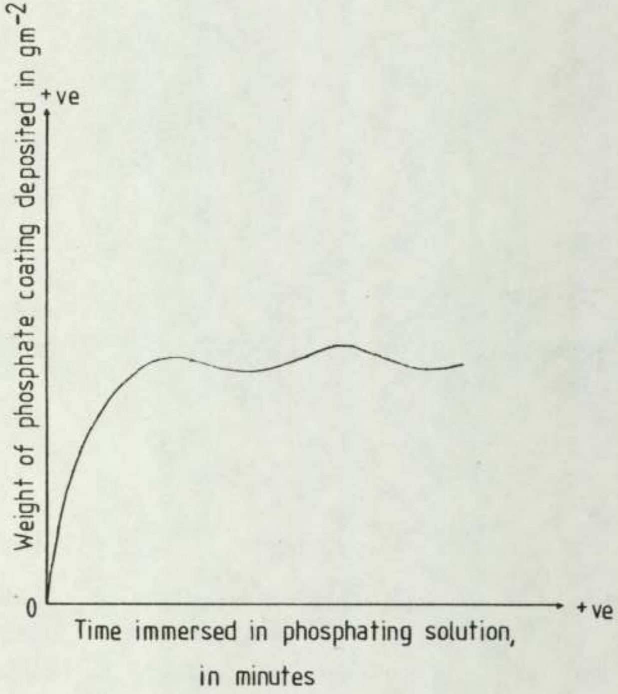


Figure 2.6 Ideal curve for the true phosphate coating weight against immersion time graph

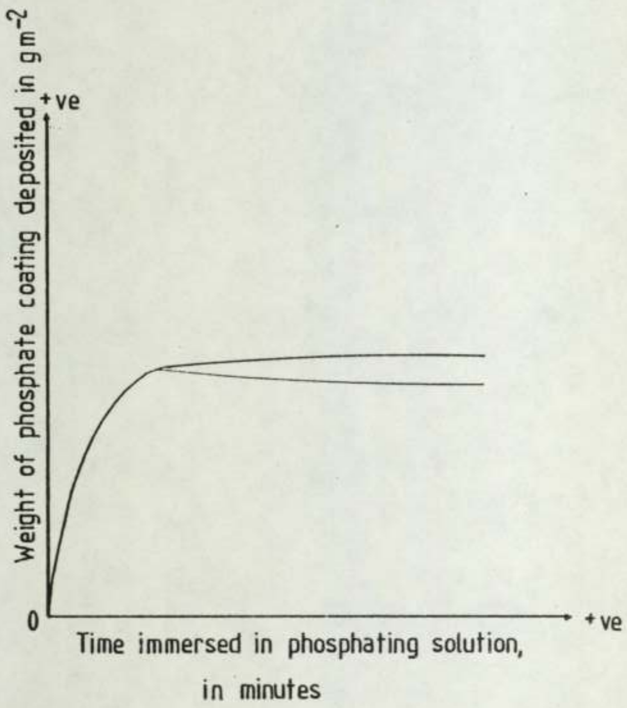


Figure 2.7 Alternative method of presentation for a true phosphate coating weight against immersion time graph

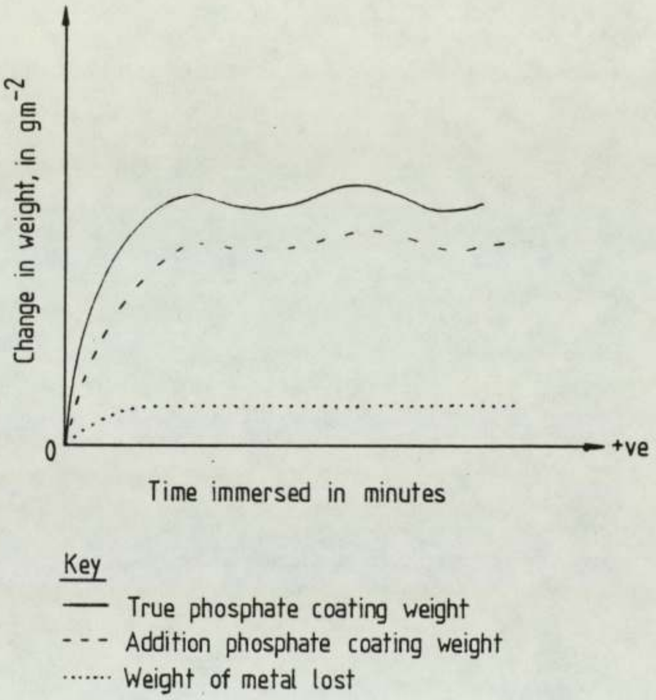


Figure 2.8 The corresponding addition coating weight and metal loss curves superimposed on the ideal coating weight curve shown in figure 2.6

lost and true coating weight curves, it also occurs at the same time for the addition coating weight curve.

2.1.11.1 Potential/time curves

There has been some work carried out on the analysis of potential time curves for the phosphating of metals. Covered in detail by Walter (31), this technique involves making the specimen to be phosphated the anode of a cell. The change in potential of the specimen with time, due to the reactions developing a non conducting phosphate coating can be measured against a reference calomel electrode. This technique allows the construction of more accurate coating weight curves from which more detailed information can be obtained (32).

2.2 The salt spray (fog) test

The corrosion tests commonly used to assess sealed phosphate coatings include the salt spray test, humidity test and water soak test. The specifications in this work require the coating to be exposed to the salt spray test.

Salt spray testing involves exposing suitable samples to a fog or mist formed by atomising a solution of sodium chloride under controlled conditions. One of the first accelerated corrosion tests, it has undergone substantial development work since it was first published by Capp 1914 (33), and is now covered by several national standards including DIN 50 021, BS AU148, and ASTM B117-73. In this work the standard used was "The salt spray (fog) test ASTM B117-73. (A review of this method will be presented comprising of two sections, firstly the work done on the basic factors of the test and secondly a critique of the test in its current form).

2.2.1 Basic factors

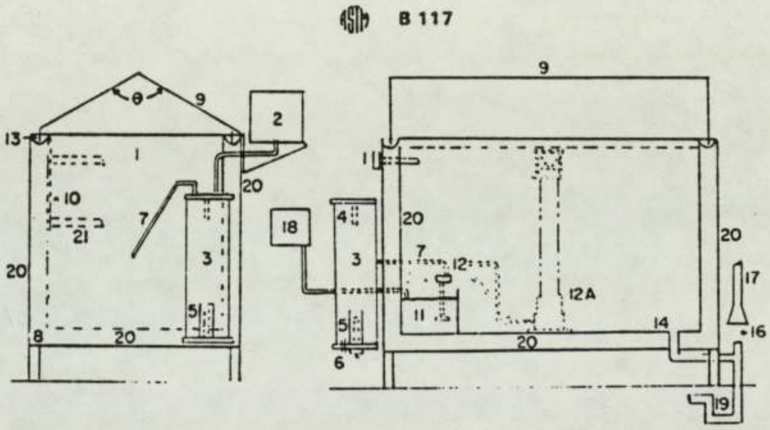
The standard ASTM B117-73 is reprinted in appendix 1. An impression of the number of changes the test has undergone is gained by comparing figure 2.9 which shows a salt spray cabinet conforming to the current standard with figure 2.10 which shows the salt spray cabinet in use at the National Bureau of Standards in 1924 (34).

2.2.1.1 Temperature inside the cabinet

Since the rate of most chemical reactions in aqueous solutions depends on temperature, the importance of controlling the temperature of the test has long been recognised. In 1924 Rawdon (35) suggested the temperature of the test should be standardised at 3o $\pm$ 1°C, and in 1928 (36) warned against use of the test over a widely varying range of temperatures. Subsequently Mutchler, Buzzard and Strausser (37) suggested that a temperature of 35 $\pm$ 2°C could be maintained in a test cabinet without cooling equipment in the summer and with heating equipment in winter. For inclusion into the test these limits were modified to 35 + 1.1 or -1.7°C and a method of heating the test cabinet included.

2.2.1.2 Temperature and humidity of the compressed air

The importance of controlling the temperature and humidity of the large volume of air used for atomising the solution to achieving a uniform temperature within a test cabint was pointed out by Waldron (38). The air needs to be heated to a temperature



θ — Angle of lid, 90 to 125 deg
1 — Thermometer and thermostat for controlling heater (Item No. 8) in base
2 Automatic water levelling device
3 — Humidifying tower
4 — Automatic temperature regulator for controlling heater (Item No. 5)
5 – Immersion heater, non-rusting
6 — Air inlet, multiple openings
7 — Air tube to spray nozzle
8 — Strip heater in base
9 — Hinged top, hydraulically operated, or counterbalanced
10 - Brackets for rods supporting specimens, or test table
11 -- Internal reservoir
12 — Spray nozzle above reservoir, suitably designed, located, and baffled
12A Spray nozzle housed in dispersion tower located preferably in center of cabinet
13 -- Water Seal
14 — Combination drain and exhaust. Exhaust at opposite side of test space from spray nozzle (Item 12), but preferably in combination with drain, waste trap, and forced draft waste pipe (Items 16, 17, and 19)
16 · Complete separation between forced draft waste pipe (Item 17) and combination drain and exhuast (Items 14 and 19) to avoid undesirable suction or back pressure.
17 Forced draft waste pipe.
18 — Automatic levelling device for reservoir
19 -- Waste trap
20 — Air space or water jacket
21 — Test table or rack, well below roof area

Figure 2.9 A salt spray cabinet conforming to ASTM B117-73

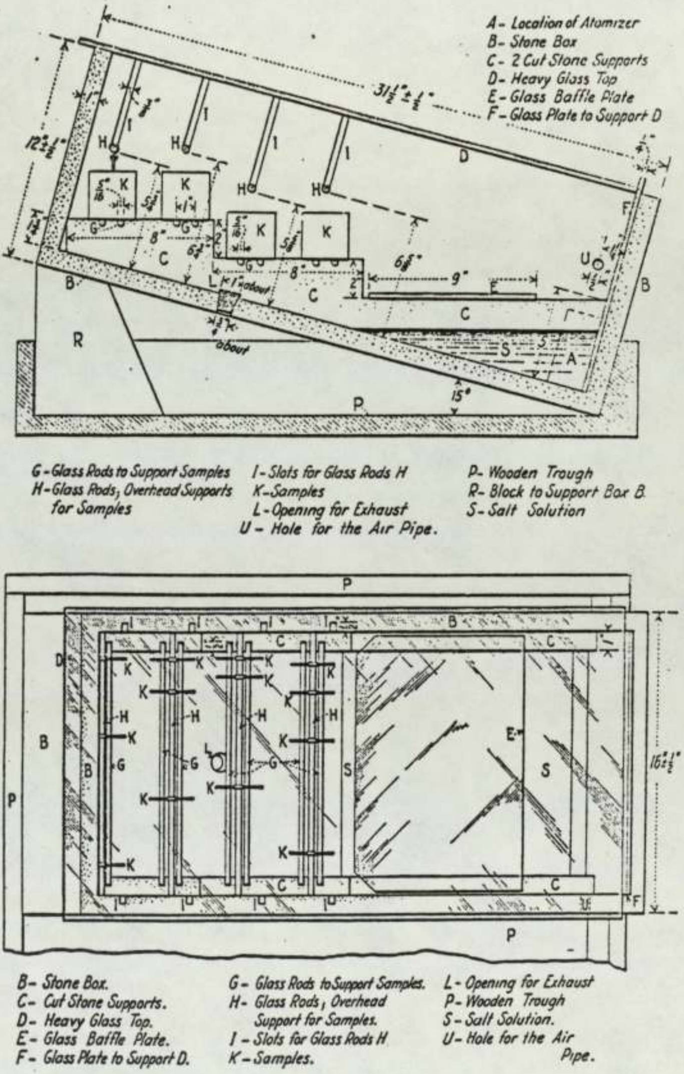


Figure 2.10 A salt spray cabinet of the type used at the National Bureau of Standards (U.S.A.) in 1924

above that of the cabinet to compensate for the drop in temperature of the air as it leaves the nozzle orifice and expands to approximately atmospheric pressure (Joule-Thomson effect). The air also requires passing through a water tower to ensure it has a humidity equal to that of the fog in the cabinet, otherwise evaporation will occur within the cabinet with an associated cooling effect.

In the specification, these two requirements are met by stipulating the compressed air is passed through a humidity tower heated to a temperature determined by the pressure of the air. To ensure that the water tower consistently works effectively there should be automatic control over the water level it contains.

2.2.1.3 Sodium chloride solution

(i) Sodium chloride content

Capp (33) originally used a solution of water saturated with salt, but subsequently changed to a 3% solution to avoid the problem of salt clogging the spray nozzle. Finn, Rawdon and Grossman (39) recommended the use of a 20% solution. However, Waldron (38) indicates the use of a 4% solution was widespread until 1932 when a 20% solution became generally used. A principal objection to the use of the 20% solution was the tendency of solid salt to deposit either on the specimen or around the spray nozzle and interfere with the test. This behaviour was attributed to the improper functioning of the apparatus, by Mutchler, Buzzard and Strausser (37), because the atomisation air contained an insufficient amount of water vapour and caused a dry fog to be sprayed. Data (40) indicated that the results from tests using a 20% solution were less affected by fluctuations in test temperature than the results from tests using a 5% solution were. However, data presented by May and Alexander (41) showed the corrosivity of iron and steel specimens by a 3% solution to be greater than that by a 20% solution. McMaster (42) subsequently presented a graph which showed the dependence of corrosivity of a salt solution used in the salt spray test on its salt content. This is reproduced in figure 2.11 and clearly shows the peak activity results from a salt solution containing between 1% and 5% salt. Consequently the current solution requires a solution containing 5 ± 1 weight per cent salt.

(ii) Recycling of solution

In the test cabinet shown in figure 2.10 corrosion products from the test specimens would build up in the salt solution as it was continuously recycled during a test. Therefore the constituents of the solution varied both during the test and also according to the types of metal under test. Work in 1925 (43) showed this caused inconsistencies in the test results and it was recommended that the test cabinet should be redesigned to prevent the recycling of solution. The current standard requires that the recycling of solution should be prevented by the design of the cabinet.

(iii) Purity of the sodium chloride

An early investigation (44) showed simply that the purity of the salt used affected the corrosivity of the salt solution, and a recommendation was made that 99.8% pure salt should be used. A

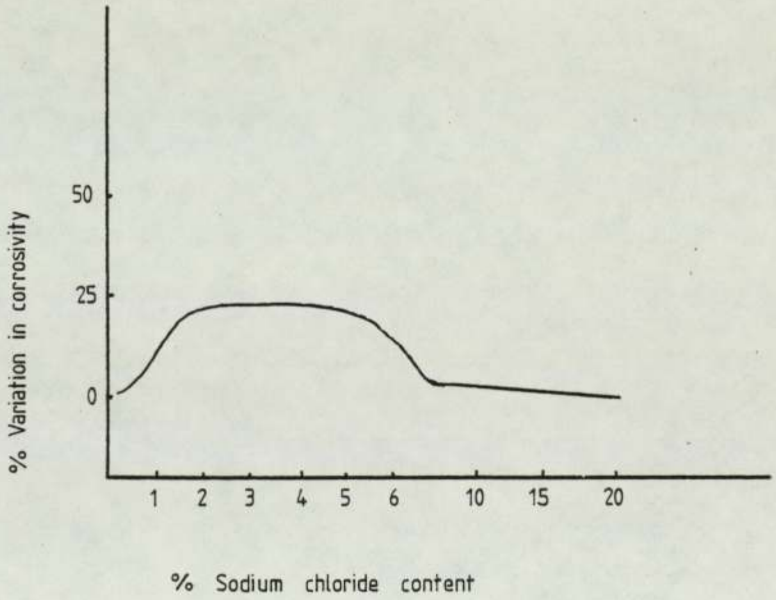


Figure 2.11 Corrosivity as a function of the sodium chloride content of the solution

later more detailed investigation (45) into the effect of metallic impurities on the corrosiveness of the salt solution led to the stricter requirement used in the present standard:- no more impurities than 0.3 per cent on the dry basis, not more than 0.1 per cent sodium iodide and substantially free of nickel and copper.

(iv) Purity of the water

Waldron (38) suggested that the solution should be made using distilled water to prevent any large differences in the composition of the tap water affecting the test results. However, if the tap water did not contain a large amount of dissolved solids it could be substituted for the distilled water. The current standard still allows the use of tap water in place of distilled water, provided the tap water contains less than 200 ppm solids.

(v) pH of the sodium chloride solution

Waldron (38) stated:

> "It is believed that the corrosion of most materials in this test will be only little affected if the solution is maintained within a narrow pH range at the neutral point."

Darsey and Cavanagh (46) in an investigation of the effect of solution temperature on pH found that after raising the temperature of a solution, based on tap water, from ambient to the test temperature of $35^{\circ}C$ and allowing it to stand for some time the pH increased from 6.9 to 8.7. This was suggested to be analogous to the difference in pH caused by saturating distilled water with carbon dioxide. Therefore the rise in pH of the salt solution was attributed to the loss of carbon dioxide caused by the rise in temperature of the solution lowering the solubility product. In the current standard there is a stipulated pH range for the solution, and the pH of the sprayed solution has to be tested.

The importance of controlling the pH of the solution can be seen from the simplified Pourbaix (47) diagram for iron presented as figure 2.12. The figure shows that at a potential of 0 volts as the solution pH falls below 7 the specimen enters the corrosion region of the diagram and as the pH of the solution rises above 7 the specimen enters the passivation region of the diagram.

2.2.1.4 Positioning of the test specimens

The importance of the angle of exposure (44) of the test specimen in the salt spray test is demonstrated by figure 2.13 which shows the variation of the corrosion rate of specimens with their angle of exposure. The corrosion rate is a maximum between 15°, and 85° to the horizontal and drops off markedly at angles outside this range. The current standard requires specimens to be exposed at angles between 15 and 30° to the vertical, or as agreed between the purchaser and supplier.

2.2.1.5 The fog

An investigation (43) into the reproducibility of results from the salt spray test revealed a large variation in the corrosion rate of nominally identical specimens in different parts of the same test cabinet and between nominally identical specimens in different cabinets.

The difference in the results from different parts of the same cabinet was suggested to be due to the difficulty of producing a uniform density of salt fog throughout the cabinet.

This led to variations in fog settling rates and corrosion

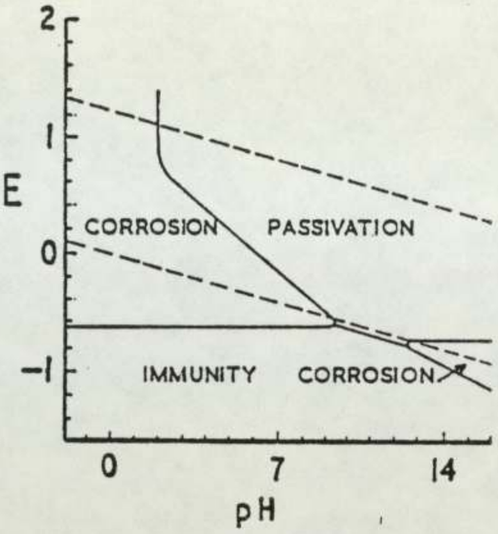


Figure 2.12 A simplified form of the Pourbaix Diagram for iron

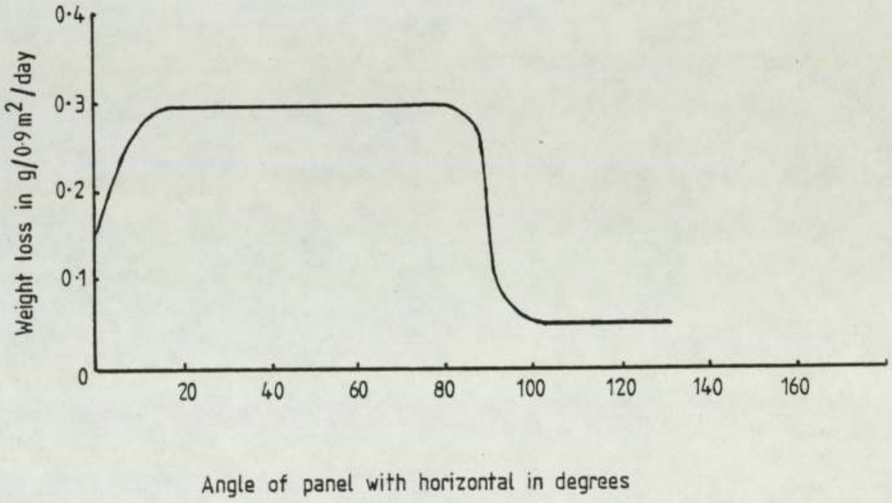


Figure 2.13 Effect of specimen angle on corrosion in salt spray cabinets

conditions in different regions of the cabinet. To improve the uniformity of the fog density changes to the fog production method were suggested. However as a uniform fog density throughout the cabinet could not be guaranteed, it was recommended that the specimens should be periodically moved around the cabinet as this would ensure that each specimen was subjected to an average of the corrosion conditions within the cabinet.

The lack of standardisation of the atomising conditions and type of atomiser (spray nozzle) was blamed (48) for the discrepancy in results between different cabinets, as cabinets could be operating with widely different fog densities and consequently fog settling rates. Darsey and Cavanagh (46) showed that a change in the fog settling rate affected the corrosion rate of specimens, and McMaster(42) subsequently reported that the trend was for an increase in the fog settling rate to increase the corrosion rate of specimens.

Darsey and Cavanagh (46) also reported that there was a critical atomisation pressure, for a nozzle, at which an abnormal increase in the corrosivity of the fog occurred. This peak in the corrosivity was shown to be avoided if fluctuations in the pressure of the air supply to the atomiser were controlled to within 0.007 bar.

The current standard takes account of this work by stipulating a maximum and minimum fog settling rate that must be achieved at a site nearest to and farthest away from the spray nozzle. The only requirement regarding the design of spray nozzle in the standard is that it should achieve the stipulated fog collection rate. The standard stipulates the range of air pressures, to the spray nozzle, which are permitted and advises that either the critical air pressure of the nozzle is determined and avoided, or the air supply to the nozzle is fitted with a pressure regulator to prevent there being a critical air pressure.

2.2.2 Critique

Much of the early criticism of the salt spray test was due to the lack of standardisation of the test method. This allowed test cabinets to operate over a range of widely differing corrosion conditions causing variations in the results obtained. Even after the first standard had been issued in 1939 (49) after a questionnaire (50) in 1942 it was reported that

> "considerable variation exists in current salt spray techniques".

and

> "from the replies it is apparent that uniform control of operating temperatures, positions of test specimens, fog density and air pressure is not accomplished by most users. It should be pointed out, however, that variations are possible even though the test is performed in accordance with ASTM B117-41T. Thus it would appear further standardisation may be necessary".

The investigations carried out to standardise the test have produced a great improvement. However the present standard is still open to the following criticisms.

(i) Failure criterion

The standard indicates the information the supplier should pass on to the purchaser regarding the results of the test. However, the failure criterion that should be applied to the test is deliberately left to mutual agreement. While it would be difficult to standardise the failure criterion, as the test is used for assessing a variety of specimen types and base metal/coating combinations, guidelines would be useful. Guidelines would help to prevent the situation where coatings are required to exhibit no defects after a set period of exposure. This requirement strictly applied can cause test specimens to be failed due to small areas of rust developing where damage has occurred to the specimen during its preparation.

(ii) Calibration of fog droplet size

Efer (51) suggests that an atomiser produces a fog made up of droplets of widely varying diameters. These droplets settle at different rates, the larger heavier droplets near the atomiser and the smaller lighter droplets away from the atomiser. He suggests that this effect combined with 'flyaway spray' caused by the large volume of air required for atomising the solution causes different fog settling rates within the test cabinet. Thus by virtue of their position in the test cabinet nominally identical samples could be exposed to different fog settling rates and give different results. He suggests firstly that the problem could be alleviated by including the requirement in the standard that at least 90% of the fog should consist of droplets of a diameter between 1 and 7 μm. Secondly, he suggests the problem could be solved by using equipment that produced an aerosol rather than a fog. An aerosol through the uniformity of the diameter of its constituent droplets, and relatively low air requirement would give a more uniform fog settling rate within the test cabinet.

(iii) Use of the test

The standard covering the salt spray (fog) test ASTM B117-73 points out that the test is designed primarily for use in quality acceptance work. Much of the criticism directed at the test has resulted from its use for corrosion research. La Que (52) in an article which was strongly critical of the test's use for research stated:

> "The salt spray test is useless as an instrument of research, but of possible worth for inspecting different lots of the same product".

In many of the published replies(53)to La Que's article the use of the salt spray test for quality assurance was indicated to be acceptable but a necessary evil. In this work the ability of certain finishes to withstand the salt spray test is assessed. Comparisons are made only between the results for specimens with the same finish, and the test is not used for predicting service life or for ranking different types of finish. The aim of the work is to improve the salt spray resistance of the finishes phosphate and oil or stain to a level where they can meet the salt spray test requirements imposed by the automotive customers. Therefore, the test is being used in its acceptable form, that is for quality purposes.

CHAPTER 3

EXPERIMENTAL METHOD

3.1 Test panels

Mild steel test panels were purchased from Sapcote Engineering Ltd., Leicester. Two sizes were used, panels 25 cm x 2.5 cm x 0.015 cm for the determination of phosphate coating weights and panels 15.3 x 10.2 cm x 0.015 cm for the evaluation of finishes. Although these panels were of a lower quality than Goldseal test panels that are produced by Pyrene Chemical Services Ltd specifically for experimental work, they were more robust. This facilitated their being cleaned by the actual industrial cleaning processes in use at Metalastik. This was preferred to using test panels, prepared to a standard that could not be achieved in the factory, to assess finishes that would ultimately be produced in the factory.

However the following process was adopted as the standard method for cleaning test panels to ensure that the results from tests could be compared. The panels were immersed in alkali stabilised trichloroethylene vapour at a temperature of between 35 and 40°C for two minutes, then blasted with G12 (British Standard 2451) chilled iron grit for ten minutes using a Tilghmann wheel-abrator, followed by a second immersion in the trichloroethylene vapour for one minute. The panels were then stored in a dessicator until they were used, or for four weeks after which they were reprocessed if the panels were not used after being reprocessed once, they were discarded, as were panels that had been used in a test.

3.2 Selection of products for testing

When products were required for tests they were taken from batches of products that represented typical production at the required stage in the manufacturing process.

3.3 Cleaning of products to be tested

When products selected for testing required cleaning they were wheelabrated with G12 (BS2454) chilled iron grit for 10 minutes using a Tilghman Wheelabrator.

3.4 Phosphating

Three sets of equipment were used for phosphating, the manual and automatic phosphating plants and laboratory equipment. The works phosphating plants theoretically contain phosphating conditioning rinses(see 2.1.7.2 and 2.1.8.1) as part of their sequence. However, the conditioning rinse prior to phosphating is not maintained by the operators, and the use of chromic acid in a post phosphating treatment has been discontinued because of the health risks (2.1.8.1) associated with its use. Therefore for the basic work aimed at improving the quality of the phosphate coating the phosphating sequence used was that actually in use on the shopfloor. All the sets of equipment contained the basic process shown in figure 3.1. The figure shows processing consisted of alkali cleaning followed by rinsing in cold water twice to prevent carry-over of the alkali chemicals into the acid phosphating solution. Phosphating was followed by three rinses to ensure thorough cleansing of the phosphate coating after which the specimens were warm air dried. The immersion times in each solution are

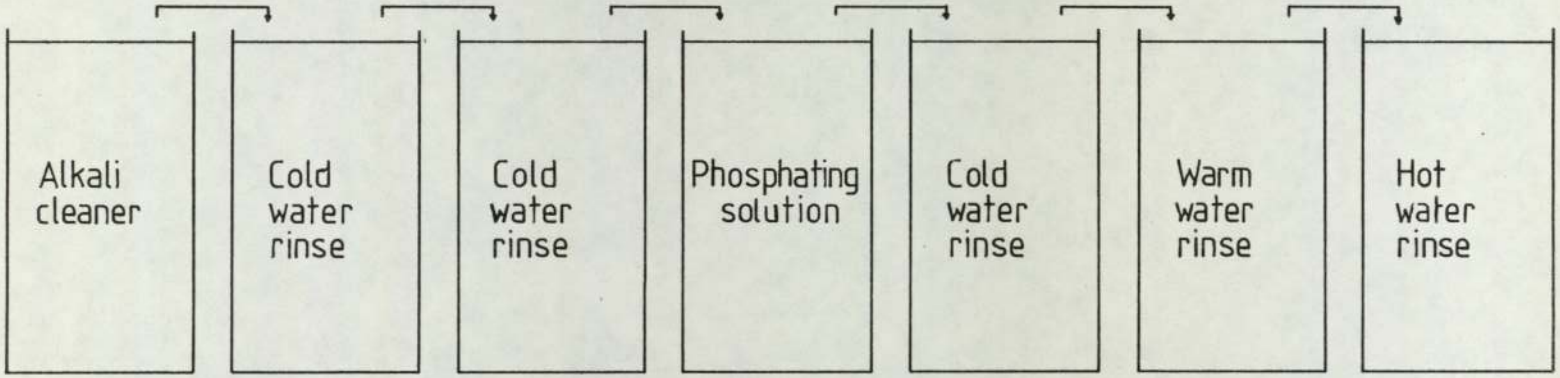


Figure 3.1 A schematic representation of the phosphating sequence used

presented in Table 3.1 and are identical to the immersion times used for production. The volume of each solution is also shown in Table 3.1 for each set of equipment. Thermostatically controlled steam coils were used for heating the manual and automatic phosphating plants, and the laboratory solutions were contained in thermostatically controlled water baths.

TABLE 3.1 COMPARISON OF PHOSPHATING PROCESSES

Solution	Tank volume (litres)			Immersion time (minutes)
	Manual plant	Automatic plant	Laboratory	
Alkali cleaner	141	659	3	4
Rinse	71	309	3	1 - 1.5
Rinse	71	309	3	1 - 1.5
Phosphating Solution	1135	1135	3	6
Rinse	254	254	3	1 - 1.5
Rinse	254	254	3	1 - 1.5
Rinse	254	390	3	1 - 1.5
Warm air dry	-	-	-	4

3.4.1 Alkali cleaner

Alkali cleaning was carried out using Pyroclean 19 a proprietary immersion alkali cleaner supplied by Pyrene Chemical Services Ltd. The solution was maintained between 85 and 90°C at a chemical strength of 55 - 60 points (0.6 Kg of Pyroclean 19 per 1000 litres of water = 1 point).

3.4.2.1 Determination of alkali pointage

The pointage of the alkali solution was determined by pipetting 10 ml of the solution into a conical flask, adding approximately 25 ml of distilled water and several drops of methyl red indicator. The resulting solution was then titrated against 0.1M hydrochloric acid until a change from clear to red indicated the end point. The pointage of the solution was given by the volume of hydrochloric acid used in the titration.

3.4.2 Rinses

The rinses were kept clean by frequent cleaning out and where possible a fresh water supply was used to overflow the rinse continuously during use.

3.4.3 Phosphating solution

Phosphating was carried out using either Bonderite 181X or Parco 95 zinc phosphating solutions, both being proprietary processes supplied by Pyrene Chemical Services Ltd. The chemicals for both solutions were supplied in two pack form, one pack for initial make up (IMU) of a solution and one pack for replenishment(R) of the chemicals in a working solution (see 2.1.5.1).

There are tests (5) available for determining the concentration of each chemical in these phosphating solutions. However in order to interpret the results of such tests, specialised knowledge of the solution is required, which the suppliers were unwilling to disclose as they were proprietary chemicals. Therefore when necessary the suppliers were asked to carry out a full analysis of the solution and comment on the results. The tests used in this work were only to determine the amounts of chemicals required to replenish the solutions. The test common to both the Parco 95 and the Bonderite 181X solution will be described next and the other control tests will be covered later.

(i) Total acid pointage

The total acid pointage of the phosphating solution was determined by pipetting 10 ml of the solution into a conical flask, adding 25 ml of distilled water and several drops of indicator phenolphthalein. The resulting solution was titrated against 0.1M sodium hydroxide until a change from colourless to pink indicated the end point. The pointage of the solution was given by the volume of sodium hydroxide used in the titration.

(1 litre of Parco 95 per 1000 litres of solution = 1 point)

1.5 litre of Bonderite 181X per 1000 litres of solution = 1 point)

3.4.3.1 Parco 95

Parco 95 is the trade name for a heavyweight immersion zinc phosphating solution which in this work was operated between 82 and 88°C with a total acid pointage between 38 and 42 points and an iron content between .25 and .35 points.

(i) Iron content

The iron content of the solution was determined by pipetting

10 ml of solution into a conical flask, adding 5 ml of a solution of 50% phosphoric acid and 50% sulphuric acid. The resulting solution was titrated against 0.02M potassium permanganate until a change from colourless to pink persisted for 45 seconds indicating the end point. The iron content of the solution was then calculated using the following equation.

The percentage ferrous iron content = volume of potassium permanganate used in titration X0.056.

(An addition of 0.6 kg of powdered iron = + 0.05%)

(An addition of 0.63 litre of Hydrogen Peroxide = -0.05%)

3.4.3.2 Bonderite 181X

Bonderite 181X is a medium to heavyweight immersion zinc phosphating solution. In this work the solution was operated as a heavyweight phosphating solution by the use of a proprietary additive chemical based on ethylene diamine tetraacetate,known as Additive 3 and supplied by Pyrene Chemical Services Ltd. The solution was operated between 64 and 68°C, a total acid pointage of 67 to 73 points, Additive 3 pointage of 7 to 10 points and maintained on the nitrite side by additions of sodium nitrite in the form of Compensating Solution 2 supplied by Pyrene.

(i) Presence of nitrite

The presence of nitrite was ascertained by dipping a strip of starch iodide paper into the solution. A change from white to blue indicated nitrite was present, no change indicated that an addition of sodium nitrite was required. If the test indicated an addition of sodium nitrite was required 1 to 2 ml of Compensating Solution 2 was added per litre of phosphating solution and the test repeated until a positive indication of the presence of nitrite was achieved.

(ii) Additive 3 pointage

Before determining the Additive 3 pointage a check was carried out to ensure that nitrite was present in the solution. The pointage was then determined by pipetting 10 ml of solution into a conical flask, adding 25 ml of distilled water, 2-3 grams of urea and 5 ml of a solution of 50% sulphuric and 50% phosphoric acid. The solution was then heated until just boiling, allowed to cool then titrated against 0.02M potassium permanganate until a change from colourless to pink persisted for 45 seconds. The Additive 3 pointage was given by the volume of potassium permanganate used in the titration.

(0.7 litre of Additive 3 per 1000 litres of solution = 1 point)

3.5 Determination of phosphate coating weight

As discussed in section 2.11 there are three weights of importance in the phosphating of metals, the true and addition phosphate coating weights and the weight of metal lost during phosphating. Determination of the true coating weight of samples is a destructive test and could not provide information on samples to be used for any purpose other than determining coating weights. For samples to be used in corrosion testing the addition phosphate coating weight was determined, as this would be expected to give an indication of the quality of the phosphate coating. The dimensions of test panels and products were determined using vernier calipers and a micrometer screw gauge.

3.5.1 Addition coating weight

The addition phosphate coating weight is given by:

$$\text{A.C.W.} = \frac{\text{Change in weight during coating}}{\text{surface area}} \quad \text{gm}^{-2}$$

3.5.2 True coating weight

To determine the true coating weight of phosphate on a sample the sample was phosphated, weighed and then the coating stripped off by immersing the sample in 1 molar hydrochloric acid inhibited with 20 gl^{-1} of antimony trioxide to prevent attack of the base metal. The panels were immersed for four minutes, dried and weighed, then immersed for further periods of 30 seconds until no significant weight loss occurred. The true coating weight is given by:

$$\text{T.C.W.} = \frac{\text{Decrease in weight during stripping}}{\text{surface area}} \quad \text{gm}^{-2}$$

3.5.3 Metal Loss

To determine the weight of metal lost during phosphating both the addition and true coating weights had to be determined for the sample. The metal loss is given by:

$$\text{M.L.} = \text{T.C.W.} - \text{A.C.W.} \ \text{gm}^{-2}$$

3.5.4 Coating weight curves

To determine coating weight curves a set of panels were phosphated (3.4) with the phosphating solution immersion times altered to 1,2,4,6,10,15 minutes and then further increments of 5 minutes until the curve achieved a constant value. To facilitate the comparison of curves they are presented with a single line rather than in the forms discussed in section 2.2.1.

3.6 Extraction of organic materials from phosphating solutions

A 100 ml sample of solution was transferred into a separating funnel, 100 ml of dichloromethane was added to the funnel which was then sealed and shaken vigorously for two minutes. The contents of the flask were then allowed to settle. The two immisible liquids separated and the dichloromethane fraction was run off into a weighed evaporating dish. This procedure was repeated twice using the same sample of phosphating solution. The evaporating dish was placed in a warmoven to prevent the evaporating dichloromethane from cooling the dish sufficiently to cause condensation to build up. After the dichloromethane had evaporated, the evaporating dish was reweighed to determine the weight of non-volatile organic material extracted.

The two methods used to try and identify the organic materials were firstly thin layer chromatography and secondly infra red spectroscopy.

3.6.1 Thin layer chromatography

A sample of the extracted organic material was dissolved in dichloromethane then small amounts of the liquid were spotted onto the bottom of a Polygram sil G precoated plastic sheet (Camlab Cambridge) using a capillary tube. Samples of known organic materials were produced for comparison with the unknown material by two methods.

(i) The known organic was dissolved in dichloromethane and spotted onto the sheet using a capillary tube.

(ii) The known organic was added to a fresh laboratory phosphating solution, the solution used then the dissolved organic materials extracted (3.6). The extracted organic material was then dissolved in dichloromethane and spotted onto the sheet using a capillary tube.

The sheet was then maintained in contact with a solution of 100 parts by volume of toluene, 1 part acetone, 5 parts ethyl acetate and removed when the liquid had nearly reached the top of the sheet. The level to which the liquid had climbed was marked and the sheet allowed to dry. It was then examined in daylight and U.V.light and the distances travelled and colours of any visible spots were noted. The distances were then converted into retention factors (R.F.).

3.6.2 Infra red spectroscopy

A sample of the organic material was dissolved in dichloromethane. Using a capillary tube small amounts of the liquid were transferred onto one of the salt plates of a cell from a Unicam SP200 infra red spectrophotometer until a thin layer of the organic material had deposited. The cell was then closed, transferred to the machine and a spectrum produced.

3.7 Supplementary finishes

3.7.1 Black stain sealant

A proprietary black stain sealant P41 supplied by Pyrene Chemical Services Ltd was used (3.7.3) at a solids content (3.7.5.2) of 10 - 12% by weight.

3.7.2 Oil sealant

A proprietary oil finish Astrolan 23/20/11 supplied by Astor Chemicals Ltd was used (3.7.3) at a solids content (3.7.5.2) of 18 - 22% by weight.

3.7.3 Application of oil or stain by dipping

Both these finishes were applied by dipping. The solutions were kept in air tight containers, stirred and the solids content checked before use and discarded and replaced with fresh solutions every four weeks.

3.7.4 Paint

At Metalastik two paints are used. One paint is a high build formulation applied by spray and is formulated to give a thick coat of paint. The other paint is applied by dipping and is formulated to give a thin coat of paint.

3.7.4.1 Application of paint by spray

Crodabond a high build etch primer finish supplied by Croda Paints Ltd was applied using a Bink Bullows Model 230 spray gun, supplied with paint by a pressure vessel. The paint was maintained at a flow time of 28 to 36 seconds (3.7.5.3) and applied at an atomisation pressure of 2.91 to 3.45 bar. After application the paint was allowed to air dry. The paint film was then examined to ensure that it was free of runs and sags and that the average thickness of the phosphate and paint film was between 25 μm and

30 μm. Samples that were to be compared were, as far as possible, sprayed at the same time.

3.7.4.2 Application of paint by dipping

Goodlass Wall etch primer finish supplied by Goodlass Wall and Co.Ltd. was applied using the Stein Atkinson dip plant. The paint was maintained at a flow time of between 50 and 60 seconds (3.7.5.3).

After application the paint was warm air dried. The coating was then checked to ensure the paint film was free of runs and sags and that the average thickness of the phosphate and paint film exceeded 12 μm. Samples that were to be compared were, as far as possible, dipped at the same time.

3.7.5 Tests on supplementary finishes

3.7.5.1 Coating weight

The sample was weighed before application of the paint and after the paint film had dried. The paint coating weight is given by:

$$\text{P.C.W.} = \frac{\text{Change in weight of the specimen}}{\text{surface area}} \quad \text{gm}^{-2}$$

3.7.5.2 Solids content

The solids content was determined in accordance with BS3900 Methods of Test for Paints part B2 Determination of volatile matter and non volatile matter.

3.7.5.3 Flow time

The flow time was determined in accordance with BS3900 Methods of Test for Paints part A6 Determination of Flow Time, using a B3 cup and the break point procedure.

3.7.5.4 Film thickness

The film thickness was determined in accordance with BS3900 Methods of Test for Paints part C5 Determination of Film Thickness using method No.5 and the permanently magnetic class of instrument.

3.8 Corrosion testing

3.8.1 Salt spray testing

Salt spray testing was carried out in a cabinet that was operated according to the American Society for Testing Materials Standard ASTM B117-73 except in two respects:

(i) the cabinet did not have a device to automatically control the level of salt solution in the reservoir. Therefore as the solution level dropped the head between the solution and the atomiser increased possibly causing a decrease in the volume of solution sprayed and consequently a decrease in the fog settling rate.

(ii) the cabinet did not have a device to automatically control the amount of water contained in the humidity tower. This could lead to fluctuations in the temperature and humidity

of the compressed air used for
atomising the salt solution (see 2.2.1.2).

To minimise the effects of these two shortcomings the two levels were maintained by frequent manual additions during periods of use. At the start of this work Metalastik agreed to purchase a new salt spray cabinet that met the requirements of ASTM B117-73, however, the cabinet was not purchased.

The test panels were exposed at an angle of 30°C to the vertical, with the side to be tested parallel with the flow of fog. Test parts were exposed with the maximum amount of surface area exposed at an angle between 15 and 30° to the vertical and parallel with the flow of fog. In view of the shortcomings of the test cabinet both the test parts and panels were moved around the cabinet during the period of testing to ensure that they were all exposed to closely similar corrosion conditions (see 2.2.1.5).

3.8.1.1.. Inspection of samples

During testing all the samples were inspected at 16 and 24 hour intervals. At the inspections the samples were washed with distilled water, dried in a gentle stream of compressed air and then two aspects of the samples were evaluated. Firstly, at each inspection the surface or surfaces of the sample under test were examined for signs of corrosion breaking through the finish. Secondly, at each 24 hours inspection the painted samples were subject to a paint adhesion test.

3.8.1.2 Appearance

The samples were left on test until the first significant signs of base metal corrosion appeared. A small number of large corrosion sites or a number of small corrosion sites were considered to be significant, but if only one or two small corrosion sites appeared that could be due to imperfections on the specimen,these were ignored (see 2.2.2.2). On the appearance of significant signs of base metal corrosion the time elapsed since the test had begun was noted and the sample was rated according to the scheme presented in figure 3.2. The average size of the corrosion sites was rated according to Chart B and the frequency of their appearance according to Chart A to give a 2 digit rating.

This rating system was originally devised by Champion for assessing the number of pits, blisters and flaking areas that were present on electroplated and anodized corrosion specimens. It was used in this work because it gave a better definition of the appearance of specimens after testing than the recommended standard ASTM D1654-74. Evaluation of painted or coated specimens subjected to corrosive environments, or the standard ASTM D610 Evaluating degree of rusting on painted steel surfaces.

3.8.1.3 Adhesion

To test the adhesion of the paint film the finish on the surface under test was scribed through to the bare metal using a blade of 25μm thickness, to produce the pattern shown in figure 3.3. Before the start of the salt spray test and at 24 hour intervals during the test the following procedure was carried out. The area

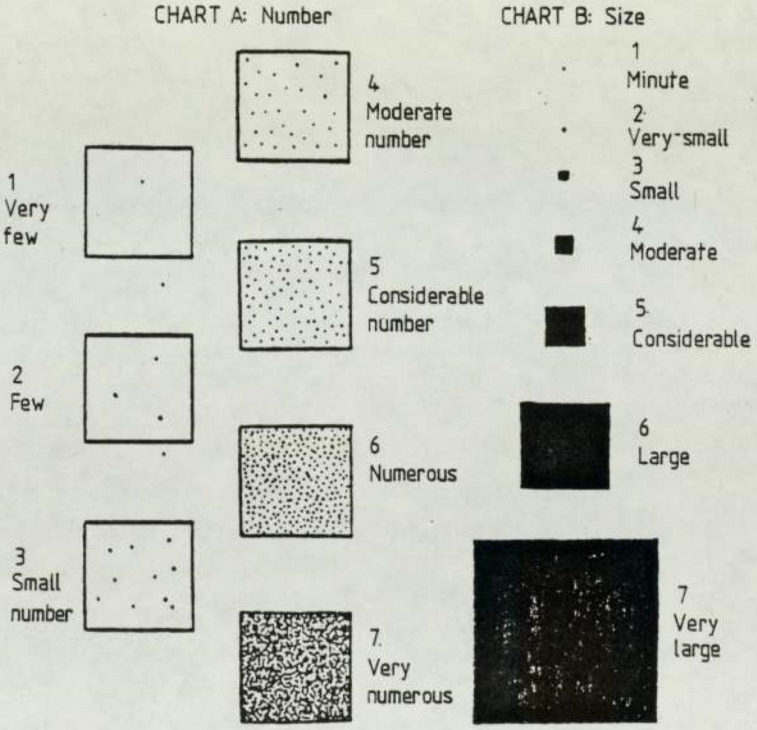
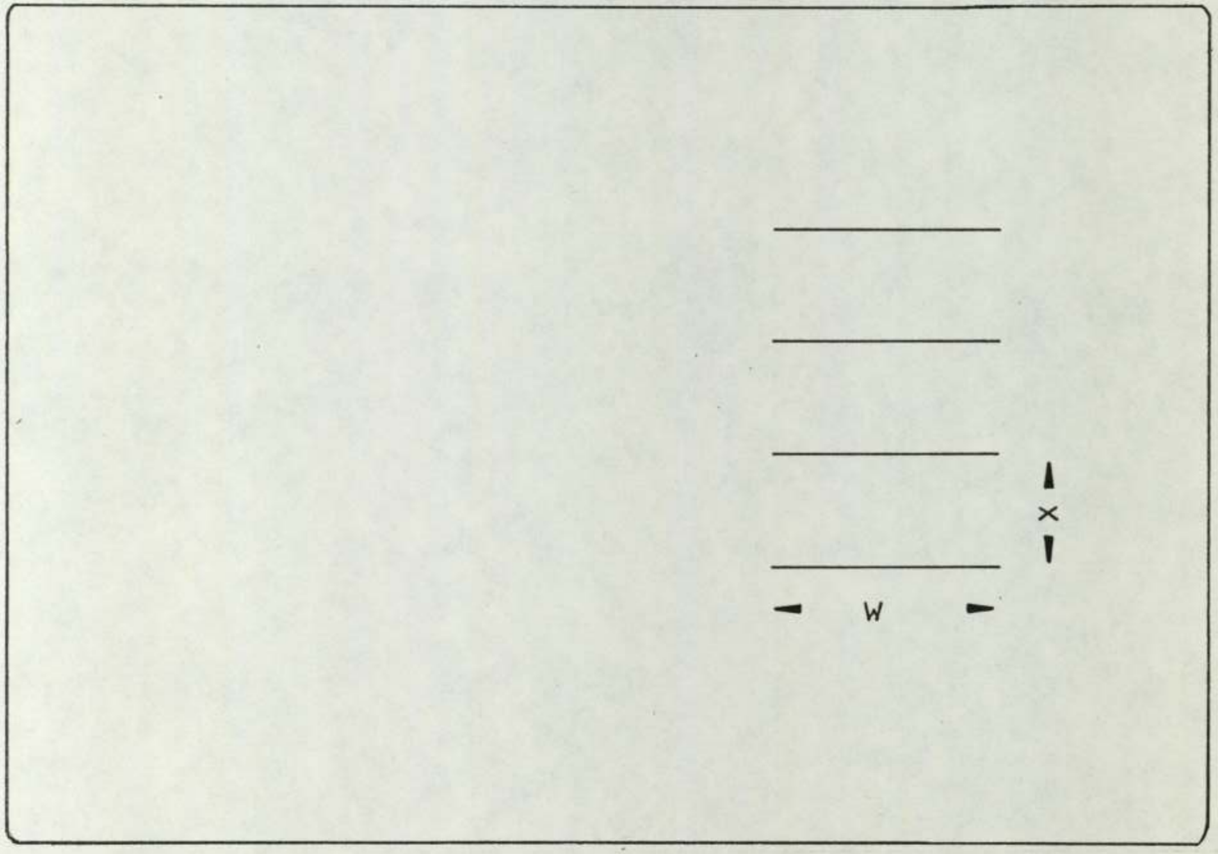


Figure 3.2 System for rating the appearance of corrosion on the surfaces of samples



All scribe lines were
25mm from edges

W = 30mm

X = 15mm

Figure 3.3 The positions of the scribe lines on the phosphated and painted panels used in the salt spray test surrounding a scribe line was gently dried using tissues and compressed air, a piece of sellotape masking tape was applied over the scribe line (using an India rubber to apply even pressure) then sharply stripped off. The distance paint was removed either side of the scribe line was measured in four places and an average value calculated. The adhesion of the paint film was judged to have failed when the average value exceeded 2 mm, or a general loss of adhesion was detected in the area surrounding the scribe line. This test is an adaptation of ASTM D1654-74 Evaluation of painted or coated specimens subjected to corrosive environments. The two major changes were firstly to use several scribe lines to allow an assessment of the variation in adhesion of the paint film with duration of the test rather than simply assessing the adhesion after a specified period of testing. Secondly, instead of rating the loss of adhesion a simple pass or fail standard of 2mm was taken because this was the criterion mainly applied by the automotive customers.

This adhesion test, an adaptation of ASTM D1654, evaluated both the general adhesion of the paint film and the resistance of the finish to corrosion creepage from a damaged area. For this reason plus its simplicity it was used in preference to other more sophisticated adhesion tests such as that described by Bullit and Prosser (54).

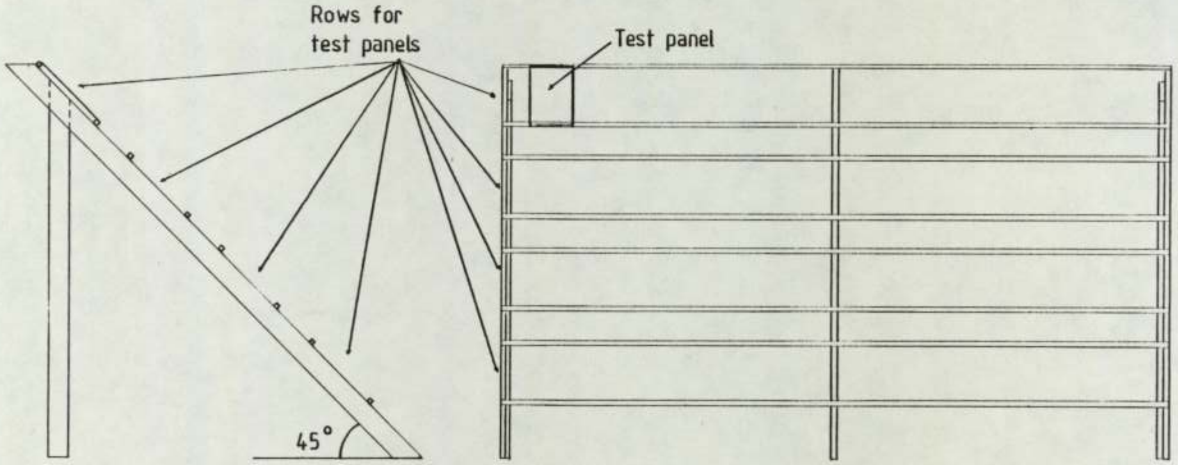
3.8.2 Atmospheric corrosion testing

Atmospheric exposure of test panels was used in preference to in-service exposure of test panels or products for the following reasons. The required test panels and products were not available until this work was near completion. Therefore insufficient time was available for the type of comprehensive test programme (55) the author suggests would be required to allow realistic comparisons between the results for the finishes.

However, an atmospheric test of the finishes allowed test panels to be exposed under exterior corrosion conditions and although an atmospheric test is usually carried out in multiples of one year (in order for the panels to be exposed to complete seasonal cycles) comparisons between specimens exposed for shorter periods are valid provided they are exposed concurrently in the same test.

As comparisons were only going to be between the panels exposed in the test and no specific assumptions with regard to in-service life were to be made from the results, only one test site was used. This was the roof of the factory at Evington Valley Road, Leicester. The rack was fixed in an area free of overhangs and discharge stacks, with the panels facing south at an angle of 45°. The test panels were fixed to the slats of a wooden rack as shown schematically in figure 3.4. Tacks, insulated from the panel to prevent bimetallic corrosion contaminating the panel, were used to mount the panels. Care was taken to ensure the panels were fixed such that no strain was introduced by the fixing method and the positioning of panels was such that the drainwater from one panel did not impinge on any other.

The top and bottom centimetre of each panel was blocked off with insulating tape to prevent edge corrosion products running down specimens and causing contamination(56). Panels were exposed



Side view

Front view

Figure 3.4 Rack for the atmospheric corrosion test as produced or with diagonal scribe lines on the panel, as shown in figure 3.5, produced using a ruler and a blade of 25 μm thickness. This pattern of scribe lines was used to allow a single assessment of the adhesion of the paint film at the end of the test.

3.8.2.1 Inspection

The panels were inspected every four weeks for general appearance and for signs of corrosion creepage from the scribe marks. The appearance was rated according to the system shown in figure 3.2. Any obvious signs of corrosion creepage from edges or scribe lines were also noted.

3.9 Examination of phosphate coatings

Scanning electron microscopy was used in preference to optical microscopy for examining the phosphate coatings, because of the greater depth of field a scanning electron microscope offers. Representative areas were carefully cut from samples for examination. These were mounted on studs and connected to earth using small spots of silver paint between the cut edges of the specimen and the stud. The specimens were examined using a Cambridge 150 scanning electron microscope operating at 25 KV detecting secondary electrons. The electrical insulation properties of the phosphate coating caused problems due to electrical charge building up on the specimen, and affecting the performance of the microscope. When this occurred the problem was alleviated by spraying the specimens with an electrically conductive coating that was known not to cause artefacts in the surface structure.

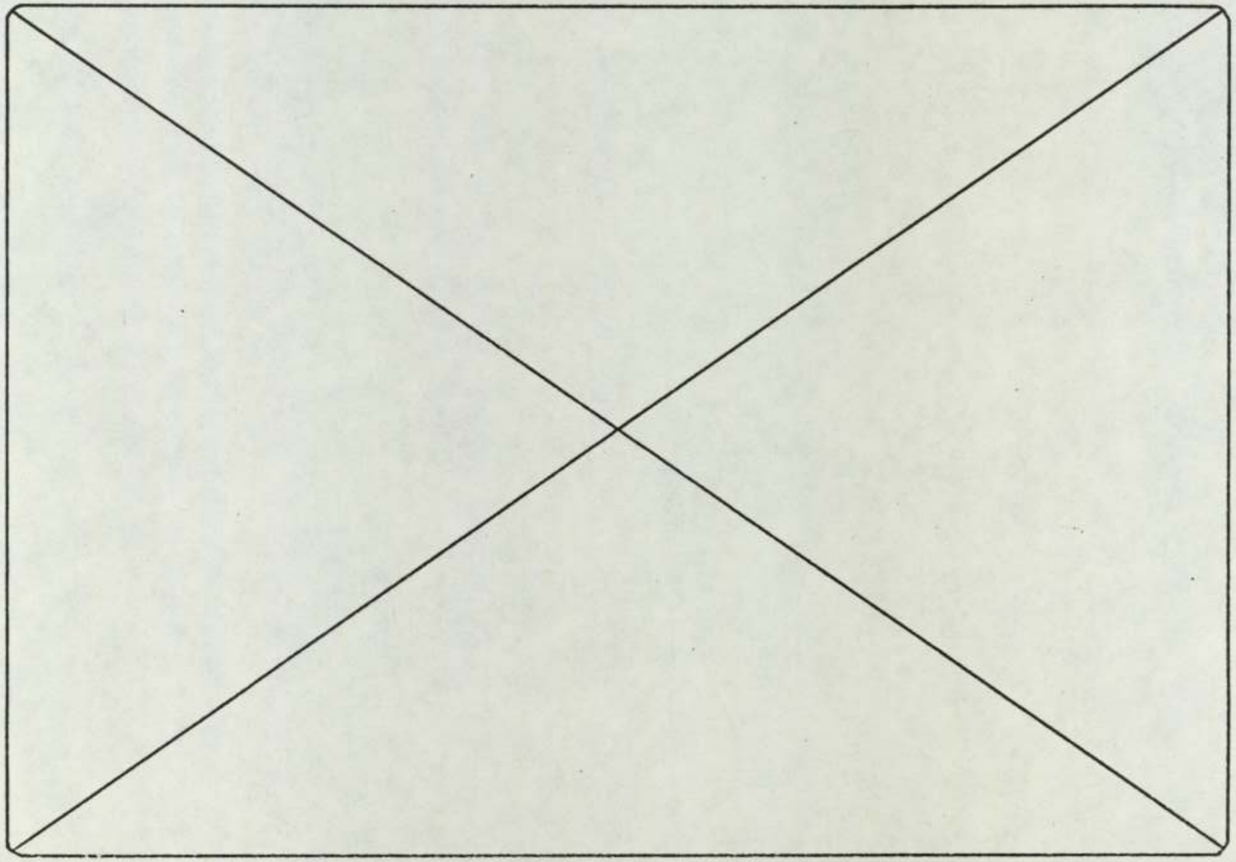


Figure 3.5 Scribe line pattern for atmospheric corrosion testing

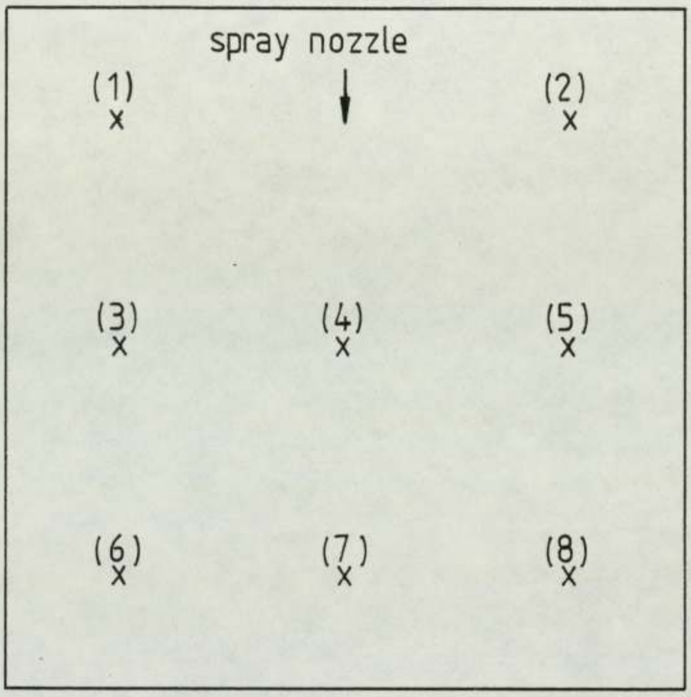
3.10 Preliminary experimental work

3.10.1 Salt spray cabinet

In view of the importance attached in the literature (see 2.2.1.5) to the fog settling rate in the salt spray test, the relationship between the atomisation air pressure and the fog settling rate for the cabinet used in this work was determined. Eight fog collection devices of the type described in ASTM B117 -73 were placed in the cabinet in the positions shown in figure 3.6. The cabinet was then operated for 24 hours at each of a range of air pressures and the fog collection rate determined. The results in Table 3.2 show that with the exception of positions 1 and 2 in the cabinet there was not a large variation in the fog collection rate with the atomisation air pressure used.

TABLE 3.2 VARIATION OF THE FOG SETTLING RATE IN THE SALT SPRAY CABINET WITH THE ATOMISATION AIR PRESSURE USED

Atomisation air pressure (bar)	For collection rate at each fog collection site (ml hr^{-1})								Average
	1	2	3	4	5	6	7	8	
0.966	1.8	1.7	1.5	1.6	1.5	1.5	1.6	1.6	1.6
1.104	1.8	1.7	1.6	1.5	1.7	1.5	1.5	1.7	1.6
1.24	1.8	1.7	1.6	1.6	1.7	1.5	1.6	1.5	1.63
1.38	1.9	1.7	1.5	1.4	1.5	1.5	1.5	1.5	1.56



Plan view of the interior of the salt spray cabinet

Key

( ) Identification number

x Position

Figure 3.6 Positions of the fog collector devices in the salt spray cabinet

With the exception of positions 1 and 2 there was also not a great variation between the fog collection rate in different parts of the test cabinet at constant atomisation air pressure. The fog collection rates achieved were within the 1 to 2 ml hr^{-1} required by the standard ASTM B117-73 for all the atomisation air pressures. However, it was decided to operate the cabinet at 1.38 bar because at that pressure the average fog collection rate was closest to 1.5 ml hr^{-1}, exactly in the middle of the 1 to 2 ml hr^{-1} range allowed by the standard, and there was also the least variation between the fog collection rates in different parts of the cabinet at that pressure. In addition it was decided not to place any specimens in the areas shown as positions 1 and 2 in figure 3.6 due to the higher collection rates that occurred in those positions which was possibly due to flyaway spray from the spray nozzle. During subsequent tests two collectors were kept in the cabinet to ensure that the fog collection rate did not alter substantially from 1.5 ml hr^{-1} and the air supply to the cabinet was fitted with a regulator to control pressure fluctuation to within 0.007 bar and avoid the possibility of their being a critical atomisation air pressure (2.2.1.5). In view of the substantial work already reported (2.2) on the salt spray test no further calibration work was carried out.

3.10.2 Coating weight curves for a laboratory solution of Parco 95

Panels for coating weight determinations (3.5) were phosphated (3.4) using a laboratory solution of Parco 95 (3.4.3.1). The true coating weight curves are presented in figures 3.7 to 3.9 for solution

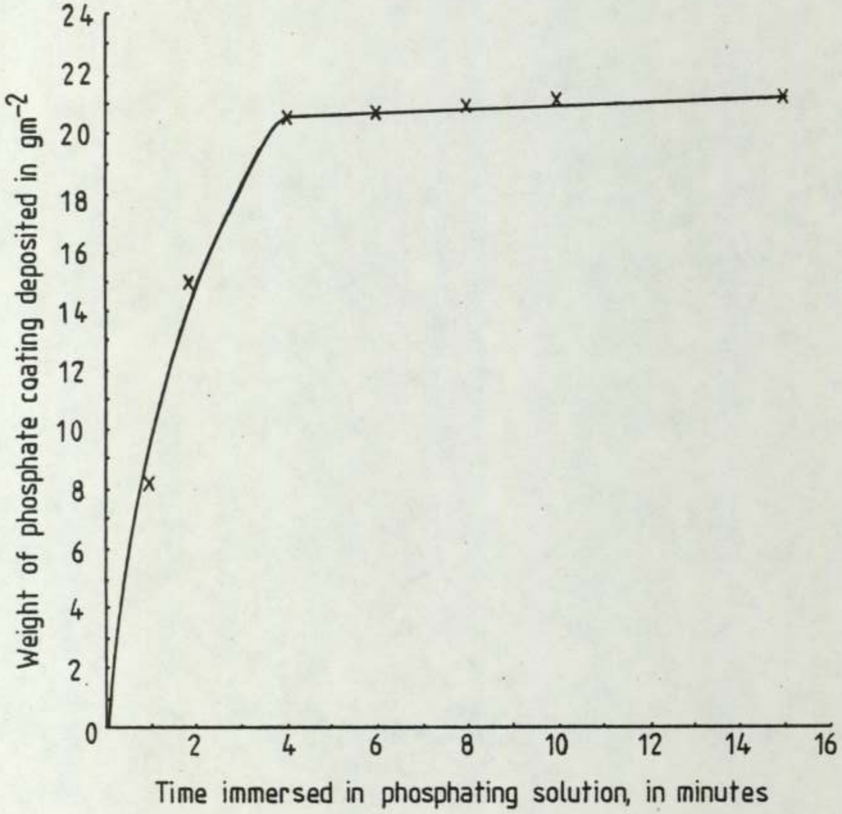


Figure 3.7 True phosphate coating weight deposited as a function of time immersed in a Parco 95 phosphating solution at 82°C

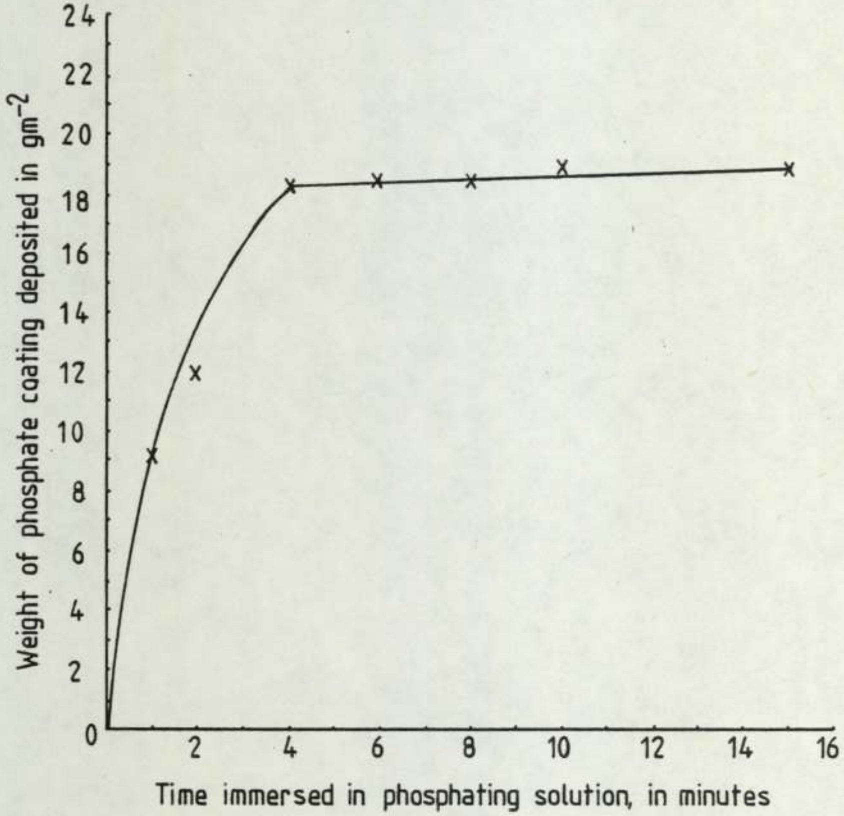


Figure 3.8 True phosphate coating weight deposited as a function of time immersed in a Parco 95 phosphating solution at 86°C

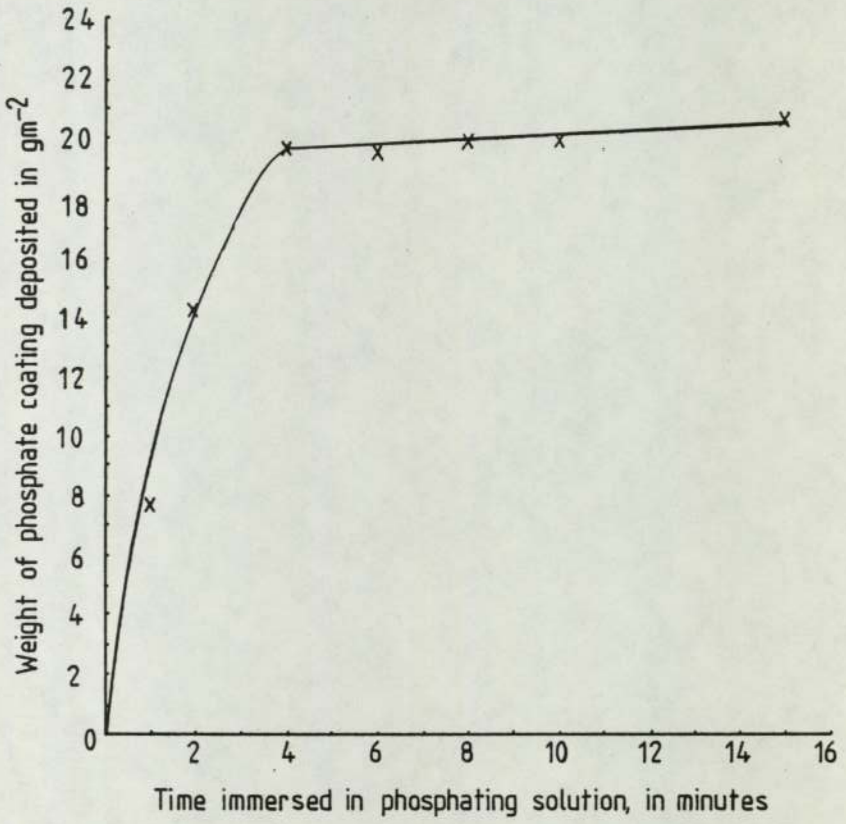


Figure 3.9 True phosphate coating weight deposited as a function of time immersed in a Parco 95 phosphating solution at 90°C

temperatures of 82, 86 and 90°C respectively. All the curves show the same trend of a steep initial gradient, with a constant coating weight achieved after 4 minutes phosphating.There are slight differences in the values of the coating weights at which each curve becomes constant (see 2.11) approximately 20.5 gm^{-2} at 82°C, 18 gm^{-2}at 86°C and 20 gm^{-2} at 90°C. These slight differences are not a linear function of temperature and are suggested to reflect slight differences in the panels used. These results show that a phosphating time of six minutes was sufficient to achieve a complete phosphate coating, and that variations in the solution temperature between 82 and 90°C would not markedly affect the state of completion or weight of the phosphate coating deposited.

The corresponding addition phosphate coating weight and metal loss curves are presented in figures 3.10 to 3.12 for the solution temperates 82, 86 and 90°C respectively. The metal loss curves show that dissolution of the metal panel had virtually ceased after two minutes immersion, although the true phosphate coating weight did not reach a constant value until 4 minutes for each temperature. Therefore although little acid attack on the panel was occurring after 2 minutes the phosphating solution was still returning to equilibrium and depositing phosphate crystals until approximately 4 minutes. The constant values reached in the metal loss curves are approximately 7.5 gm^{-2} for solutions operated at 82 and 86°C but 5 gm^{-2} for the solution operated at 90°C.

The addition phosphate coating weight curves follow the same trend as the true coating weight curves, at each solution temperature. After a sharp initial gradient, a constant value is attained after

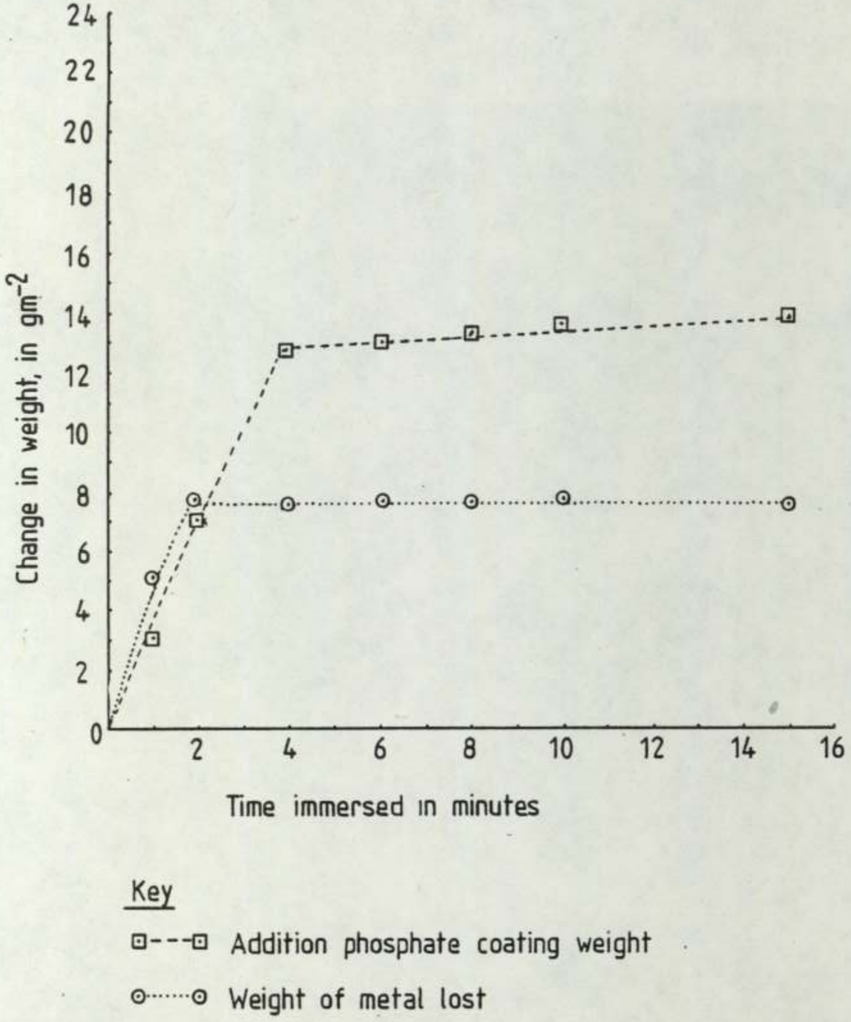


Figure 3.10 Addition phosphate coating weight and weight of metal lost as a function of time immersed in a Parco 95 phosphating solution operated at 82°C

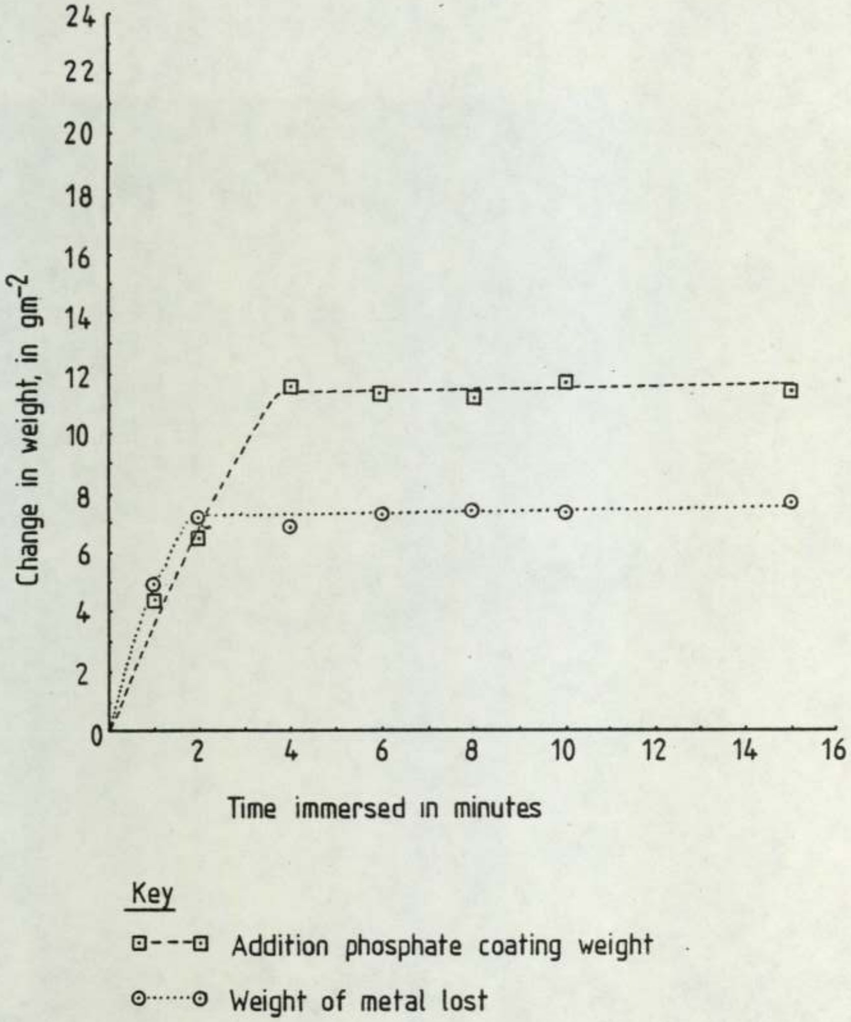


Figure 3.11 Addition phosphate coating weight and weight of metal lost as a function of time immersed in a Parco 95 phosphating solution operated at 86°C

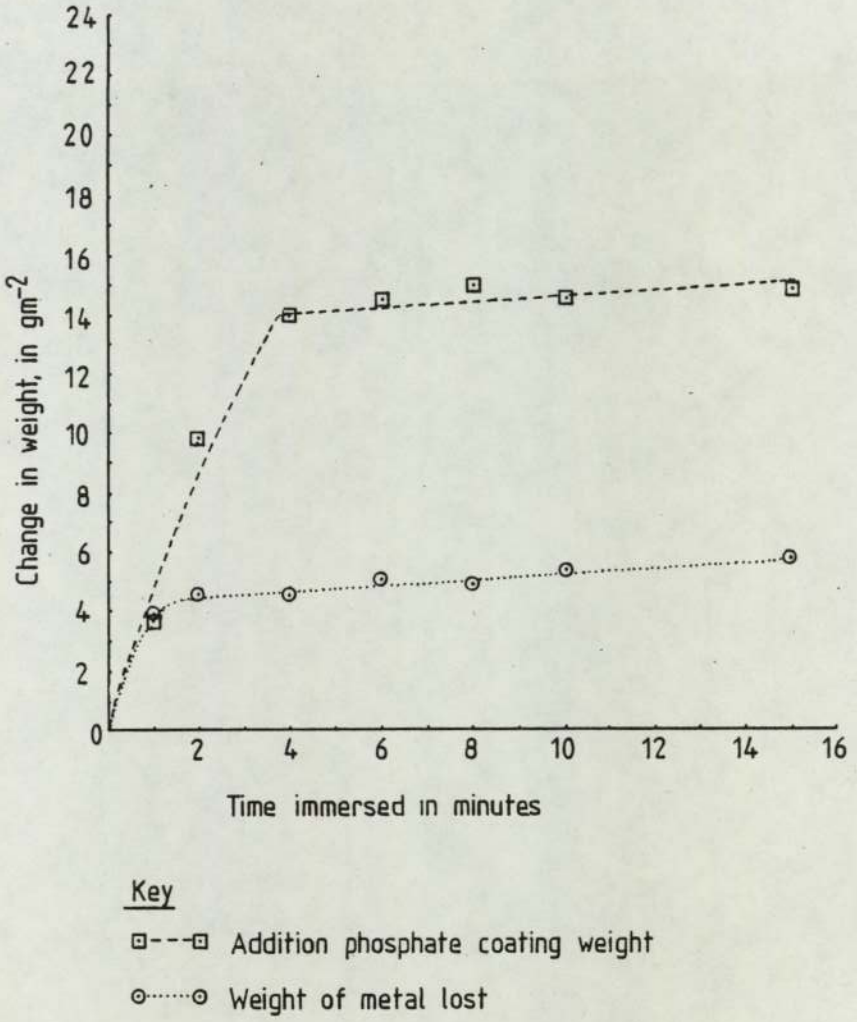


Figure 3.12 Addition phosphate coating weight and weight of metal lost as a function of time immersed in a Parco 95 phosphating solution operated at 90°C

approximately 4 minutes immersion. The constant values reached are 13 gm^{-2} at 82°C, 12 gm^{-2} at 86°C and 15 gm^{-2} at 90°C. Because there was some experimental variation in the addition coating weights when the addition coating weight was used to ensure that panels for corrosion testing had received a reasonable phosphate coating, only panels with addition coating weights greatly different from the band 12-15 gm^{-2} were rejected.

3.10.3 Effect of the coating weight of P41 stain finish on the corrosion resistance of the phosphate and stain finish

The phosphate and stain finish was expected to show less resistance to the salt spray test than the phosphate and oil finish. The phosphate and stain finish was thus used to assess any improvements in the protective value of the phosphate coating, which had the advantage that testing times were much shorter. Therefore it was decided to investigate whether the resistance to the salt spray test of the phosphate and stain finish depended on the coating weight of stain applied.

Twelve test panels were phosphated (3.4) using a laboratory solution of Parco 95 (3.4.3.1). Batches of P41 stain were then prepared at percentage solid contents (3.7.5.2) of 8.4, 9.6, 10.8 and 11.6, and three test panels stained (3.7.1) in each batch, the coating weight of stain determined (3.7.5.1)and then the panel salt spray tested (3.8.1) and evaluated (3.8.1.2).

Figure 3.13 shows that the coating weight of stain deposited on a panel decreased approximately linearly with the decrease in the solids content of the stain used. However, the results in Table 3.3 show that over the range tested there was no relationship between the

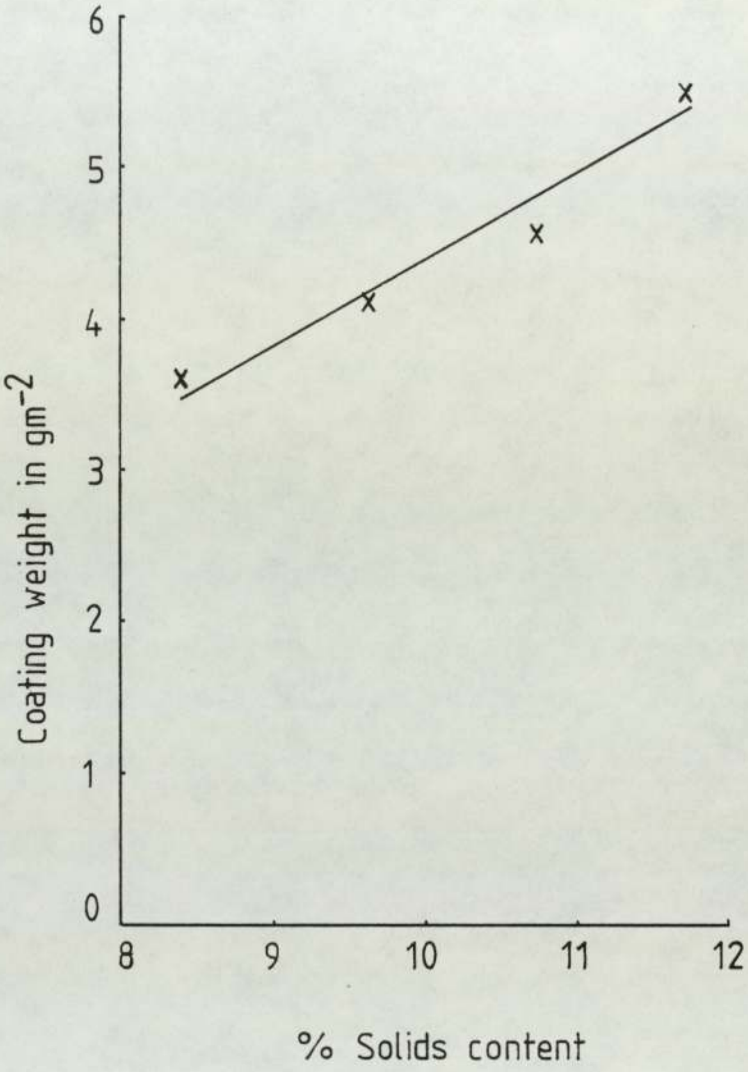


Figure 3.13 Coating weight of stain finish deposited as a function of the solids content of the stain

coating weight of stain on a panel and its salt spray resistance as all the panels took 72 hours or more to fail at failure ratings of 4.1 or 5.1 irrespective of the coating weight of stain on the panel.

Therefore the stain was used as received with a solids content of 10 to 12 per cent, and when the coating weight of stain deposited on test panels for corrosion testing was checked (3.7.5.1) only results outside the range 4 to 6 gm^{-2} were considered unsatisfactory and the panel rejected.

TABLE 3.3 INVESTIGATION INTO THE RELATIONSHIP BETWEEN THE COATING WEIGHT OF STAIN ON A TEST PANEL AND ITS SALT SPRAY RESISTANCE

Coating weight of stain (gm^{-2})	Resistance to the salt spray test (hours)	Rating at failure
3.6	88	4.1
4.1	72	4.1
4.5	72	5.1
5.6	88	4.1

3.10.4 Use of a standard specimen in the salt spray tests

A standard specimen was included in each salt spray test, as a control, to assess whether the corrosion conditions in the test cabinet were normal. The standard specimen was a laboratory Parco 95 (3.4.3.1) phosphated(3.4)and stained (3.7.1) panel, which the results in section 3.11.3 had indicated should withstand between 72 and 88 hours exposure to the test before breaking down. Any test in which the control panel failed to withstand 72 hours exposure, were rejected and repeated.

CHAPTER 4

PREPARATION OF THE METAL SURFACE FOR PHOSPHATING

4.1 Cleaning methods

Critical to the development of a good phosphate coating is the condition of the metal's surface. At Metalastik there are principally two production routes (1.2) prior to anti-corrosion finishing, either wheelabrating followed by selective application of adhesive or chemical cleaning followed by non selective application of adhesive. After moulding there is a subsidiary branch to each route of a metal manipulation operation which caters specifically for bushes. This operation causes the metal surfaces to become work hardened and although the products are alkali cleaned immediately afterwards, traces of lubricant contamination usually remain. As summarised in figure 4.1 these routes cause products to arrive at the metal finishing stage in four categories of surface condition, each of which may be exacerbated by the presence of rust if the products have suffered long delays between the manufacturing stages. However, the problem of rusting is not considered here as a short term solution to the problem, acid pickling, was already in existence. In the long term Metalastik was changing the shopfloor layout to a system based on Group Technology (57), one of the advantages of this being a reduction in the time products spend on the shopfloor and are hence at risk of rusting.

To prepare each category of surface condition for phosphating requires a combination of cleaning methods (see 2.1.7.1). In Table 4.1 a matrix is presented of the soils making up the range of surface conditions and the possible cleaning methods. Each cleaning

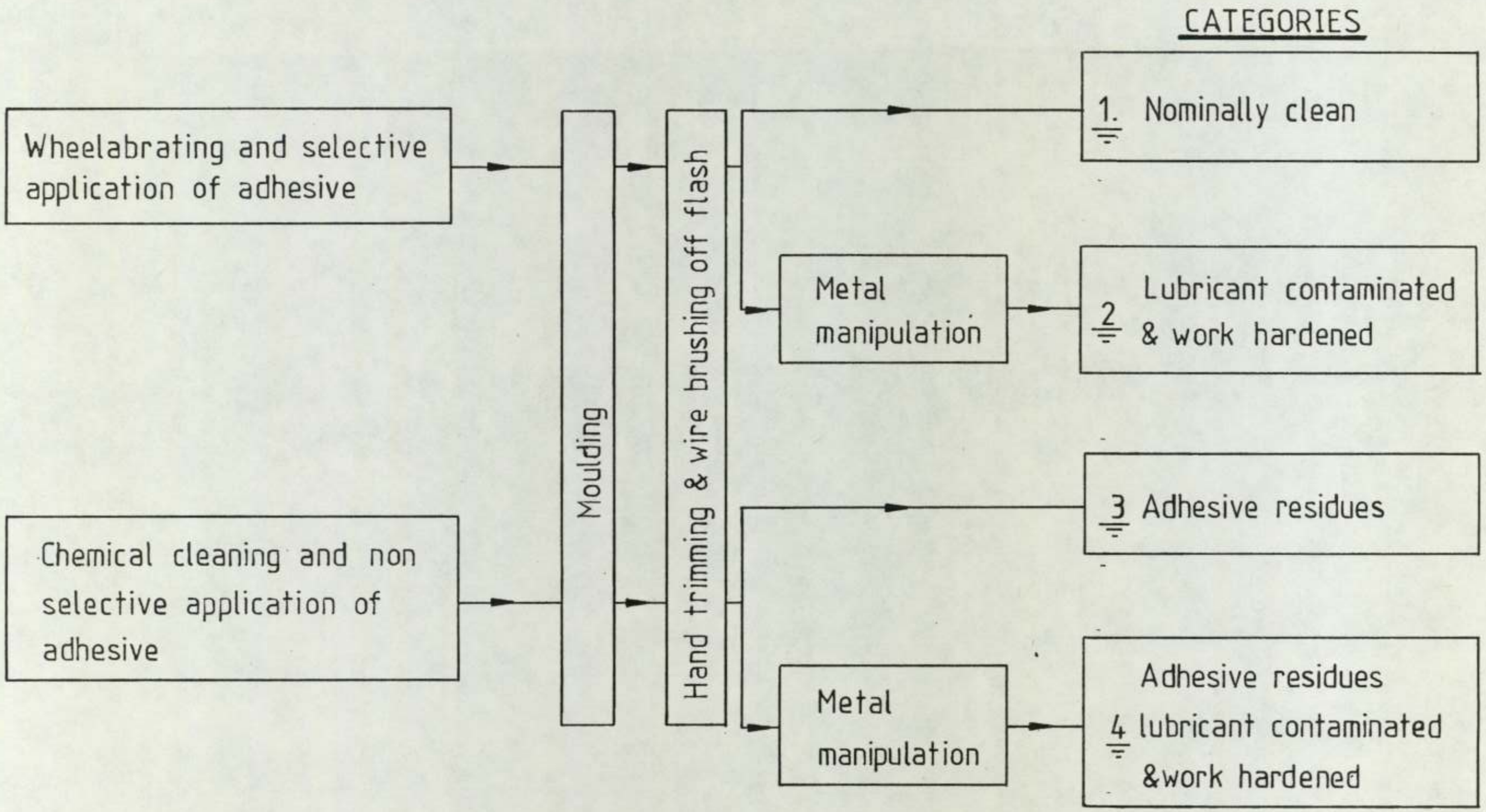


Figure 4.1 Surface conditions of the products at the metal finishing stage

method is considered against each soil and awarded 1 point if it is capable of removing it or 0 points if it is not. Solvent cleaning is not considered as an option due to the presence of the rubber-to-metal bond.

Table 4.1 Matrix of cleaning methods and soils

Soil	Cleaning Methods		
	acid pickling	alkali cleaning	abrasive cleaning
Lubricant contamination	0	1	0
work hardened surfaces	1	0	1
adhesive residues	0	0	1

Table 4.1 shows no one cleaning method is capable of dealing with all the categories of surface condition and the only combination of two cleaning methods capable of coping with all the soils is alkali and abrasive cleaning. However, the only routine cleaning operation prior to immersion in the phosphating solution was alkali cleaning which Table 4.1 shows to be capable of dealing with parts in surface condition category 1 only. Therefore to determine the percentage of products for which this cleaning operation catered, the percentage of production arising in each category of surface condition was determined. To simplify this work a Pareto's analysis was carried out on the products that were phosphated. This showed that 23% of the number of different products phosphated represented

78% of the production volume. The production route for each of the products contained in the 23% was found from the manufacturing records, and the category of surface condition of each product at the anti-corrosion finishing stage could be determined by applying this information to figure 4.1. Table 4.2 shows the percentage of products that arrive in each category of surface condition.

Table 4.2 Category of surface condition of the products that make up 78% of the volume of work phosphated

	Category of surface condition			
	1	2	3	4
No. of Products	16	14	5	13
Percentage	33	29	11	27

Table 4.2 shows that the routine alkali cleaning operation prior to phosphating could only deal with the 33% of products arriving in surface condition category 1. It is suggested that this situation arose because the adverse affects of two of the manufacturing processes on the surface condition of the products to be phosphated were not recognised. Firstly, the work hardening of the metal surfaces caused by the metal manipulation operations was not considered to be deleterious to the development of a phosphate coating. Secondly, the presence of adhesive residues was not considered to be important as the phosphate coating was expected to develop on the areas of exposed metal, which combined with the

corrosion resistance of the adhesive residues to provide a reasonable level of corrosion protection.

4.2 Comparison of the existing cleaning method with the optimum cleaning method

Samples of products representing each category of surface condition in figure 4.1 were obtained (3.2): Six of each surface condition were phosphated (3.4) using Parco 95 (3.4.3.1) and stained (3.7.1), and a further six samples were wheelabrated (3.3) phosphated (3.4) using Parco 95 (3.4.3.1) and then stained (3.7.1). The samples were salt spray tested (3.8.1) and evaluated (3.8.1.2) in two representative batches. The addition phosphate coating weights of the samples (3.5.1) are presented in Table 4.3. These results show that the samples in surface conditions 2,3, and 4 achieved a significantly higher coating weight when wheelabrated prior to phosphating. While the results for category 1 do show an increase in coating weight for those samples that were wheelabrated, this is not considered sufficient to be significant as the wheelabrating operation could increase the surface area of a sample (5).

The salt spray test results of the samples are presented as one set in Table 4.4 as the duplicate tests gave virtually identical results. The results for the products representing categories 1 and 2 show no difference in performance between those which were wheelabrated prior to phosphating and those that were not, both having a failure rating of 4.1 at 72 hours. The results for the products representing categories 3 and 4, however, show a marked

TABLE 4.3 COMPARISON OF THE ADDITION PHOSPHATE COATING WEIGHTS ON THE DIFFERENT SURFACE CONDITIONS

Treatment	Surface category*	Mean addition phosphate coating weight(gm^{-2})	σ
Phosphated	1	10.99	1.22
	2	6.29	1.03
	3	1.2	0.79
	4	1.73	0.51
Wheelabrated and phosphated	1	14.66	1.76
	2	12.48	1.66
	3	4.74	0.23
	4	5.72	0.6

* see figure 4.1

TABLE 4.4 EFFECT OF THE DIFFERENT CLEANING METHODS ON THE SALT SPRAY RESISTANCE OF THE STAINED PHOSPHATE COATING

Treatment	Surface Category**	Salt spray* resistance (hours)	* Rating at failure
Phosphated	1	72	4.1
	2	72	4.1
	3	16	7.4
	4	16	7.4
Wheelabrated and phosphated	1	72	4.1
	2	72	4.1
	3	72	4.1
	4	72	4.1

* Typical result representative of the products tested.
** See figure 4.1.

improvement from a failure rating of 7.4 at 16 hours when phosphated and stained only to a failure rating of 4.1 at 72 hours when wheelabrated prior to phosphating and staining.

Products representing category 3 showed a marked improvement in phosphate coating weight, because the wheelabrating removed the adhesive residues and allowed a phosphate coating to develop over the complete metal surface. The improvement in coating weight that occurred as a result of wheelabrating products within category 2 resulted from the abrasive removal of the work hardened surface layer (2.1.3.1) that had resulted from the metal manipulation operation. A combination of these two reasons resulted in the products within category 3 showing an improvement in coating weight as a result of wheelabrating.

The identical salt spray test results for products in surface condition category 1, whether wheelabrated or not, confirms alkali cleaning, to be sufficient for this category. Category 2 products also showed identical resistance to the salt spray test, wheelabrated or not, indicating that the work hardened surfaces do not prevent the deposition of a complete phosphate coating. The lower coating weight on the unwheelabrated products, however, suggests the work hardening results in the formation of more nucleation sites on the metal surface causing the coating to complete more quickly but with smaller phosphate crystals and consequently a lower coating weight. The marked improvement in salt spray resistance shown by the products in surface condition categories 3 and 4 must therefore be a result of the wheelabrating removing the adhesive residues. It is suggested that the adhesive residues interfered with the anodic/cathodic reaction mechanism (2.1.4) by producing small chemically inert non conducting sites on the damaged metal surfaces. This would cause the development of a grossly porous phosphate coating with consequent poor corrosion resistance.

The benefits of wheelabrating can be summarised as shown in Table 4.5.

Table 4.5 Benefits of wheelabrating prior to phosphating

Category	% of product types	Coating weight	corrosion resistance
1	33%	no change	no change
2	29	improved	no change
3	11	improved	improved
4	27	improved	improved

An improvement in the phosphate coating weight would be beneficial in decreasing the problem of internal Quality Control. A thin phosphate coating causes poor retention of the black stain and consequent visual defects which often leads to a refusal (by Q.C) to despatch products. As it was the addition phosphate coating weight that was measured, the results indicate that the improvement in true phosphate coating weight that could be expected for categories 3 and 4 would bring the products up to the 7.5 gm^{-2} minimum coating weight, required by the automotive customers specifications listed in Table 1.2. The associated improvement in salt spray resistance for these two categories would bring them up to and in some cases in excess of the salt spray resistance requirements of the same specifications. As the products investigated represent 78% of the volume of work phosphated and were all supplied to automotive customers both aspects were of importance.

The first method to be considered to achieve this improvement was to eliminate the causes of the categories of surface condition 2,3 and 4.

4.2.1 Adhesive residues

Adhesive residues result from the non selective application of adhesive to the metal sections as described in section 1.2.2. To apply the adhesive selectively to the metal sections of these products would mean changing from a relatively low labour content dipping operation to either labour intensive manual, or specialised automatic, selective application techniques. This option had already been investigated by Metalastik as a way of reducing the amount of adhesive wasted by the unnecessary coating of metal surfaces not to be bonded. However trials had shown that the increase in labour costs and the wastage of adhesive involved in the selective application methods combined to far outweigh any savings.

4.2.2 Work hardened and lubricant contaminated surfaces

These two conditions result from the metal manipulation operations carried out on bushes. To remove the need for the operation would require high pressure moulding to maximise the volume of rubber injected into the product, thus minimising the subsequent shrinkage of the rubber after moulding. However, work by Metalastik has already shown that although this method could reduce the shrinkage stress, the reduction is not sufficient to obviate the need for the metal manipulation operations.

4.3 Options for achieving the optimum cleaning method

As the causes of the surface conditions could not be removed, possible ways of achieving the combination of alkali and abrasive cleaning were considered. The possibilities were either to purchase a wheelabrator and introduce an extra cleaning operation, or replace the existing Revel plant used for degreasing products after metal manipulation by a plant capable of simultaneous abrasive and alkali cleaning. This latter option was chosen as it had the following two advantages. Firstly, the Revel plant was due for replacement and it is simpler to justify the replacement of an existing operation than the introduction of a new operation. Secondly, the products in categories 2 and 4 are bushes and would automatically be processed through a replacement for the Revel plant. Only products in category 3 would require the extra operation of being processed through a replacement for the Revel plant to be justified.

4.4 Identification of machine required

In this section of the work the author was responsible for the technical evaluation of the processes and Mr. N.C.Constantinou, Production Methods Engineer was responsible for the production engineering aspects. Four companies were asked to offer processes. The companies and the processes they offered are listed in Table 4.6.

Table 4.6 The cleaning processes offered by companies

Company	Process offered
Dynajet Ltd	High speed jetting of solution at products.
Flowfast Ltd	High speed jetting of solution at products.
Osro Ltd	Vibration of products in a slurry of abrasive particles and degreasing solution.
Abrasive Developments Ltd.	Vaqua D process:- Blasting of products with alumina or glass beads in a degreasing solution.

The processes offered by Flowfast and Dynajet were not taken further as they did not offer the combined abrasive and alkali cleaning action required. The processes offered by Osro and Abrasive Developments Ltd were assessed by sending samples of products representative of the worst surface condition, category 4 for cleaning. After cleaning the products the two companies packed them in air tight bags containing silica gel and returned them. The products were then phosphated (3.4) using Parco 95 (3.4.3.1) stained (3.7.1) and salt spray tested (3.8.1). Table 4.7 presents the addition phosphate coating weights and the salt spray test results (3.8.1.2) for the products.

The results in Table 4.7 show the products cleaned using the Abrasive Developments process achieved a higher average addition phosphate coating weight of 6.33 gm^{-2} compared with the average value of 4.24 gm^{-2} for the products cleaned using the Osro process. The salt spray resistance result of the products cleaned using the Abrasive Developments process is correspondingly better at an average value of 72 hours rating 4.1 compared with 24 hours rating 7.4 for the products cleaned using the Osro process. This difference is suggested to be due to the superior cutting action of the Abrasive Developments Vaqua D process (58) promoting a coherent phosphate coating by removing more of the adhesive residues. These results led to the Osro process being dropped from consideration.

Little difference is evident between the average addition phosphate coating weight of 6.33 gm^{-2} and salt spray test result of 72 hours rating 4.1 for the Abrasive Developments cleaned products of the average addition phosphate coating weight of 5.72 gm^{-2} and salt spray test result of 72 hours rating 4.1 for the same category of product alkali cleaned and wheelabrated, see Tables 4.3 and 4.4. Therefore, as the Abrasive Developments process was able to cope with the worst category of surface condition, which incorporated all the soils associated with the other surface conditions no further definitive testing of the process was carried out.

TABLE 4.7 EVALUATION OF THE CLEANING PROCESSES OFFERED BY OSRO LTD AND ABRASIVE DEVELOPMENTS LTD

Treatment	mean, addition phosphate coating weight(gm^{-2})	σ	salt spray resistance (hours)*	* Rating at failure
Cleaned by Osro Ltd process and phosphated	4.24	0.16	24	7.4
Cleaned by Abrasive Developments Ltd process and phosphated	6.33	0.51	72	4.1

* Typical result representative of the products tested.

4.5 Purchase of the machine

Although the Abrasive Developments Vaqua D process had been identified as capable of cleaning the products, to try to avoid the situation of purchasing from a monopoly supplier attempts were made to identify an alternative supplier. However no alternative supplier of a combined degreasing and abrasive cleaning process was found. The Production Methods Engineering Department then discussed the size of machine required, its purchase price and running costs with Abrasive Developments. The author's involvement in this side of the work was restricted by internal politics within the company and also by commitments to the other work reported in this thesis. The following cash flow analysis was then drawn up, comparing the cost of alkali cleaning followed by wheelabrating with the cost of the Abrasive Developments machine. A number of assumptions inherent to this type of analysis were made, some of which were:

(i) Constant sales (revenue)
(ii) Constant product mix
(iii) Constant prices and costs

Cost savings associated with purchasing of an Abrasive Development Vaqua D machine

Running cost of alkali cleaning and wheelabrating	0.81 p/lb
Running cost of Abrasive Developments Vaqua D machine	0.42 p/lb

Cost saving per lb = 0.81p - 0.42p = 0.39p

Weekly production = 28 tons

Cost saving per week = 28 x 2240 x 0.39p

= £244

Cost saving per annum = £11,468

Sale of old machine = zero assuming scrap value = removal cost

CASH BENEFIT

	Cash outflow £	Cash inflow £
Assuming asset is depreciated at 20% with zero scrap value		
Total savings = 5 years x 11,468		= 57,340
Purchase of new machine	20,000	
Purchase of associated loading and unloading equipment	7,000	
	27,000	57,340
		- 27,000
Gain		£ 30,340

A report was distributed which summarised the benefits of improving the cleaning products received prior to phosphating, and presented the cash flow analysis for the two methods of achieving this improvement. The report recommended that the best course of action would be to replace the Revel degreaser with a Vaqua D machine from Abrasive Developments.

The report was accepted and the Works Manager, General Manager and Divisional Director completed the necessary procedures to allow the order for a machine to be placed. While waiting for the Abrasive Developments machine, an extra operation of wheelabrating products in categories 2,3 and 4 prior to phosphating was introduced.

4.6 Commissioning of Abrasive Developments machine

The machine was ready for delivery in the last month of the 1979 Financial Year. When the Production Methods Engineering department inspected the finished machine at Abrasive Developments works several faults were found, however the machine had to be accepted immediately for the capital expenditure to be associated with the 1979 Financial Year. Consequently after installation the machine was not operational for approximately two months, during which time it was altered. The author then issued the internal company documents attached as appendix 2, which detail the machine, its operation and maintenance. In addition, the author trained the operators who were assigned to work the machine. However when the machine was ready to be officially 'handed over' to the production department the shopfloor workers union went into dispute with the company over the annual wage negotiation. This resulted in the machine being 'blacked', as one of the sanctions imposed was a refusal to work any new machine. This dispute lasted approximately two months after which the operators were given a refresher course in operating the machine and it was officially handed over.

Figure 4.2 shows the machine in its final form on the shopfloor.

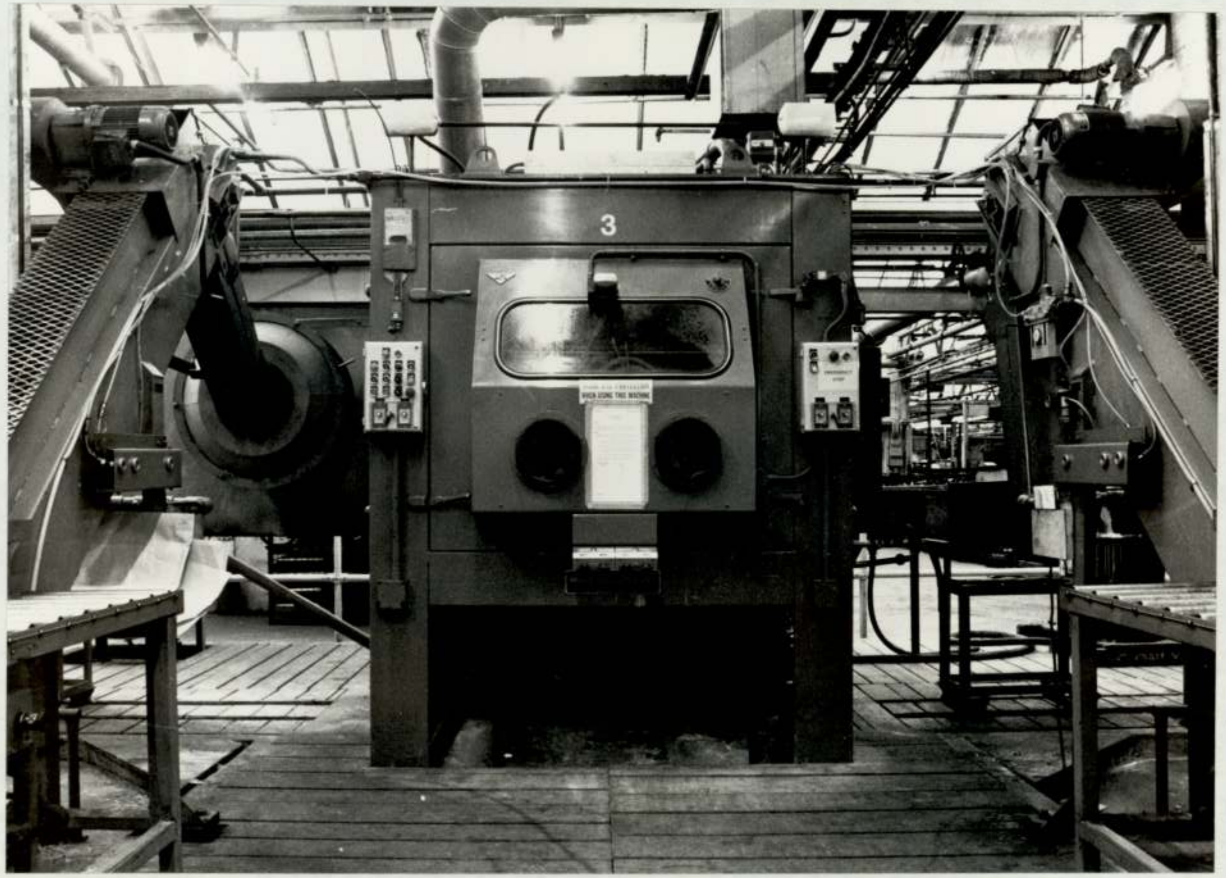


Figure 4.2 Vulcan Vaqua D machine in position on the shop floor at Metalastik

CHAPTER 5

PHOSPHATING SOLUTION

The results in Chapter 4 show that a Parco 95 phosphate coating, produced on a properly cleaned surface using laboratory equipment, when stained achieved 72 hours or more resistance to the salt spray test. The next step was to determine the resistance to the test of a stained Parco 95 phosphate coating that had been produced on a properly cleaned surface using works equipment. In this work test panels with properly cleaned surfaces were used to assess phosphating solutions, because as a result of the work reported in Chapter 4 the majority of products phosphated in the factory would be properly cleaned.

5.1 Comparison of phosphate coatings produced using works and laboratory equipment

Nine test panels were phosphated (3.4) using Parco 95 (3.4.3.1) and stained (3.7.1). Three were phosphated and cleaned using the manual phosphating plant, 3 using the automatic phosphating plant and 3 using laboratory equipment. The panels were then salt spray tested (3.8.1) and evaluated (3.8.1.2.). The results in Table 5.1 show that the panels processed using works equipment (the manual and automatic phosphating plants) failed after 16 hours exposure with a failure rating of 7.5, while the panels processed using laboratory equipment failed after 72 hours with a failure rating of 4.1. The large differences between the times to failure and the rating at failure indicated that there was a major difference between the phosphate coatings, the only other variable had been eliminated by staining all the panels in the same batch of stain. The cause of the

TABLE 5.1 COMPARISON OF THE RESISTANCE TO THE SALT SPRAY TEST OF PARCO 95 PHOSPHATE COATINGS PRODUCED IN THE WORKS WITH THOSE PRODUCED IN THE LABORATORY

Treatment	Salt spray resistance (hours)*	Rating at failure*
Laboratory equipment	72	4.1
Manual phosphating plant	16	7.5
Automatic phosphating plant	16	7.5

* Typical result representative of the panels tested.

poor phosphate coatings produced using the works equipment was not immediately obvious as both the automatic and manual sets of equipment had deficiencies and also suffered from poor maintenance of the processing solutions. The possible causes of the poor phosphating were:-

(i) Substandard cleaning of the metal surfaces to be phosphated

Infrequent dumping and renewal of the alkali cleaning solutions caused contamination to build up on the surface of the solution. As products or specimens were withdrawn from the cleaner their surfaces would become contaminated. This contamination would prevent access of the phosphating solution to the metal surfaces, inhibiting the phosphating reactions.

(ii) Chemicals dragged over into rinse tanks, causing substandard rinsing

Some of the rinses were fed with fresh water by a spray bar at the top of the tank, as shown in figure 5.1. This caused the fresh water to skim across the surface of the tank and over the weir to the drains failing to renew the main body of contaminated rinse water. This could have caused inadequate rinsing of corrosive residues on the phosphate coating, lowering its protective value.

(iii) Failure of thermostats to maintain solutions within the required temperature ranges

Solutions were often outside their recommended optimum temperatures because of defective thermostats.

(iv) Shortening of immersion times

Inadequate control over plants and operators often resulted in products not being processed for the specified times.

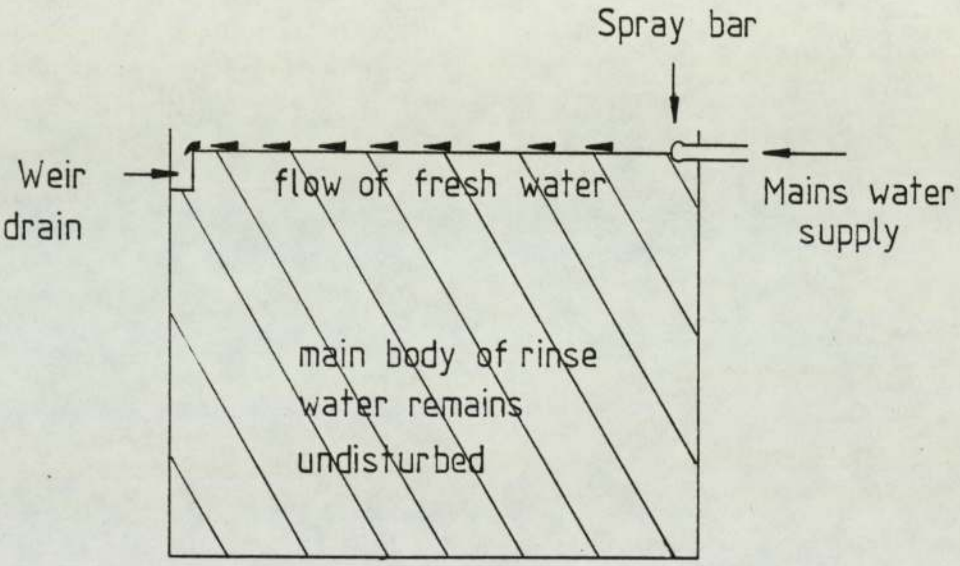


Figure 5.1 Inefficiency of using a spray bar for replacing the water in a rinse tank

(v) The use of live steam for heating solutions

This practice could result in the transfer of chemicals from the steam supply into the heated solutions which might then interfere with the phosphating reactions.

When test panels were phosphated in the works equipment it was ensured that the possible causes of poor phosphating associated with the defective equipment (iii) and (iv) were avoided. As the remaining causes were associated with the nature of various solutions the following experiment was carried out to identify the defective solution.

Using the laboratory phosphating equipment, a series of test panels were phosphated. One set of three panels was phosphated (3.4) using Parco 95 (3.4.3.1) in an all laboratory sequence. Further sets of three panels were phosphated using the sequence with one works solution substituted for a laboratory solution.Each solution was substituted until all the solutions shown in figure 3.1 had been used from both of the works phosphating plants. The panels were then stained (3.7.1), salt spray tested (3.8.1) and evaluated (3.8.1.2). The results in Table 5.2 show that poor corrosion resistance was evident only when the works Parco 95 phosphating solutions were substituted for the laboratory Parco 95 phosphating solution, failure being at 16 hours rating 7.5. All the other combinations produced test panels which lasted 72 hours or more in the salt spray test, at failure ratings of 4.1 or 5.1.

To ensure that chemical depletion of the works phosphating solutions, due to being overworked, had not occurred, samples of both works phosphating solutions were left to stand for 1 day and 7 days. After checking the total pointage (3.4.3) 3 panels were

TABLE 5.2 RESISTANCE TO THE SALT SPRAY TEST OF PARCO 95 PHOSPHATE COATINGS PRODUCED USING LABORATORY EQUIPMENT AND WORKS SOLUTIONS

Treatment	Salt spray resistance (hours)*	Rating at failure*
All laboratory solutions	88	4.1
Works solution substituted into sequence		
Works alkali cleaner (M.P.)	72	4.1
Works alkali cleaner (A.P.)	72	4.1
Works rinse 1 (M.P.)	96	4.1
Works rinse 1 (A.P.)	88	4.1
Works rinse 2 (M.P.)	88	4.1
Works rinse 2 (A.P.)	88	5.1
Works phosphating solution (M.P.)	16	7.5
Works phosphating solution (A.P.)	16	7.5
Works rinse 3 (M.P.)	88	4.1
Works rinse 3 (A.P.)	88	5.1
Works rinse 4 (M.P.)	96	4.1
Works rinse 4 (A.P.)	72	4.1
Works rinse 5 (M.P.)	88	4.1
Works rinse 5 (A.P.)	72	4.1

Key A.P. = Automatic phosphating plant

M.P. = Manual phosphating plant

Solution numbers - see figure 3.1

* Typical result representative of the panels tested.

phosphated using the laboratory sequence (3.4) with these phosphating solutions. The panels were then stained (3.7.1), salt spray tested (3.8.1) and evaluated (3.8.1.2). The results in Table 5.3 show that the panels phosphated using the solution stood for one day failed after 16 hours with a rating of 7.5 and the panels phosphated using the solution stood for seven days failed after 16 hours with a rating of ½ 7.5 ½ 5.4. There was a slight improvement in the failure rating after seven days standing but the failure time remained the same at 16 hours indicating the problem was not chemical depletion.

5.2 Variation of the salt spray resistance of the Parco 95 phosphate coatings produced using the manual and automatic works equipment

Three test panels were processed (3.4) through both the manual and automatic phosphating plants twice a week for a period of six weeks. The panels were stained (3.7.1), salt spray tested (3.8.1.) and evaluated (3.8.1.2). The results presented in Table 5.4 show that the panels generally failed the salt spray test after 16-24 hours, with a rating of 7.5. However panels processed on the manual plant did show a notable change in corrosion resistance on day 22 of the test. This improvement coincided with the complete renewal of the Parco 95 phosphating solution in that plant. This result indicates that the Parco 95 phosphating solution, when first made up in the plant was capable of producing an improved phosphate coating approaching the corrosion resistance of a Parco 95 phosphate coating produced using a laboratory phosphating solution. However, as the subsequent results show the corrosion resistance of the phosphate coating decreased rapidly with use of the plant. Complete changes of the phosphating solution were rare as, due to the cost of replacing

TABLE 5.3 THE EFFECT OF RESTING A WORKS PARCO 95 PHOSPHATING SOLUTION

Time allowed to rest	Plant solution taken from	Salt spray resistance (hours)*	Rating at failure *
1 day	Manual	16	7.5
	Automatic	16	7.5
7 days	Manual	16	½ panel 7.5 ½ 5.4
	Automatic	16	½ panel 7.5 ½ 5.4

* Typical result representative of the panels tested.

TABLE 5.4 VARIATION OF THE SALT SPRAY RESISTANCE OF PARCO 95 PHOSPHATE COATINGS PRODUCED USING THE MANUAL AND AUTOMATIC WORKS EQUIPMENT

Test day number	Results from manual plant		Results from automatic plant	
	Salt spray resistance (hours)*	Rating at failure*	Salt spray resistance (hours)*	Rating at failure*
1	16	7.5	32	5.1
3	16	7.5	24	6.4
8	16	7.5	16	7.5
10	16	7.5	16	7.5
15	16	7.5	16	7.5
17	16	7.5	16	7.5
22	48	5.1	16	7.5
Factory shutdown				
36	40	5.1	32	6.4
38	24	6.4	24	6.4
43	24	6.4	24	6.4
45	16	7.5	32	6.4
50	16	7.5	16	7.5
52	16	7.5	16	7.5

* Typical result representative of the panels tested.

a complete solution it was usual to decant off a phosphating solution into holding containers, carry out any necessary cleaning out or other work on the plant, then return the solution and top it up with I.M.U. chemical. Therefore the majority of production was processed through old solutions and consequently received an inferior phosphate coating.

5.3 Coating weight curves for a works Parco 95 solution

Coating weight curves were produced (3.5) using the Parco 95 (3.4.3.1) solutions on the manual and automatic plants. As both phosphating solutions exhibited the same trends only the curves for the manual phosphating solution are presented in figure 5.2. Comparison of the true phosphating coating weight curve in this figure with that for a laboratory solution of Parco 95, operated at 86°C, presented in figure 3.8 indicated the following differences:

(i) The initial gradient of the laboratory solution curve is far steeper than the initial gradient of the works solution curve.

(ii) The time to reach a constant true coating weight is substantially different. The Parco 95 laboratory solution reaches a plateau value after approximately 4 minutes at 86°C, whereas the works solution took 25 minutes at 88°C.

(iii) The metal loss curve for the Parco 95 works solution reaches a constant value after 25 minutes, compared with 4 minutes for the laboratory solution.

(iv) The true coating weights at which the curves become constant are substantially different at 48 gm^{-2} for the manual solution and 18 gm^{-2} for the laboratory solution.

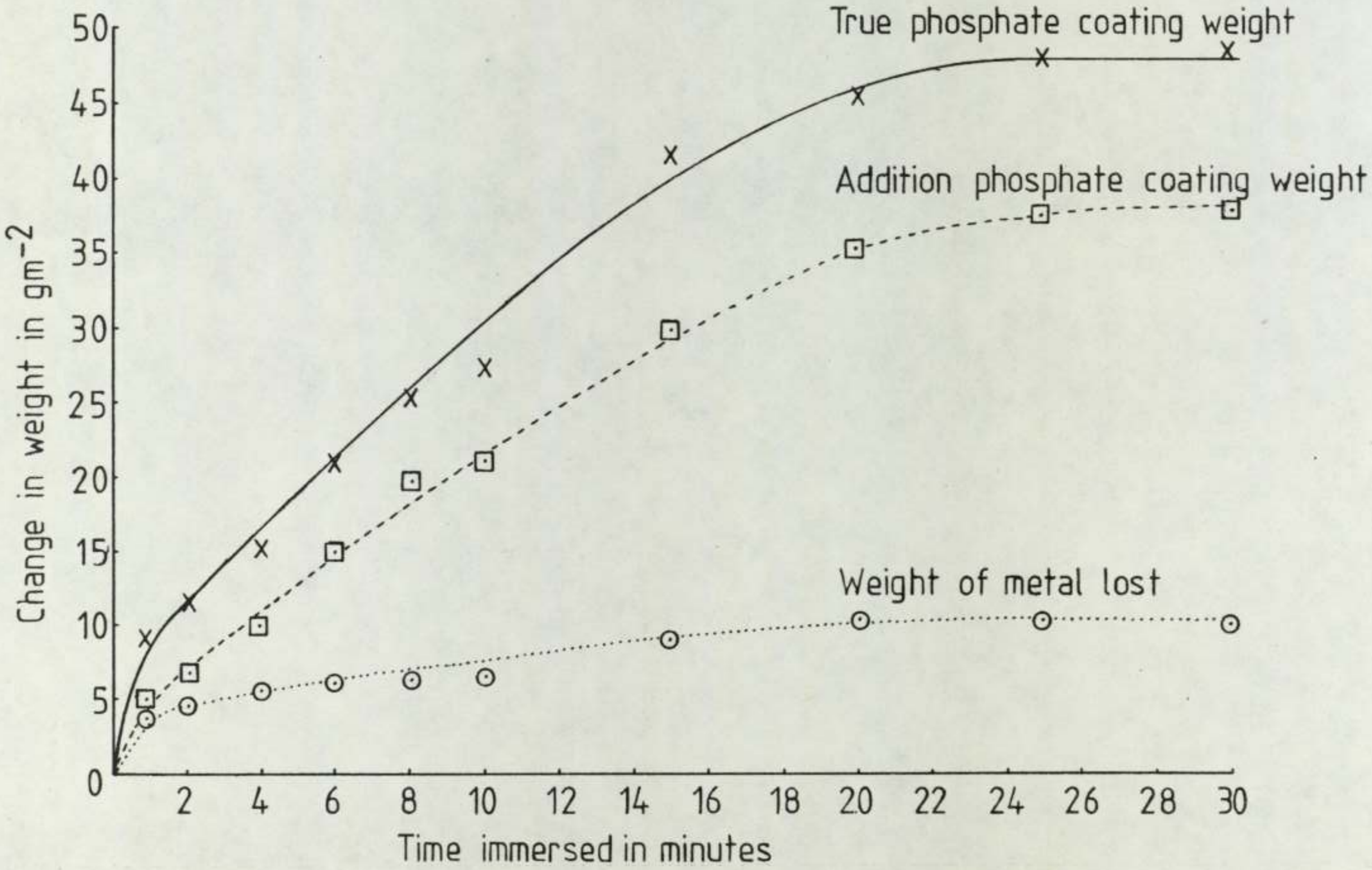


Figure 5.2 Coating weight curves for a works Parco 95 phosphating solution

Comparison of the addition phosphate coating weight and metal loss curves from figure 5.2 with their corresponding curves for a laboratory solution shown in figure 3.11 indicated similar differences.

Although all the curves exhibit differences, the addition coating weight determination, that was being used (see 3.5 and 3.10.2) to check that the phosphate coating on panels for testing were of acceptable quality gave no indication of any problem. This was because, as figure 5.2 shows, after six minutes immersion in a works Parco 95 solution the value of the addition coating weight was 15 gm^{-2} which was within the acceptable range of 12 to 15 gm^{-2} (3.10.2). This reflects the limitation, of using the coating weight deposited on one sample in a set immersion time, for quality control purposes, that it only gives a snapshot view of the coating weight curve, and does not indicate whether the curve has achieved the constant coating weight normally associated with a complete phosphate coating having deposited.

The coating weight curves for the laboratory Parco 95 solution indicate that the phosphate crystals nucleate and coalesce more rapidly on a metal surface immersed in the laboratory Parco 95 solution than when in the works Parco 95 solution. At this stage in the work there appeared to be two possible explanations for the differences between the two solutions:-

either (a) that a thin phosphate coating having deposited and covered the metal surface, the phosphate crystals continued to grow by some form of hydrolysis reaction (see section 2.1)

or (b) that the phosphate crystals were taking longer to coalesce and cover the metal surface. Accordingly while the phosphate crystals were nucleating and growing to cover the areas of bare steel at which acid attack would be continuing, the phosphate crystals already present were continuing to grow away from the surface, leading to a complete phosphate coating of high coating weight.

In favour of explanation (b) were three facts. Firstly, the metal loss curve for the works solution shows that metal was continually being lost until the true phosphate coating weight curve reached a constant value after 25 minutes. Therefore there must have been areas of exposed metal for the acid to attack until the coating completed. Secondly, a problem frequently encountered with the manual and automatic phosphating plants was that products immersed in the works Parco 95 phosphating solution for the normal 6 minutes, would become discoloured brown after immersion in the post phosphating rinses. It is likely that this was a rapid rusting process occurring at highly active surfaces (30,59) exposed by an incomplete phosphate coating. Thirdly, the presence of an incomplete phosphate coating on test panels phosphated using the works Parco 95 solutions would explain the poor resistance to the salt spray test.

To test explanation (b) three test panels were phosphated (3.4) using the two sets of works equipment, but with the phosphating times extended to the times at which the coating weight curves for each solution reached a constant value. These panels were then stained (3.7.1) and salt spray tested (3.8.1) and evaluated (3.8.1.2). A complete phosphate coating should have been deposited on these panels which when stained should be as resistant to the salt spray test as a laboratory produced coating. The results presented in Table 5.5 show that the panels failed at 72 and 88 hours with ratings

TABLE 5.5 SALT SPRAY RESISTANCE OF PHOSPHATE COATINGS PRODUCED BY EXTENDED IMMERSION TIMES IN A WORKS PARCO 95 PHOSPHATING SOLUTION

Treatment	Resistance to salt spray test (hours)*	Rating at failure *
Automatic plant	72	5.1
Manual plant	88	5.1

* Typical result representative of the panels tested.

of 5.1. These results seemed to confirm explanation b.

5.4 Analysis of phosphating solutions

Samples of the two works Parco 95 phosphating solutions were sent to the suppliers for analysis and comment (3.4.3). The results of the two analyses were reported to be normal except that the iron content was slightly low and the presence of organic contaminants was noted. The suppliers could offer no explanation for the poor phosphate coatings produced by these solutions. The concentration of the organic materials in the auto and manual phosphating solutions was then determined by extracting (3.6) the materials using a suitable solvent. The extracts had a tar-like consistency and were dark brown. The concentrations were .023 gl^{-1} and .028 gl^{-1} in the manual and automatic phosphating solutions respectively.

To determine the variation in concentration of the organics with time a completely new phosphating solution was made up in the automatic phosphating plant. Samples were taken from the solution periodically over a period of 4 weeks, and the concentration of the organic materials determined. The results are presented in figure 5.3. This shows that the concentration built up rapidly to 0.035 gl^{-1} after 2 days, then fluctuated and did not reach a stable value. The failure to reach a stable value could be due either to variations in the rubber compound and therefore types of organic material passing through the plant, or due to the inaccuracy of the technique of using a 100 ml sample to represent the average contents of a 1135 litre solution.

However the initial rapid build up in the concentration of organics does correlate with the rapid drop in the corrosion

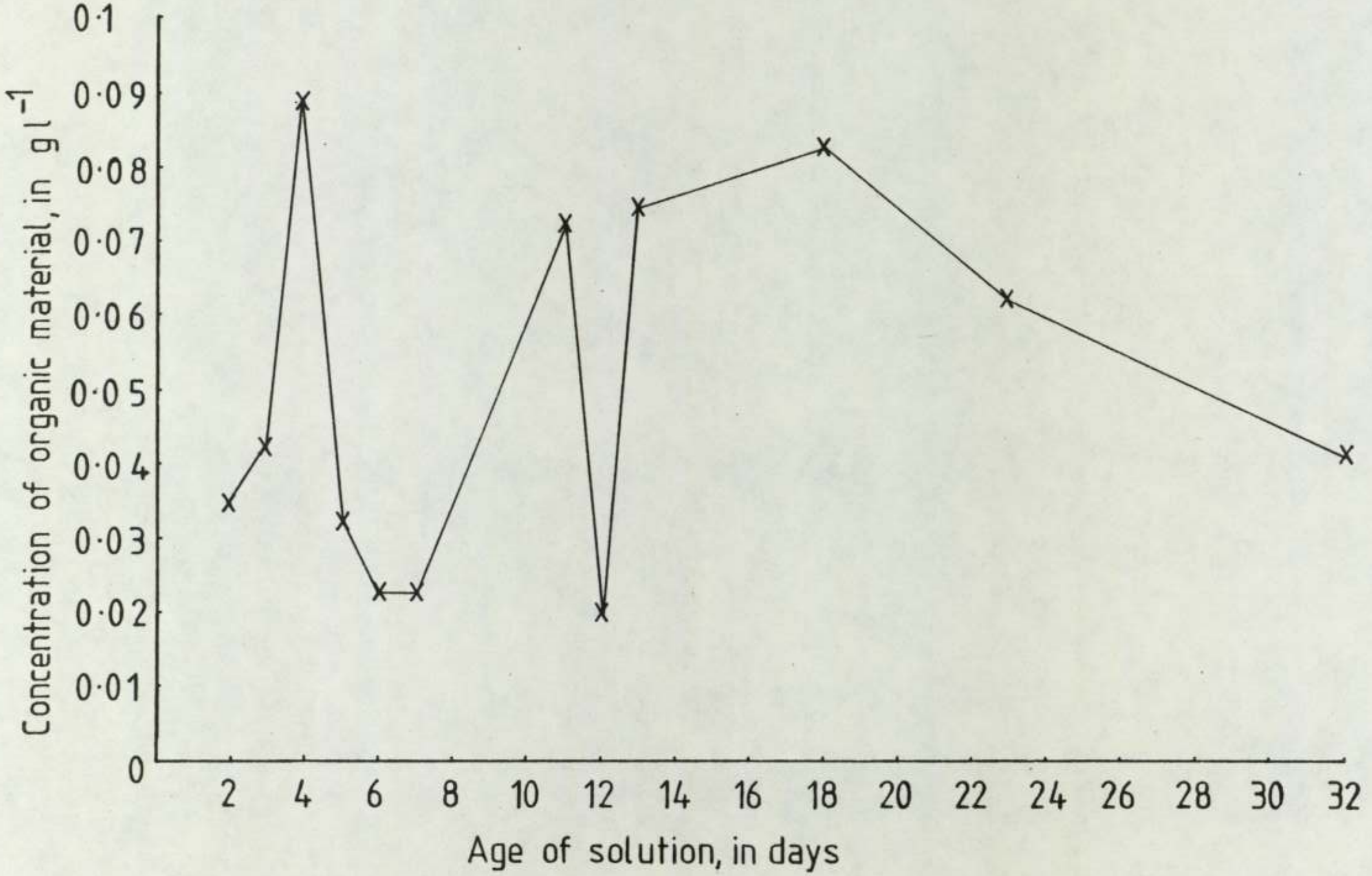


Figure 5.3 Variation in the concentration of organic material in a works Parco 95 solution

resistance of the phosphate coating produced using the works Parco 95 phosphating solution (see 5.2), after a new solution had been made up. Also the fluctuation in the concentration of organic materials could explain the occasional marginal improvements in the corrosion resistance of phosphate coatings produced using a contaminated works solution, if there was a threshold value below which the organic materials did not interfere with the phosphating reactions. The suppliers could offer no alternative explanation for the poor phosphate coatings, and agreed that it could be due to the presence of the organic materials. Therefore it was decided to try and identify these organic materials.

5.4.1 Identification of the organic materials

The possible sources of the organic materials were:-

(i) The use of contaminated, recycled, water in the works solutions.

(ii) The unofficial use of live steam heating on the plants, transferring additives in the steam supply into the solutions.

(iii) The solution leached out ingredients from the rubber sections.

Sources (i) and (ii) were removed by having the live steam heating taken off the plants, and converting the supplies of recycled water on the plants to fresh mains water, however tests showed the continued presence of organic material. The remaining possible source of the organics was the rubber sections. In the rubber sections the organics most likely to escape were those not chemically bound into the structure, the extending oils and the anti-oxidants. Of these two it was most likely to be the anti-oxidants, as some of those used were known to be water soluble (60).

Using the Pareto's analysis discussed in Chapter 4 the anti-oxidants used in 78% of the volume of work phosphated were found. These materials, described in Table 5.6, were used as standards in the tests carried out to identify the organic materials present in the phosphating solution.

5.4.1 Infra red spectroscopy

Spectra were produced (3.6.2) of the organics extracted from the automatic and manual phosphating plants. The two spectra were nominally identical, and a representative spectrum is presented in figure 5.4. This was compared with those produced (3.6.2) by the materials listed in Table 5.6. The only material to show spectral similarities with those of the extracted organics was C as shown in figure 5.5 Comparing figure 5.4 and 5.5 most peaks occur at the identical wavenumbers. However the extra peaks in the trace for the unknown organics pointed to the presence of organics additional to C.

5.4.2 Thin layer chromatography

Thin layer chromatography (3.6.1) analysis was carried out on samples extracted from both the works phosphating solutions (3.6) and on the materials listed in Table 5.6 by method (3.6.1(i)). The spot colours and RF heights for C were also present in the organic extract, as shown in Table 5.7. In addition there were five spots of colours and RF heights that did not correlate with those of the standards used. These results confirmed that C and other organics

TABLE 5.6 ANTI-OXIDANTS

Code	Trade Name	Chemical Name
A	Permanax BL	Diphenylamine/acetone condensation product.
B	Permanax B	Diphenylamine/acetone condensation product.
C	Permanax IPPD	N-isopropyl - n'-phenyl p-phenylenediamine.
D	Permanax 6 PPD	N-1,3 dimethylbutyl-N'-phenyl-p-phenylenediamine.
E	Flectol Flakes	2,2,4 trimethyl -1,2 dihydroquinoline.

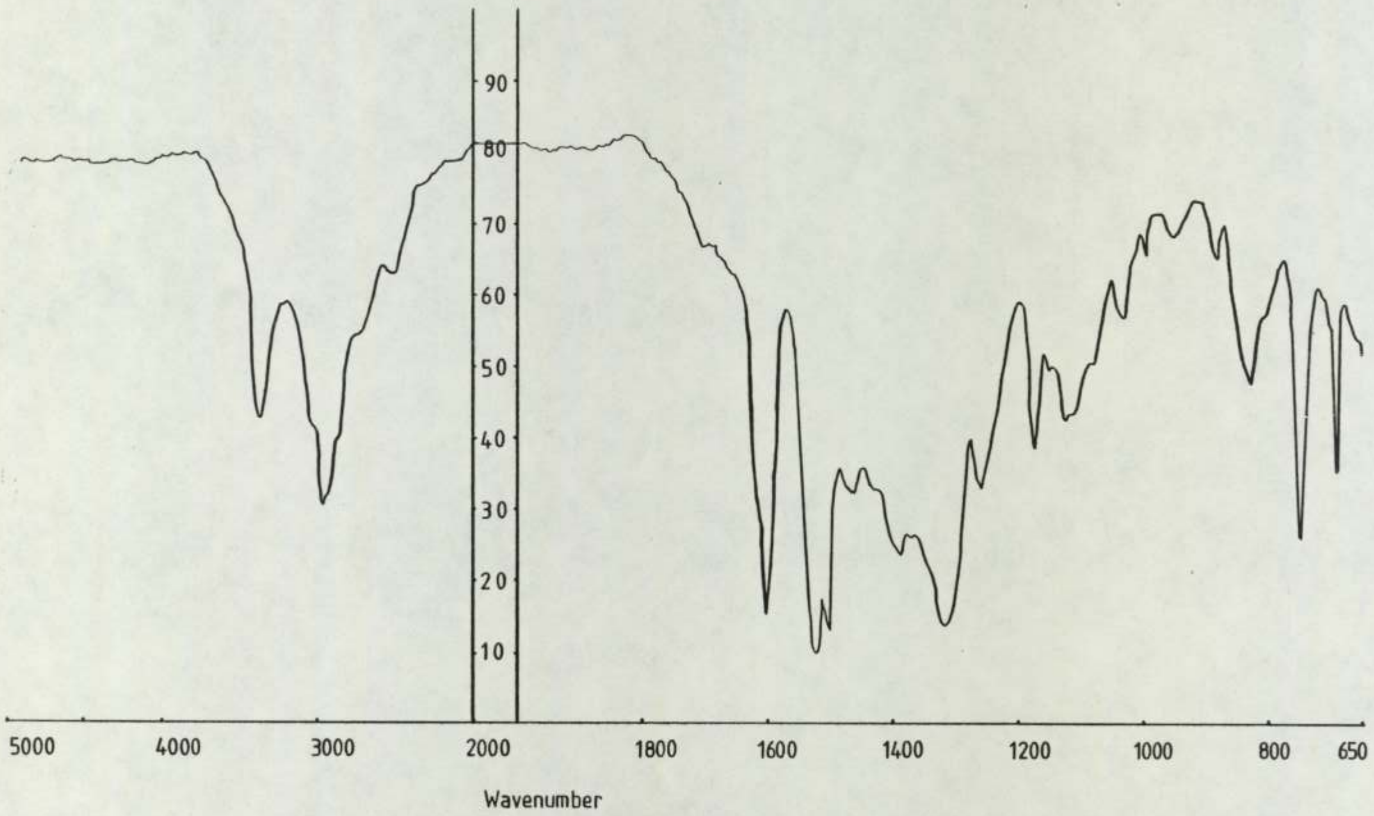


Figure 5.4 Infra-red spectrum of the organic material extracted from a works Parco 95 phosphating solution

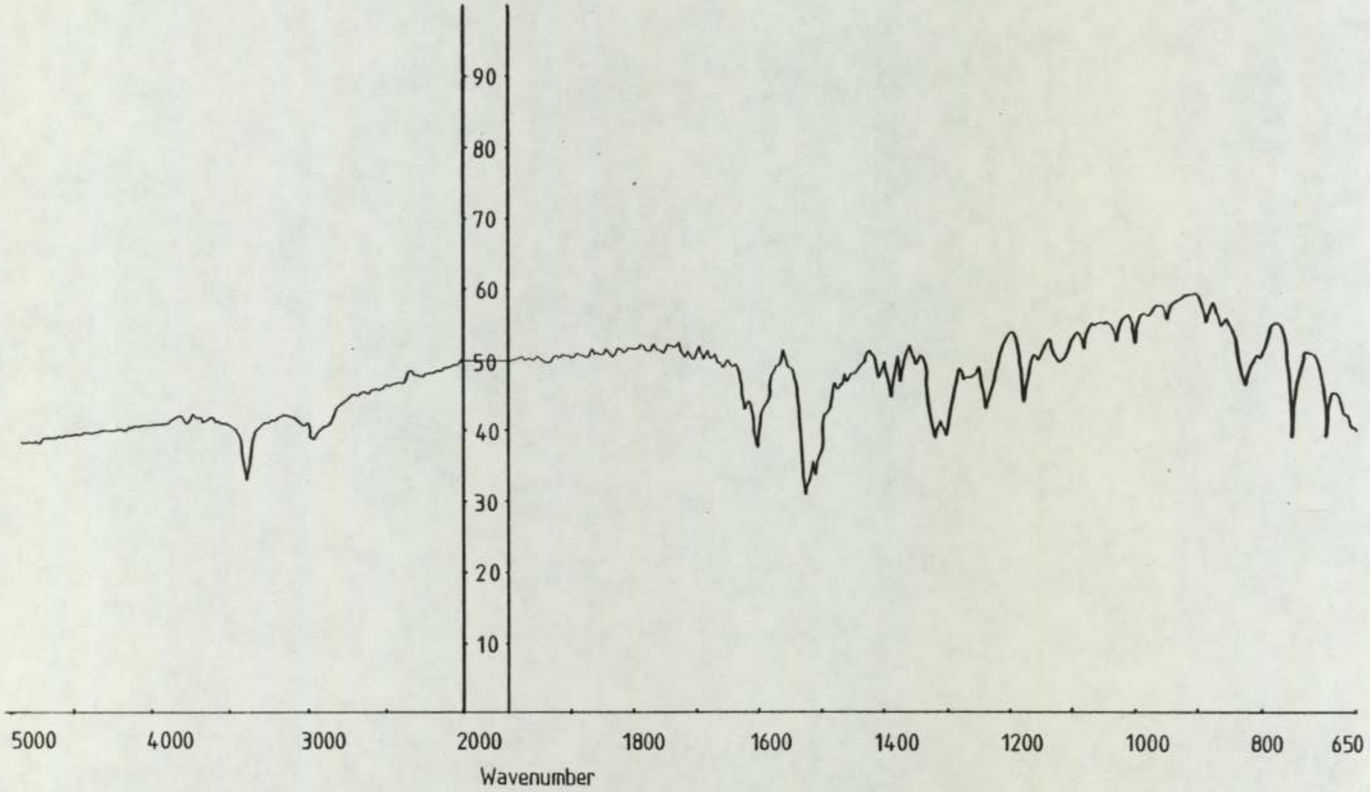


Figure 5.5 Infra red spectrum of as received C

TABLE 5.7 SPOT COLOURS AND RF VALUES FOR MATERIALS ANALYSED USING THIN LAYER CHROMATOGRAPHY

RF Values			
Material extracted from phosphating solution	As received C	Treated(3.6.1.1 (ii)) A	Colour of spot
-	-	.06	Maroon
.09	-	.09	Yellow
.15	.15	-	several with green outer
* .19	-	-	Blue
.23	-	.24	Yellow
.31	.31	-	Mauve
* .37	-	-	Yellow
.48	-	.49	Blue

were present in the solution. In order to identify the remaining unknown organics, chromatograms of the materials in Table 5.6 were produced by method (3.6.1(ii)) to ascertain whether the unknown organics were breakdown or reaction products of the materials in Table 5.6. The spot colours and RF values for A analysed by this method were also present in the organic extract as shown in Table 5.7. The spots marked with a * in Table 5.7 did not correlate with those of the materials in Table 5.6 produced by both method (3.6.1(i)) and method (3.6.1(ii)). However to identify the remaining organics would have required broadening the experiment to testing all the organic materials used in the rubber. In view of the large number of organic materials used, and the time required to analyse them the identification work was not taken further.

5.5 Duplication of the poor phosphating under laboratory conditions

The organics listed in Table 5.6 were added to laboratory Parco 95 phosphating solutions to try and duplicate the problems occurring with the works phosphating solutions. In each case a sufficient amount of organic material was added to achieve a concentration of 3 gl^{-1}, as this would be well in excess of the maximum concentration of organic material found in a works phosphating solution. All the materials listed in Table 5.6 were used as, although only materials A and C had been identified as present in a works solution, other organic materials were still unidentified that could be related to the materials in the Table.

Each material listed in Table 5.6 was added to an individual laboratory phosphating solution , and to determine whether the poor phosphating was a result of two or more organic materials combining to interfere with the phosphating reactions all of the materials listed in Table 5.6 were added to one solution.

Three panels were then phosphated (3.4) using each Parco 95 (3.4.3.1) solution stained (3.7.1), salt spray tested (3.8.1) and evaluated (3.8.1.2). The results in Table 5.8 show that the experiment failed to duplicate the poor phospahting as all the panels failed between 72 and 96 hours with a rating of 4.1 or 5.1. This pointed to the unidentified organic material in the works phosphating solutions playing a role, either alone or in concert with the identified organic materials, in interfering with the phosphating reactions.

A further experiment was carried out to try and duplicate the problems under laboratory conditions by phosphating (3.4) 40 typical products using a laboratory solution of Parco 95 (3.4.3.1). Three test panels were then phosphated (3.4), stained (3.7.1), salt spray tested (3.8.1) and evaluated (3.8.1.2). However results of 72 to 96 hours to failure and failure ratings of 4.1, show the experiment failed.

The phosphating chemical suppliers also took away a number of products and attempted to reproduce the problem in their laboratory without success.

5.6 Possible mechanisms of interference of the organic materials with the phosphating reactions

The work has shown that the organic contaminants rapidly built up in the works phosphating solutions, and at the same time the corrosion resistance of the phosphate coatings produced using the works solutions rapidly decreased. Thereafter the organic content

TABLE 5.8 RESISTANCE TO THE SALT SPRAY TEST OF PHOSPHATE COATINGS PRODUCED USING LABORATORY PARCO 95 SOLUTIONS TO WHICH ORGANIC MATERIALS HAD BEEN ADDED

Treatment	Resistance to salt spray* test (hours)	Rating at failure *
phosphating solution containing		
C	72	4.1
A	88	5.1
B	72	5.1
E	96	4.1
D	72	4.1
All of the above	88	4.1

* Typical result representative of the panels tested.

of the works solutions fluctuated and the corrosion resistance of phosphate coatings produced using a normal immersion time of six minutes was poor while,the corrosion resistance of a phosphate coating produced using extended immersion times was good. The only abnormalities reported from the analyses of the solutions were a slightly low iron content and the presence of organic materials. In the light of this information it was decided to expand theory (b) (see 5.3) to include mechanisms of how the organic materials could be interfering with the phosphating reactions and causing the deposition and coalescing of the phosphate crystals to take longer.

(i) The materials were anti-oxidants, which could interfere with the depolarisation of the cathodic sites by reacting with the accelerators (oxidising agent). If the cathodic sites were not depolarised this would prevent the approach of the phosphating solution to these areas and prevent the deposition of hopeite crystals (2.1.4.2). The phosphate coating would then grow slowly by the phosphyllite crystals in the anodic sites spreading sideways, forcing the hydrogen off the surface, a process similar to that originally suggested by Wulfson (see 2.1.3.2).

(ii) The organics present are complexing agents, which could redissolve one of the phosphate crystals types as it was deposited. The phosphate coating would then grow slowly, the other crystal type spreading sideways by a process similar to either the anodic theory suggested by Wulfson (2.1.3.2) or the cathodic theory suggested by Machu (2.1.3.1) depending on the type of phosphate crystal being deposited.

(iii) As the organics were complexing agents they could complex with the metal ions in the phosphating solution at the metal/solution interface (see 2.1.4). This would reduce the availability of the ions for the phosphating reactions and would also explain the low iron content reported by the suppliers (see 5.4).

5.7 Examination of the phosphate coatings

Rather than carry out a more detailed analysis of the phosphating process using techniques such as the time potential method it was decided to investigate the interference with the phosphating reactions by examining the phosphate coatings using the scanning electron microscope.

A set of coating weight panels (3.5.4) were phosphated (3.4) using each works Parco 95 (3.4.3.1) phosphating solution and the panels used for examination of the phosphate coatings using a scanning electron microscope (3.9). Figures 5.6 to 5.8 show the phosphate coatings produced using the laboratory solution after 1,2 and 4 minutes respectively. Figure 5.6 shows that after 1 minute immersion deposition of the phosphate crystals had begun, but areas of exposed metal were still visible. Figure 5.7 shows that after 2 minutes immersion the phosphate coating had virtually completed. Two types of phosphate crystal are evident, a thin acicular crystal marked X and platelets marked Y which are hopeite and phosphyllite respectively (see 2.1.6). After four minutes immersion, the time taken for the coating weight curves of a laboratory Parco 95 solution to achieve a constant value, the coating was complete as shown by figure 5.8. This figure shows both

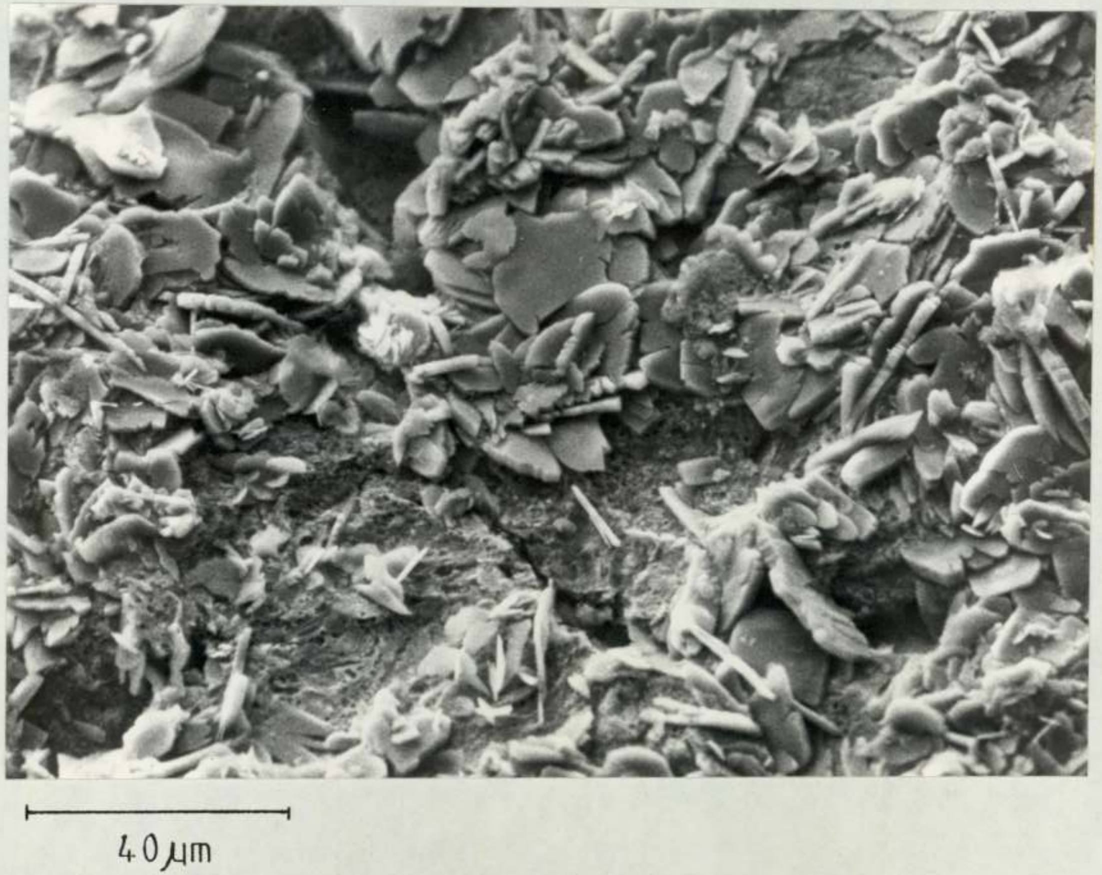


Figure 5.6 Phosphate coating produced by one minute's immersion in a laboratory Parco 95 solution

<u>Figure 5.7</u> Phosphate coating produced by two minutes immersion in a laboratory Parco 95 solution

Figure 5.8 Phosphate coating produced by four minutes immersion in a laboratory Parco 95 solution

the crystal types are well developed and there is no obvious porosity. No major difference was evident in the phosphate coatings examined when phosphating had been for longer than four minutes.

The micrographs of phosphate coatings produced using the two works phosphating solutions showed the same trends and therefore only one set of typical micrographs is presented here. Figure 5.9 shows that the appearance of the phosphate coating after 1 minute immersion was similar to that of the laboratory produced phosphate coating after the same time. The phosphate crystals had begun to deposit on the metal surface but areas of bare metal are visible. Figure 5.10 shows the phosphate coating after 4 minutes immersion. This shows that unlike the laboratory produced phosphate coating, large areas of exposed metal are visible as the phosphate coating had not completed. Figure 5.11 shows the phosphate coating after 10 minutes immersion. Two types of phosphate crystal are now clearly evident, but areas of bare metal are still visible as shown by a higher magnification of the same area in figure 5.12. This type of porosity was evident until coatings were examined after 25 minutes immersion, the time taken for the coating weight curve for a works solution (see 5.3) to reach a constant value. Figure 5.13 shows the phosphate coating after 25 minutes, to be similar to the phosphate coating achieved in a laboratory phosphating solution after four minutes shown in figure 5.8. However, comparing the two figures the phosphyllite crystals appear to be larger in the works coating than in the laboratory coating, while the hopeite crystals appear to be sparser and smaller. This points to the phosphyllite crystals depositing on to the metal surface first and then continuing to grow while hopeite crystals slowly deposit to complete

Figure 5.9 Phosphate coating produced by one minutes immersion in a works Parco 95 solution

Figure 5.10 Phosphate coating produced by four minutes immersion in a works Parco 95 solution

Figure 5.11 Phosphate coating produced by ten minutes immersion in a works Parco 95 solution

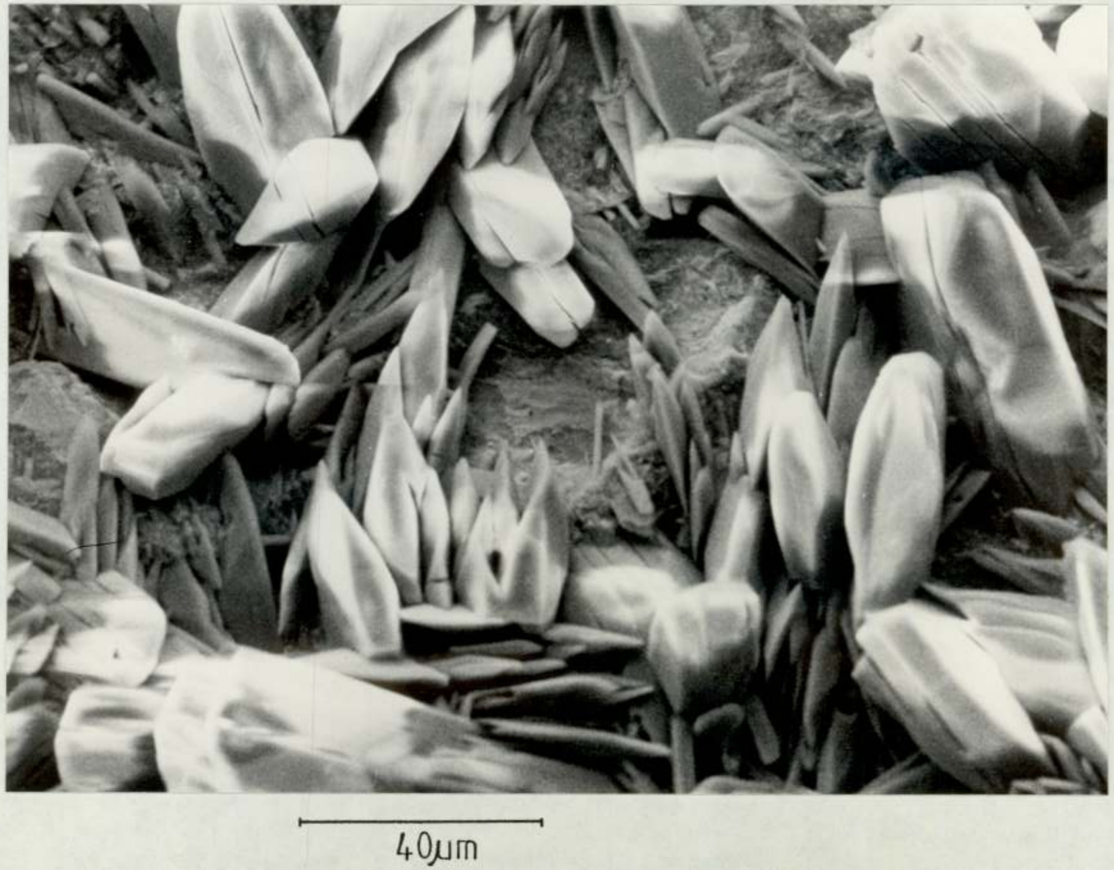


Figure 5.12 Higher magnification of the area shown in figure 5.11

Figure 5.13 Phosphate coating produced by 25 minutes immersion in a works Parco 95 solution

the coating.

These micrographs confirm that the phosphate coatings produced in works solutions, with the standard immersion time of six minutes would be grossly porous. This porosity would decrease the protective value of the phosphate coating and lead to the poor corrosion resistance already reported for a works Parco 95 phosphate coating. As both phosphate crystals are evident in the works phosphate coating after 25 minutes immersion, and none of the coatings examined showed any signs of resolution of the phosphate crystals the micrographs disprove theory (ii) (see 5.6) regarding the interference with the phosphating process. The longer time taken to achieve a complete phosphate coating in the works solution points to either theory (i), or theory (iii)or a combination of the two being correct. However, theory (i) does require modification as the micrographs show that the cathodic reaction is slowed down, not prevented, as the coating does eventually complete with both hopeite and phosphyllite crystals present not just phosphyllite crystals. This suggests the phosphating solution had reverted to an unaccelerated solution of the type originally patented (16) in which the phosphate coating deposited very slowly without the aid of accelerators. However, theory (i) alone is insufficient to explain the phenomenon, in that if the organic materials were reacting with the accelerator, the amount of accelerator available for containing the iron content of the solution would be limited and a high iron content would be expected (2.1.5.1). The analyses of the works solutions had however consistently indicated a slightly low iron content and it is suggested that this indicates there was a complexing effect of the organic materials with the metal ions as suggested in theory (iii).

Therefore the micrographs appear to show that it is a combination of theories (i) and (iii)that describes the process of interference with the phosphating reactions. These theories are not taken further as all the organic materials in the works solution had not been identified.

The coating weight curves for the works Parco 95 solution and for the laboratory Parco 95 solution are presented schematically in figure 5.14 and 5.15. These figures show the regions of coating weight deposition and completion together with the resulting corrosion resistance of the phosphate coatings.

5.8 Options for overcoming the problem

The ways of overcoming the effects of the organic materials that were considered were:-

(i) Phosphating the metals at some stage prior to bonding the rubber and metal sections, to avoid contaminating the phosphating solution with organic materials.

(ii) Dumping the phosphating solution when it becomes contaminated and making up a fresh solution.

(iii) Continously filtering the organic materials from the works solutions.

(iv) Decanting the solution into a holding tank and dosing it with chemicals to precipitate out the organic materials.

(v) Change to using a phosphating solution in which such interference by the organic materials would not occur.

(vi) Changing to using a phosphating solution in which the phosphating reactions would react with and 'neutralise' the organic materials, and deposit a complete phosphate

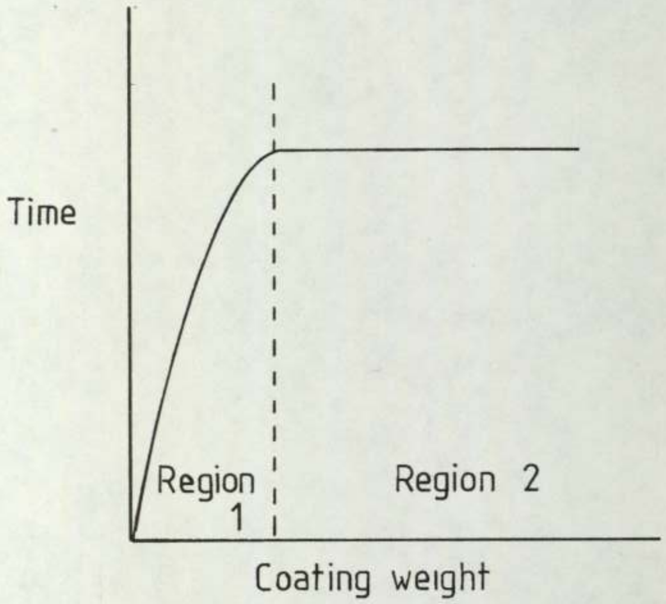


Figure 5.14

A schematic representation of the true phosphate coating weight curve for a laboratory Parco 95 solution

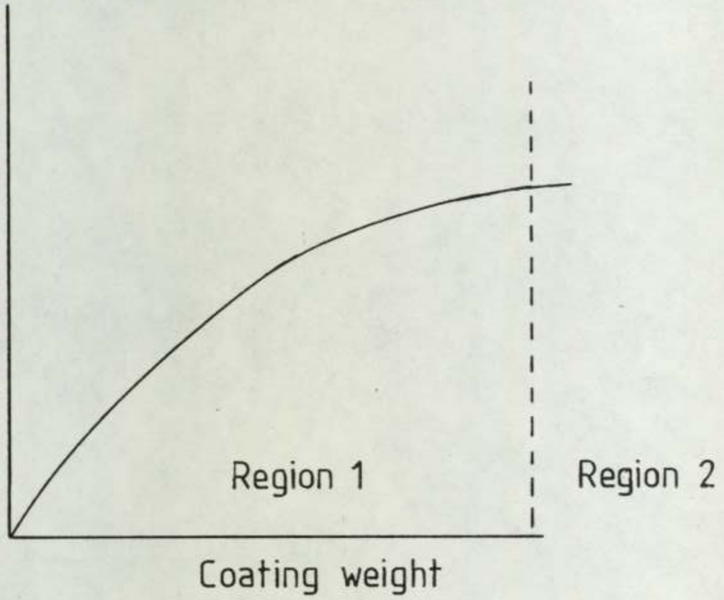


Figure 5.15

A schematic representation of the true phosphate coating weight curve for a works Parco 95 solution

Key

Region 1	Incomplete phosphate coating, poor corrosion resistance
Region 2	Complete phosphate coating, good corrosion resistance

coating.

Option (i) was discounted because the phosphate coating would become damaged by the operations involved in the moulding and deflashing stages of manufacture.

Options (ii) to (iv) were discounted on the grounds of cost, because of the rapid initial increase in the concentration of organic materials, and correspondingly rapid decrease in the corrosion resistance of the phosphate coating produced. A works situation would require the complete solution to be treated or dumped every two days.

Pyrene, the Parco 95 suppliers were contacted and they offered an alternative phosphating solution they believed would comply with option (v) or (vi), Bonderite 181X. As described in section (3.4.3.2) this solution was to be operated on the nitrite side (see (2.1.5.1) with an organic additive (see 2.1.5.2) to convert it from a medium to a heavyweight phosphating solution and at a processing temperature of between 50 and 70°C.Pyrene suggested that Bonderite 181X might comply with option (v) because at the lower processing temperature of 50 to 70°C less organic material might be leached from the rubber sections and in addition the solution is tolerant to the presence of organic materials because it is used with an organic additive. Furthermore, they suggested, Bonderite 181X might comply with option (vi)'s requirements because as extra accelerator can be added, any accelerator lost by reaction with the organic materials, suggested in section 5.6, could be replaced.

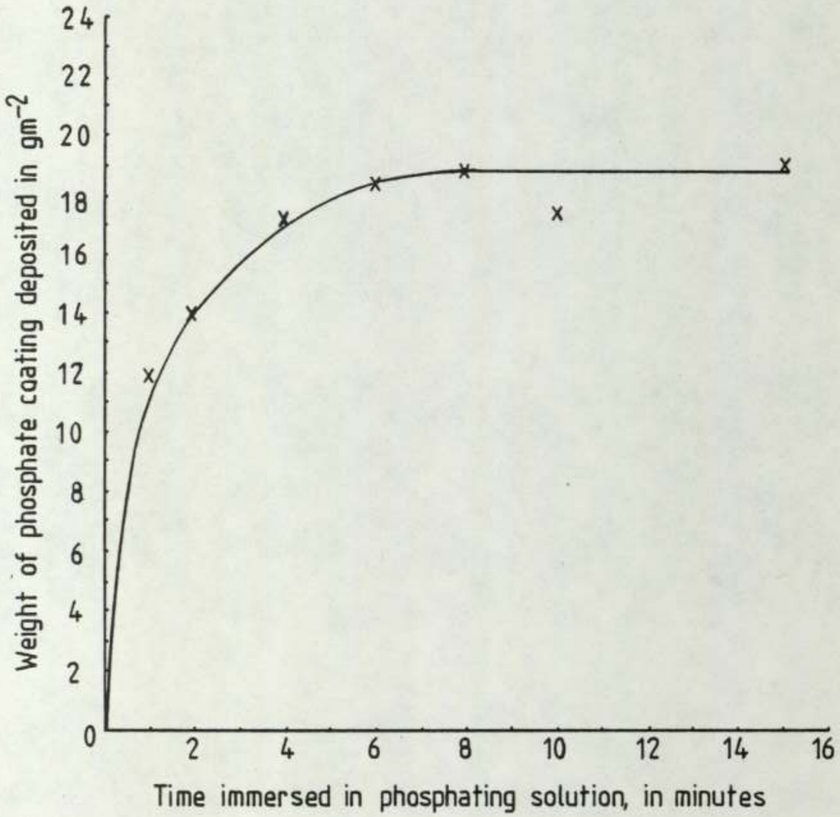
5.8.1 Laboratory trial of Bonderite 181X

To assess the suitability of Bonderite 181X as a replacement for the Parco 95 phosphating solution the following laboratory trials were carried out.

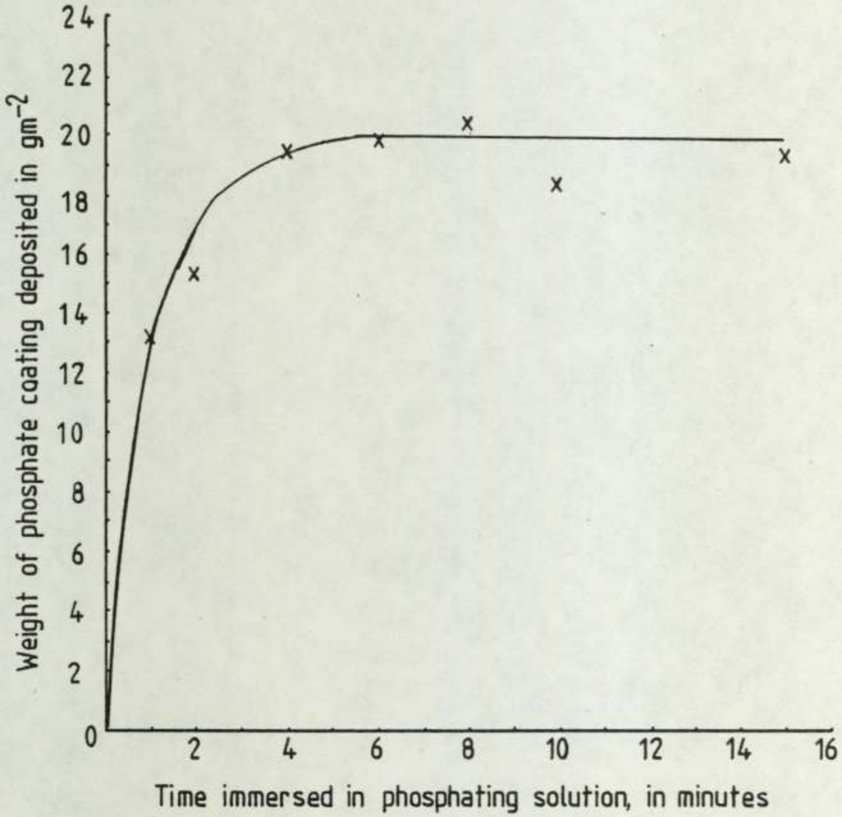
5.8.1.1 Coating weight curves

Panels were phosphated (3.4) using the Bonderite 181X solution (3.4.3.2) at temperatures of 56,60,64 and 68°C and the coating weights determined (3.5.4). The true phosphate coating weight curves for each temperature are presented in figures 5.16 to 5.19 respectively. These show that at solution temperatures of 56 and 60°C the coating weight curves do not reach a constant value indicating the phosphate coating had completed until six minutes phosphating. It was not practical to increase the production phosphating time to more than six minutes because it would increase the cost of the phosphating process. Therefore a phosphate coating completion time of six minutes meant solution temperatures of 56 and 60°C were not practical. At solution temperatures of 64 and 68°C the coating weight curves reach a constant value after two minutes, a time compatible with the production phosphating time of six minutes. Comparing the curves for these two temperatures with figures 3.7 and 3.8 for a Parco 95 laboratory phospating solution at its working temperatures, no major differences are evident. Although the final coating weight achieved by the 181X phosphating solution is slightly higher than that for the Parco 95 solution this was not considered to be detrimental.

The metal loss and addition phosphate coating weight curves for the Bonderite 181X solution are presented in figures 5.20 and 5.21 for solution temperatures of 64 and 68°C respectively. The metal loss curves show that metal was lost up to an immersion time of 4 minutes, a slightly longer time than for a specimen immersed in a



<u>Figure 5.16</u> True phosphate coating weight deposited as a function of time immersed in a Bonderite 181X phosphating solution operated at 56°C



<u>Figure 5.17</u> True phosphate coating weight deposited as a function of time immersed in a Bonderite 181X phosphating solution operated at 60°C

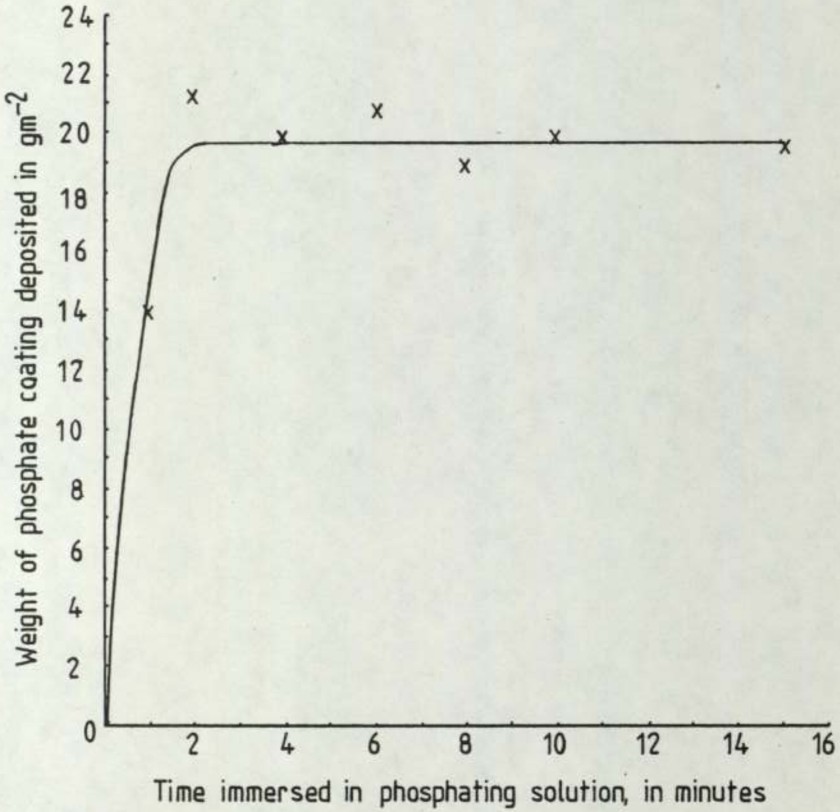


Figure 5.18 True phosphate coating weight deposited as a function of time immersed in a Bonderite 181X phosphating solution operated at 64°C

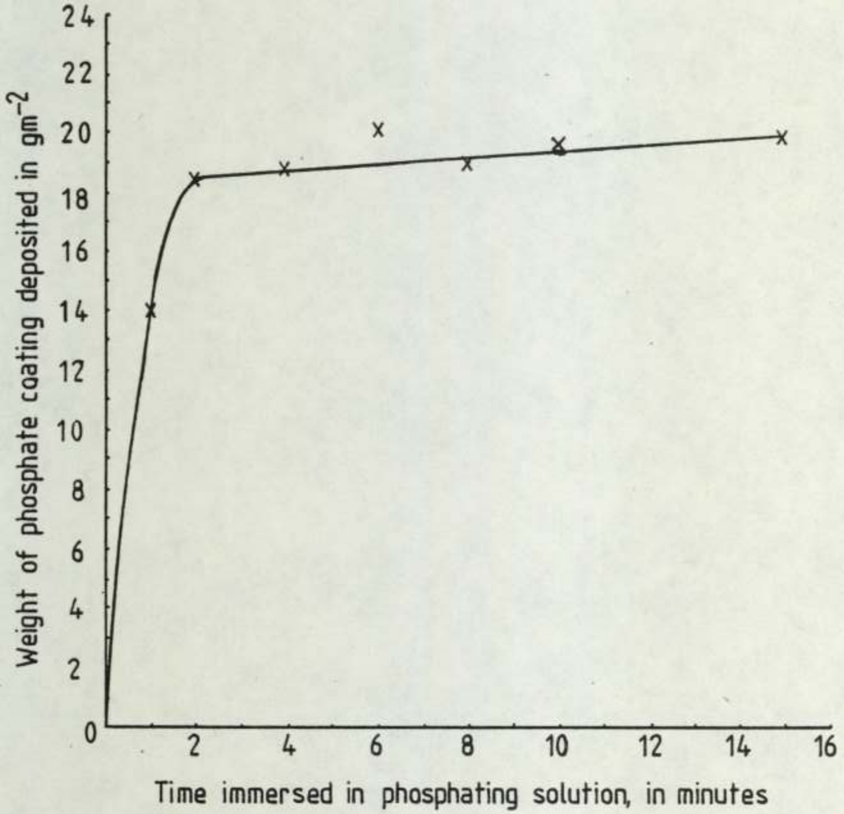


Figure 5.19 True phosphate coating weight deposited as a function of time immersed in a Bonderite 181X phosphating solution operated at 68°C

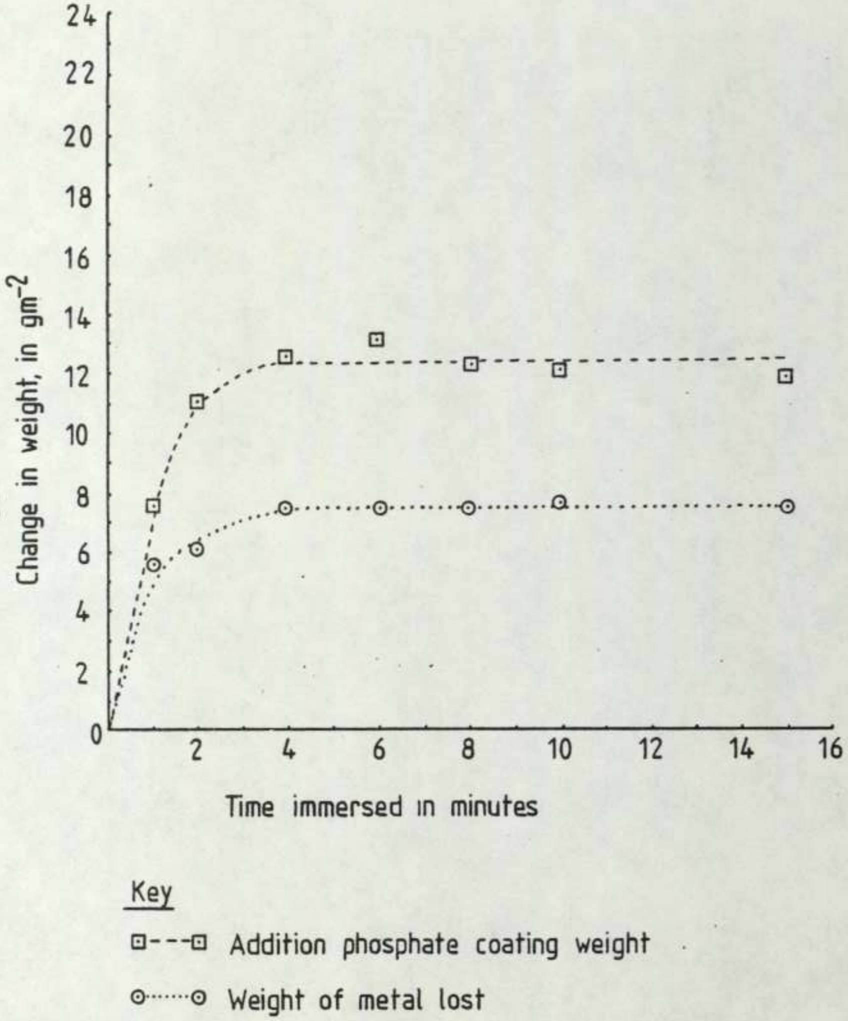


Figure 5.20 Addition phosphate coating weight, and weight of metal lost as a function of time immersed in a Bonderite 181X phosphating solution operated at 64°C

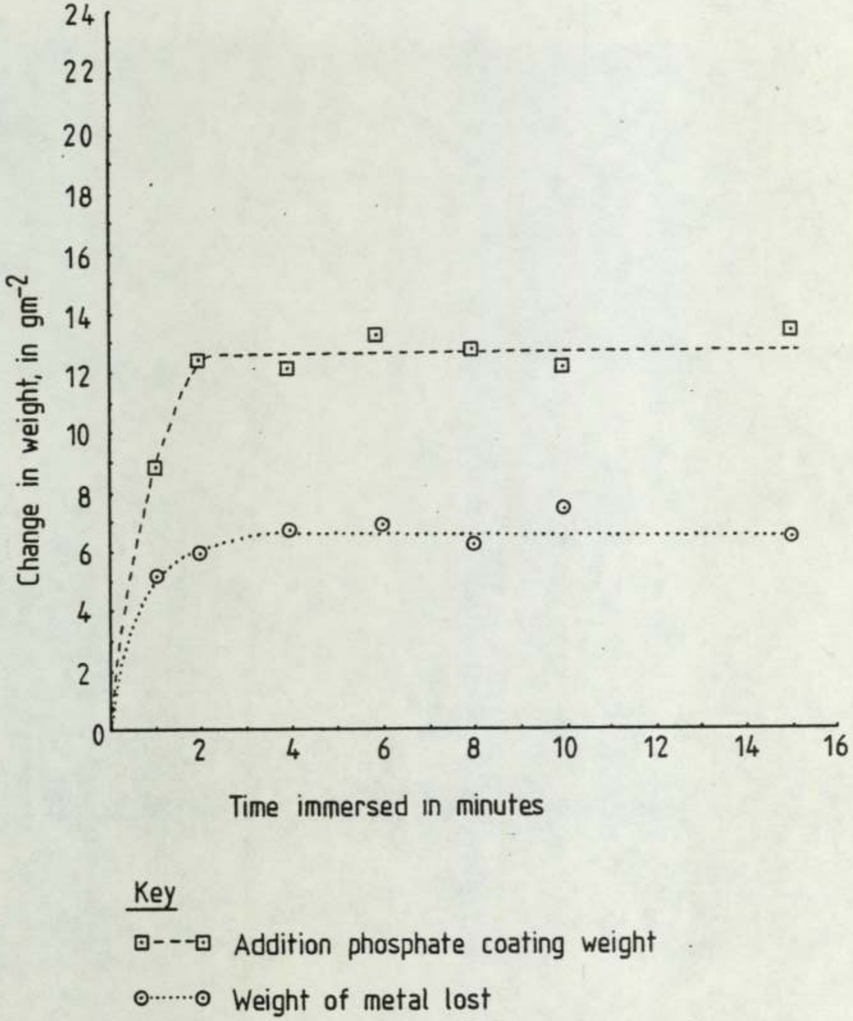


Figure 5.21 Addition phosphate coating weight, and weight of metal lost as a function of time immersed in a Bonderite 181X phosphating solution operated at 68°C

Parco 95 solution at working temperature, but still a sufficiently short-time to be compatible with the production phosphating time of 6 minutes. However the constant values of between 6 and 7 gm^{-2} that the Bonderite 181X curves reach are similar to those achieved by the Parco 95 curves (see 3.10.2).It is suggested that the longer time taken by the metal loss curve to achieve a constant value in the Bonderite 181X solution reflects the different ways in which a heavyweight phosphate coating is deposited by the two solutions. The Parco 95 solution uses a temperature between 82 and 88°C with moderately accelerated phosphating reactions compared to the high level of acceleration combined with an organic additive and lower temperature range of 64 to 68°C used in a Bonderite 181X solution. The addition phosphate coating weight curves reach a constant value of between 12 and 13 gm^{-2} after 4 minutes.

5.8.1.2 Examination of the Bonderite 181X phosphate coating

A test panel was phosphated (3.4) using a laboratory solution of Bonderite 181X (3.4.3.2) and the resulting phosphate coating examined using a scanning electron microscope. A representative area is shown in figure 5.22. This shows the phosphate coating to have completed at six minutes immersion. It also shows the coating consists predominantly of the phosphate crystal hopeite as would be expected for a highly accelerated zinc phosphating solution (2.1.6).

5.8.1.3 Protective value of a Bonderite 181X phosphate coating

Although the indications from the previous work were that Bonderite 181X produced a phosphate coating with similar

<u>Figure 5.22</u> Phosphate coating produced by six minutes immersion in a laboratory solution of Bonderite 181X

characteristics to a Parco 95 coating it was not known whether the protective value of the finishes based on a phosphate coating would be detrimentally affected by a change from Parco 95 to Bonderite 181X. Although the performance of a laboratory produced Parco 95 phosphate coating was not matched by the performance of a corresponding works coating, it was the former performance that was sought. Therefore the protective value of a Bonderite 181X laboratory produced phosphate coating was compared with that of a Parco 95 laboratory produced phosphate coating by preparing test panels of each finish based on a phosphate coating. In the following tests, six panels were phosphated (3.4) using a laboratory solution of Parco 95 (3.4.3.1) and six panels using a laboratory solution of Bonderite 181X (3.4.3.2),before the relevant supplementary finishes were applied. Three panels were used in each of two duplicate tests, however, as there were no marked differences between the results from the two tests the results are presented as one set in each case.

(i) Phosphate and stain

The phosphated panels were stained (3.7.1), salt spray tested (3.8.1) and evaluated (3.8.1.2). The results in Table 5.9 show that there was no major difference between the times to failure of the panels at 88 hours but a slight difference in the rating at failure. The Parco 95 and stain coatings failed with a rating of 4.1, while the typical failure rating of the Bonderite 181X and stain coating was 5.1. This difference is suggested to be due to the different phosphate crystal structures. The platelet and acicular crystal types that make up a Parco 95 coating provide a range of shapes and sizes of phosphate crystal which pack together well as they grow out from the surface. In comparison the single crystal type of the

TABLE 5.9 COMPARISON OF THE RESISTANCE TO THE SALT SPRAY TEST OF A PARCO 95 AND A BONDERITE 181X PHOSPHATE COATING WHEN STAINED

Treatment	Resistance to salt spray* test (hours)	Rating at * failure
Phosphated using Bonderite 181X	88	5.1
Phosphated using Parco 95	88	4.1

* Typical result representative of the panels tested.

Bonderite 181X phosphate coating is unable to provide the same range of crystal shapes, therefore the crystals are not able to pack together so closely and cover the base metal as efficiently. Thus the Bonderite 181X coating has more weak spots than a Parco 95 coating, leading to more corrosion spots. However, this difference was judged not to be significant as both coatings were able to meet the requirements of the relevant specifications listed in Table 1.2

(ii) Phosphate and oil

The panels were oiled (3.7.2) then salt spray tested(3.8.1) and evaluated (3.8.1.2). The results in Table 5.10 show that none of the test panels had failed after 192 hours exposure. Testing was halted at this stage as the coatings had easily exceeded the requirements listed in Table 1.2.

(iii) Phosphate and a thin coat of paint

In addition to testing the resistance to the appearance of corrosion the adhesion of the paint film was tested. The panels were painted (3.7.4.2),then salt spray tested (3.8.1) and evaluated (3.8.1.2)(3.8.1.3). The results in Table 5.11 show that the times to failure and rating at failure were identical at 48 hours and 4.3 respectively. The times to failure of the adhesion of the paint film were also identical at 24 hours.

(iv) Phosphate and a thick coat of paint

The panels were painted (3.7.4.1) then salt spray tested (3.8.1) and evaluated (3.8.1.2)(3.8.1.3). The results in Table 5.12 show all the Parco 95 phosphated panels failed after 192 hours exposure with a rating of 5.1, and the paint adhesion failed after 72 hours. There is some variability in the results for the Bonderite

TABLE 5.10 COMPARISON OF THE RESISTANCE TO THE SALT SPRAY TEST OF A PARCO 95 AND A BONDERITE 181X PHOSPHATE COATING WHEN OILED

Treatment	Resistance to salt spray test * (hours)
Phosphated using Bonderite 181X	192
Phosphated using Parco 95	192

* Typical result representative of the panels tested.

TEST 5.11 COMPARISON OF THE RESISTANCE TO THE SALT SPRAY TEST OF A PARCO 95 AND A BONDERITE 181X PHOSPHATE COATING WHEN PAINTED (3.7.4.2)

Treatment	Resistance to salt spray test (hours)*	Rating at failure*	Time to failure of adhesion test*
Parco 95	48	4.3	24
Bonderite 181X	48	4.3	24

* Typical result representative of the panels tested.

TABLE 5.12 COMPARISON OF THE RESISTANCE TO THE SALT SPRAY TEST OF A PARCO 95 AND A BONDERITE 181X PHOSPHATE COATING WHEN PAINTED (3.7.4.1)

Treatment	Resistance to salt spray test (hours)	Rating at failure	Time to failure of adhesion test
Phosphated using Parco 95	192*	5.1*	72*
Phosphated using Bonderite 181X	192**	5.1	192**
Phosphated using Bonderite 181X	144**	5.1	48**

* Typical result representative of the panels tested.

** Two typical results are presented for the Bonderite 181X phosphated panels as each value represents 3 test results.

181X phosphated panels, 3 gave a slightly poorer performance than the Parco 95 panels failing after 144 hours exposure with a rating of 5.1 with the paint adhesion failing after 48 hours. The other 3 gave an equivalent performance failing after 192 hours exposure with a rating of 5.1 and a better paint adhesion result of 192 hours to failure.

In terms of visual corrosion all the panels passed the requirements of the specifications listed in Table 1.2. The adhesion results for 3 of the Bonderite 181X panels were far superior to the results for the Parco 95 panels, and 3 were marginally poorer. Therefore a change to Bonderite 181X was judged to be acceptable for this finish as well as the other 3 finishes based on a phosphate coating.

5.8.1.4 Preproduction trial

Samples of several product configurations were obtained (3.2) and wheelabrated (3.3). Half of the samples were phosphated (3.4) using a laboratory solution of Bonderite 181X (3.4.3.2) and half using a laboratory solution of Parco 95 (3.4.3.1). The samples were then coated with the four supplementary finishes, stain, oil, a thin coat of paint and a thick coat of paint with normal production batches under unsupervised conditions. No problems were found for samples with either phosphate coating and no differences were apparent when samples of each finish were examined visually.

5.8.1.5 Laboratory duplication of contamination with organic materials

It had not been possible to duplicate in the laboratory the effect that the organic materials had in the works Parco 95 phosphating solutions. Therefore it was not possible to assess in the laboratory whether a Bonderite 181X phosphating solution would be similarly affected by the presence of the organic materials. The only way to assess the system was to subject Bonderite 181X to a works trial in one of the works phosphating plants.

5.8.1.6 Critical path analysis of the work required for a works trial of Bonderite 181X

A simple critical path analysis for the works trial of Bonderite 181X is presented in figure 5.23. The lead up to the trial included the need to obtain health and safety approval for the solution and, permission to use the phosphating plant before an order for the required chemicals could be placed. The three stages of receiving the chemicals, obtaining the necessary repairs to the phosphating plant and communicating information regarding the trial to key personnel then had to be completed prior to starting the trial. The final stages are shown as being the actual cleaning out of the plant and making up of a Bonderite 181X phosphating solution.

5.8.1.7 Health and safety aspects of using Bonderite 181X

Before pressing the case for a works trial of Bonderite 181X approval of the solution was sought from the Dunlop Divisional Health and Safety Manager. The need for this arose because the solution would require regular additions of sodium nitrite a chemical which had, where possible, been withdrawn from use when

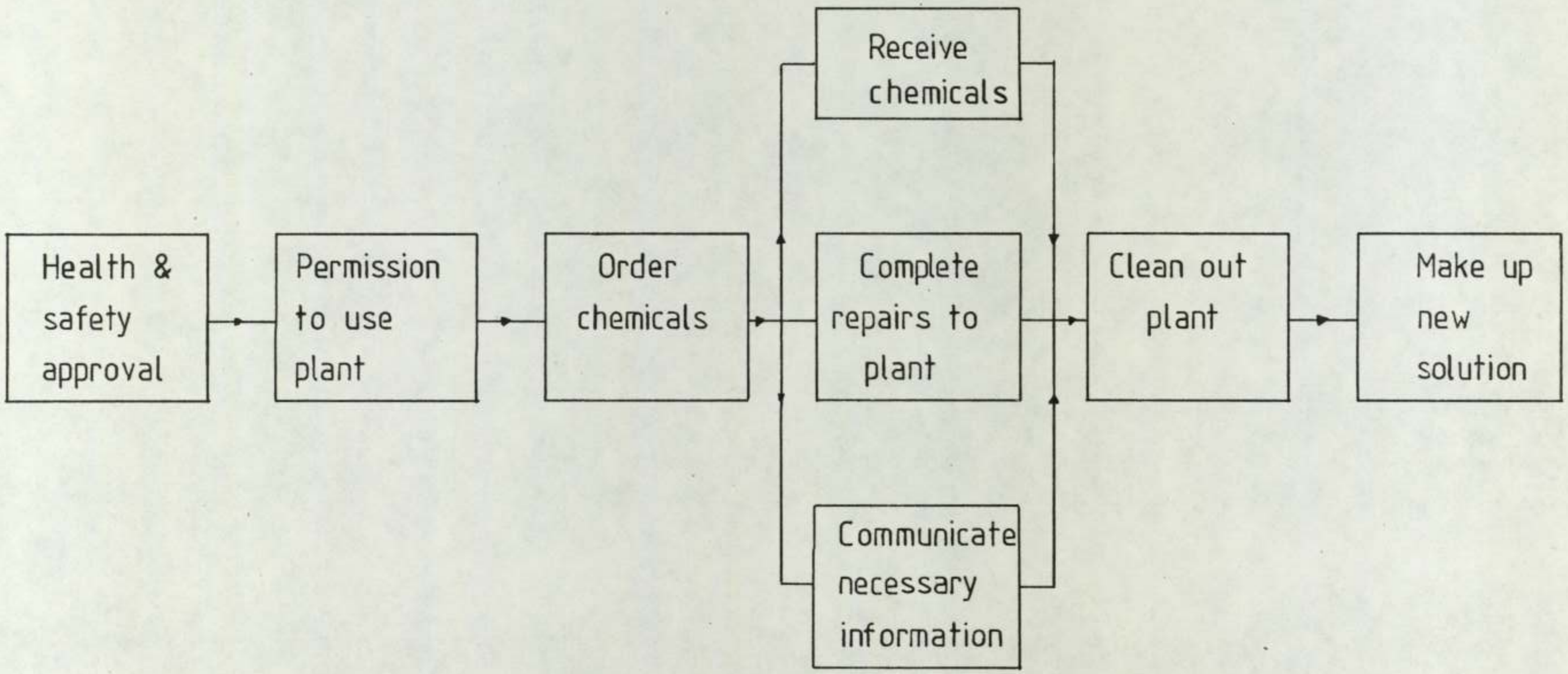


Figure 5.23 Critical path analysis of the work required prior to the works trial of the Bonderite 181X phosphating solution

direct contact with a rubber was involved. Work has shown that nitrite in contact with secondary amines under certain conditions can form nitrosamines (61), some of which are potent carcinogens in animals (62). After discussing the situation with the Divisional Health and Safety Manager and the Scientific Adviser it was decided that a consultation with the Environmental Health Manager for the Dunlop Group was necessary. A memorandum (appendix 3a) sent to the Environmental Health Manager stated that whilst the Division was pursuing a policy of preventing the use of sodium nitrite-containing materials in contact with rubber, it was not possible to find alternative materials in all cases. In the case of the phosphating solution the risk involved in the use of sodium nitrite was believed to be negligible for three reasons. Firstly, the possibility of their being secondary amines at the surface of the rubber was small, secondly, the concentration of sodium nitrite in the phosphating solution was low, and thirdly, the conditions prevalent in the phosphating solution would not be conducive to the formation of stable nitrosamines.

In a reply to this memorandum (appendix 3b) permission to use the Bonderite 181X process was given. Further consultation was carried out with the Environmental Health Manager to ensure that he was aware of the use to which the solution was to be put. Samples of the solution were also taken to Central Research, Analytical section, and permission to use the process was not withdrawn.

5.8.2 Works trial of Bonderite 181X

A memorandum summarising the need to replace the Parco 95 phosphating solution, and indicating that a comparison of the Parco 95 and Bonderite 181X phosphating solutions had shown that they were interchangeable was issued (appendix 3c). The memo was followed by a talk to the Production Managers on the work reported in this chapter. After the talk the need to carry out repairs to the plants before a trial was strongly pressed. A compromise was reached whereby it was agreed to bring the automatic phosphating plant up to the required standard, but repairs to the manual phosphating plant would be held in abeyance until the results of the trial were known.

After the talk a memorandum was received from the Works Manager (appendix 3d) urging that a phosphating solution to replace the Parco 95 solution should be introduced as soon as possible.

Sufficient chemicals were ordered to run the automatic plant for eight weeks(appendix 3e). Shortly before the trial was due to commence a meeting was held to finalise arrangements for the trial (appendix 3f) and the necessary Health and Safety documents were issued on a temporary basis (appendix 3g).

On May 19th 1979 a Bonderite 181X solution was made up in the automatic phosphating plant and for comparative purposes a fresh solution of Parco 95 was made up in the manual phosphating plant. At the start of the trial, the repairs to the automatic plant had not been completed, which caused the author to supervise the operation of the plant for its use of two shifts per day, particularly to ensure that the temperature of operation was kept between 64 and $68^{\circ}C$.

5.8.2.1 Variation of the corrosion resistance of the phosphate coating

During the first four weeks of the trial 3 test panels were phosphated regularly using the works Parco 95 solution (3.4.3.1) and using the works Bonderite 181X solution (3.4.2.2). The panels were then stained (3.7.1), salt spray tested (3.8.1) and evaluated (3.8.1.2).

The results in Table 5.13 show that the panels produced using the Parco 95 solution dropped from a salt spray resistance of 72 hours with a rating of 4.1 to a resistance of 16 hours with a rating of 7.5 after 6 days. Thereafter the panels produced using the Parco 95 solution, typically failed at 16 hours with a rating of 7.5, with occasional improvements to 48 hours resistance with a failure rating of 5.1. The improvements did not appear to coincide with any particular incidents. In comparison the panels produced using the Bonderite 181X solution typically failed after 40 or 48 hours with a failure rating of 5.1 or 4.1, irrespective of the age of the solution. The variations from this typical value were improvements to a resistance of 64 hours or more with a rating of 4.1 or 5.1 or drops to 24 hours rating 5.1. Towards the end of this evaluation the trend was for the higher corrosion resistance of 72 hours or more, rating 4.1 or 5.1 to be maintained by the panels processed in the Bonderite 181X solution. This is suggested to be due to better control being achieved over the sodium nitrite content of the solution towards the end of the trial. Two changes contributed to this, firstly, thermostats were fitted to the plant. These allowed closer control over solution temperatures, and in particular prevented the temperature of the phosphating solution

TABLE 5.13 VARIATION OF THE RESISTANCE TO THE SALT SPRAY TEST OF PARCO 95 AND BONDERITE 181X PHOSPHATE COATINGS.

Age of solution days	Phosphated using Parco 95*		Phosphated using Bonderite 181X*	
	Salt spray resistance (hours)	Rating at failure	Salt spray resistance (hours)	Rating at failure
1	72	4.1	72	4.1
2	48	5.1	24	5.1
3	24	6.4	24	5.1
4	48	5.1	72	5.1
5	24	7.5	48	4.1
6	16	7.5	40	5.1
10	16	7.5	48	4.1
11	48	5.1	40	4.1
16	16	7.5	48	5.1
17	16	7.5	48	4.1
18	16	7.5	24	5.1
22	48	5.1	24	5.1
24	16	7.5	64	5.1
25	24	7.5	16	4.1
29	40	5.1	64	4.1
30	16	7.5	32	5.1
31	16	7.5	88	4.1
32	16	7.5	88	4.1
38	16	7.5	72	5.1
39	16	7.5	72	4.1

*Typical result representative of the panels tested.

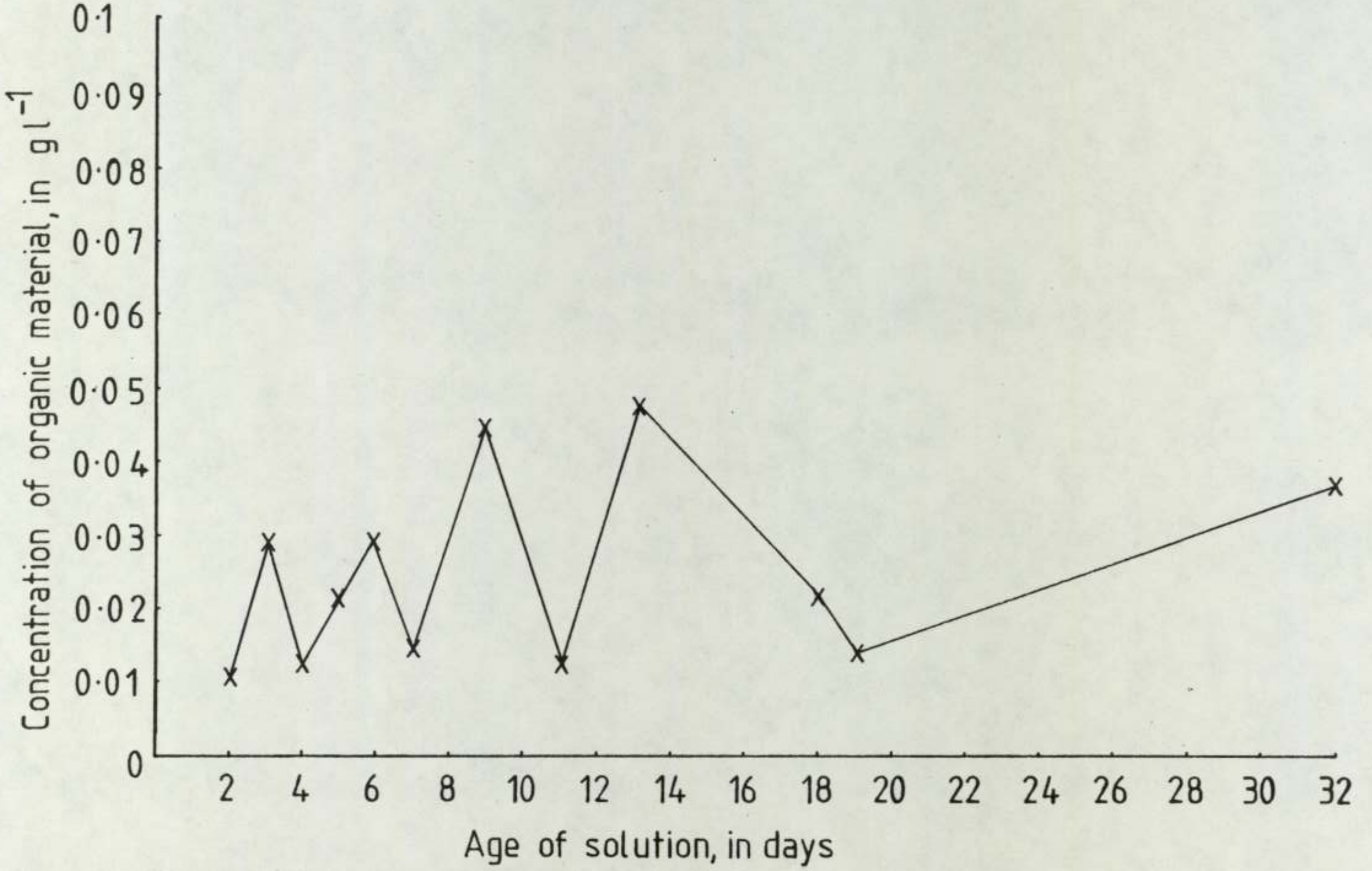
exceeding 70°C as had happened on occasions. Above 70°C sodium nitrite decomposes (30) in a phosphating solution and on the occasions the temperature exceeded 70°C the Bonderite 181X solution quickly changed to running on the iron side (see 2.1.5.1). Secondly, during the trial it was found that twice daily additions of sodium nitrite were required to maintain the solution on the nitrite side. Additions of sodium nitrite were not made at that frequency at the start of the trial as the Bonderite 181X solution should have generated sufficient nitrite during use not to need external additions (see section 2.1.5.1). During the early part of the trial this resulted in the solution changing to running on the iron side several times. The need for additions of sodium nitrite is suggested to indicate that it was taking part in a reaction that would not normally occur in a Bonderite 181X phosphating solution. This reaction could be with the organic materials, preventing their interference with the phosphating reactions (see 5.8). Further evidence in support of this was that when the Bonderite 181X solution did change to running on the iron side the phosphate coatings produced were discoloured brown.As a Bonderite 181X solution running on the iron side deposits a phosphate coating by similar reactions to a Parco 95 solution running on the iron side, this could be due to organic materials, no longer being neutralised by the sodium nitrite when they entered the solution, causing the deposition of an incomplete phosphate coating.

5.8.2.2 Concentration of organic materials in the works Bonderite 181X phosphating solution

During the first four weeks of the trial, samples of the phosphating solution were taken twice weekly and the organic materials extracted (3.6). The results in figure 5.24 show that the concentration of organic material in the Bonderite 181X solution, started at .0275 gl^{-1}, which represented the Additive 3 content (see section 2.1.5.2) and was part of the make up of the solution, and subsequently fluctuated between .01 and .0475 gl^{-1}. To ascertain whether this fluctuation was due to variation in the Additive 3 content of the solution, or due to other organic materials entering the solution, the extracted organic materials were analysed using thin layer chromatography (3.6.1). The results of these analyses showed no difference in the organics extracted from the solution as made up before or during its use. This confirmed that either the organic materials were not being leached into the solution because of its lower operating temperature, or that the organic materials were reacting with chemicals in the phosphating solution and being precipitated as sludge. The fluctuations in the concentration of organic materials in the Bonderite 181X solution is suggested to reflect the disadvantage of making large daily additions of Additive 3 to the solution, instead of regular small additions.

5.8.2.3 Report on the works trial

During the period of the trial a memo (appendix 3h) was received from the Product Design and Development Manager enquiring about the validity of unofficial reports he had received of an improvement in the quality of the phosphate coatings being produced at Metalastik. However, it was not until the results reported in the last two sections had been obtained that sufficient confidence was felt to issue a report on the trial. The report attached as



<u>Figure 5.24</u> Variation in the concentration of organic material in a works Bonderite 181X phosphating solution

appendix 3j was then issued summarising the results, and indicating that the improvement in the phosphate coating, resulting from the use of Bonderite 181X, merited an immediate change to that solution. The following cost benefit analysis of the change was included.

Cost benefit analysis of a change from Parco 95 to Bonderite 181X

Accurate usage rates of the Parco 95 chemicals were only available on a yearly basis as the amount issued from works stores. The information on the additions authorised each day to the plants was grossly inaccurate due to the unofficial additions made by the plant operators. Therefore the following comparison was based on yearly usage.

Chemical Costs

Cost of chemicals for a Parco 95 solution

Chemical	Annual consumption kg	Cost/kg	Annual Cost	Total
Parco 95 R	7,700	57p	£4,389	
Parco 95 IMU	1,162	57p	£ 662	
				£5,051

Pyrene give the average consumption rates of chemicals as:-

Chemical	Average usage rate in grammes used per square metre processed
	g/m^2
Parco 95	2.5
181X	3.5

Therefore an increase in the usage of chemicals of 40% would be expected on changing from Parco 95 to Bonderite 181X.

Cost of chemicals for a Bonderite 181X solution

Chemical	Estimated annual consumption	Cost/kg	Annual Cost	Total
Bonderite 181X R	10,780	61p	6,576	
Bonderite 181X IMU	1,136	61p	693	
Additive 3	1,540	80p	1,232	
Compensating solution No.2	220	31p	68	
				£8,569

Increase in chemical costs £3,518

Cost of solution renewals

Parco 95 solution

Number of renewals (1978)	Hours per renewal	No. of men	Cost per man hour	Annual cost
15	6	2	£3	£540

Bonderite 181X

Estimated number of renewals required	hours per renewal	No. of men	Cost per man hour	Annual cost
12	6	2	£3	£432

Saving in labour costs £108

Cost of heating solutions

Tank	Temperature using Parco 95	Temperature using Bonderite 181X	Reduction in Temp.	Saving in £s/annum
Phosphating	88°C plus	70°C or less	18°C	2,445*
Post-phosphating				
Rinse 2	90°C	70°C	20°C	1,005
Rinse 3	90°C	70°C	20°C	-
		Saving on heating		£3,450

* steam costed at £2.50 per 1000 lbs.

Total saving per annum resulting from a change to Bonderite 181X

Increase in chemical costs £	(£3,518)
Saving on labour costs	£ 108
Saving on plant heating	£3,450
Total	£ 40

Thus even assuming a 40% increase in chemical usage the process shows a cost saving before taking into account the benefits of a decrease in production problems, a decrease in the amount of chemicals wasted and an improvement in quality.

The report was presented at a meeting of the Production Managers. A memorandum (appendix 3k) from the Quality Assurance Manager was the first reaction to the report in which it was urged that the recommendations of the report should be implemented. Shortly afterwards a memorandum (appendix 3l) was received from the Works Manager accepting the findings of the work and asking that the recommendations of the report be implemented.

5.8.3 Introduction of Bonderite 181X as the standard phosphating solution

A memorandum (appendix 3m) was sent to the Purchasing Department advising them of the change to Bonderite 181X, and asking for a meeting to discuss the changeover. At the meeting it was agreed to use up the remaining stocks of Parco 95 in the manual phosphating plant and continue using Bonderite 181X in the automatic phosphating plant. Purchasing also agreed to negotiate with Pyrene regarding the price of the Bonderite 181X chemicals, and a further memorandum (appendix 3n) was sent outlining the reasons for believing the chemicals to be overpriced.

As a lever in the negotiations with Pyrene the Purchasing Manager indicated to Pyrene that the Division would not change to Bonderite 181X unless the prices were reduced. In order to convince them he refused to order any further supplies of Bonderite 181X until a price reduction was obtained. During the period of negotiations the stocks of Bonderite 181X chemicals were finished and the stage was reached when consideration was given to changing the automatic plant back to Parco 95. However at this stage an emergency order for Bonderite 181X chemicals was forced through the Purchasing Department. Had the order not been forced through the cost of the lost production on the automatic phosphating plant and the cost of having to change the phosphating solution from Bonderite 181X to Parco 95 and then back to Bonderite 181X would have more than accounted for the first years savings resulting from the reduction in price to 56p per kg for the Bonderite 181X Rand IMU chemicals that was eventually achieved. This illustrates the departmental attitude that exists within Metalastik, where each department attempts to optimise its own function and is oblivious to the costs and problems this creates for other departments. T.McCrae (65) suggests this attitude is characteristic of organisations facing a complex and uncertain world.

The chemicals were made stock items and the Health and Safety information re-issued on a permanent basis. A memorandum was then sent to the Engineering Department (appendix 3p) outlining the repairs required to the manual phosphating plant in preparation for converting it to Bonderite 181X.

It was not until March 1980 that the stocks of Parco 95 were finished. This was due to the large stock held, and disputes outside the Division causing the introduction of a short working week for a period.

5.8.3.1 Performance of Bonderite 181X in the manual phosphating plant

Three test panels were phosphated (3.4) weekly using the Bonderite 181X (3.4.3.2) phosphating solution in the manual phosphating plant, over the first four weeks of its operation. These were then stained (3.7.1), salt spray tested (3.8.1) and evaluated (3.8.1.2). The results in Table 5.14 show that the panels failed the salt spray test after 72 or more hours with a rating of 5.1. The better performance of the Bonderite 181X solution in this plant than reported for the early part of the trials in the automatic plant is suggested to be due to better control over the temperature of the solution, and the sodium nitrite content, being achieved from the start of the trial.

5.8.3.2 Reduction in the production of discoloured phosphate coatings

The corrosion resistance of the phosphate coatings produced using works phosphating solutions had increased as a result of changing from Parco 95 to Bonderite 181X but it was not known whether there had also been a reduction in the number of discoloured phosphate coatings produced. For this assessment the manual phosphating plant was used since it was more open to abuse because of the degree of control the operator had over this plant. The number of discoloured phosphate coatings was assessed by examining visually at random 100 tote tins of products that had been phosphated

TABLE 5.14 RESISTANCE TO THE SALT SPRAY TEST OF PHOSPHATE COATINGS PRODUCED USING BONDERITE 181X IN THE MANUAL PHOSPHATING PLANT

Number of weeks of using Bonderite 181X in the manual plant	Resistance to * salt spray test (hours)	Rating at * failure
1	72	5.1
2	96	5.1
3	72	5.1
4	88	5.1

* Typical result representative of the panels tested

under unsupervised conditions.

The bar chart in figure 5.25 shows the number of tote tins containing a percentage of defective coatings when the plant was using Parco 95, and figure 5.26 shows the results of the same study carried out when the plant was using Bonderite 181X. The results show a dramatic decrease in the production of defective coatings from 73 tote tins containing 90-100% discoloured coatings when using Parco 95 to virtually no discoloured coatings when the plant was using Bonderite 181X.

5.8.3.3 Assessment of the resistance to the salt spray test of the finishes based on a works Bonderite 181X phosphate coating

To assess whether using the Bonderite 181X under shopfloor conditions was causing any decrease in performance the following experiments were carried out, assessing the finishes based on a works Bonderite 181X phosphate coating. In each of the tests three test panels were phosphated (3.4) using a works solution of Bonderite 181X (3.4.3.2) and then the supplementary finish applied.

(i) Phosphate and stain

The phosphated panels were stained (3.7.1), salt spray tested (3.8.1) and evaluated (3.8.1.2). The results in Table 5.15 show that the panels failed after 64 hours testing with a rating of 5.1. This result for the test was slightly poorer than that reported for a laboratory coating of Bonderite 181X and some of the results of the works trials but was sufficient to meet the customer requirements listed in Table 1.2.

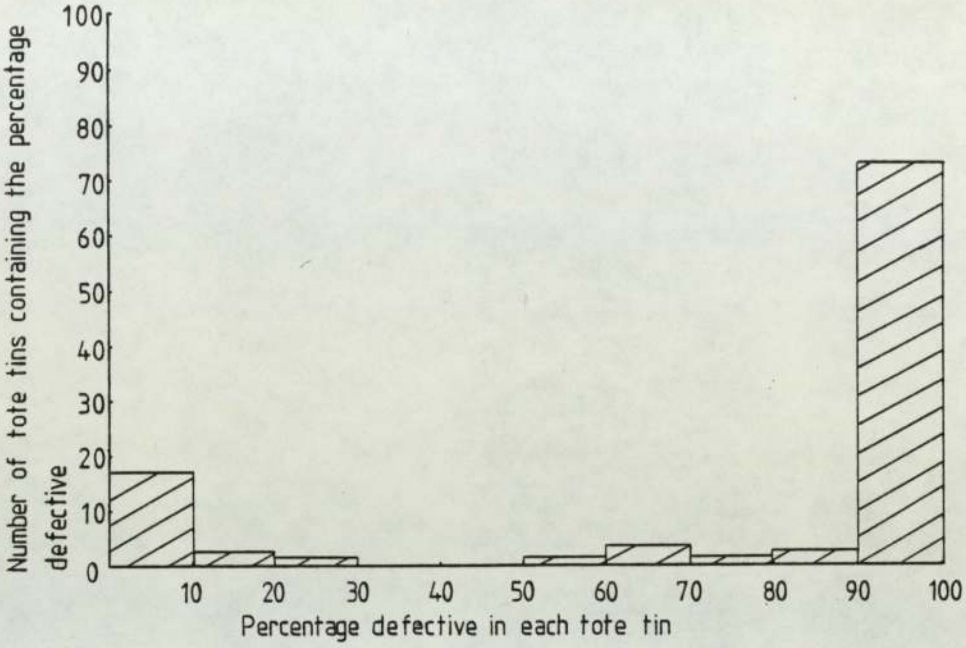


Figure 5.25 Production of defective phosphate coatings on the manual plant when using Parco 95

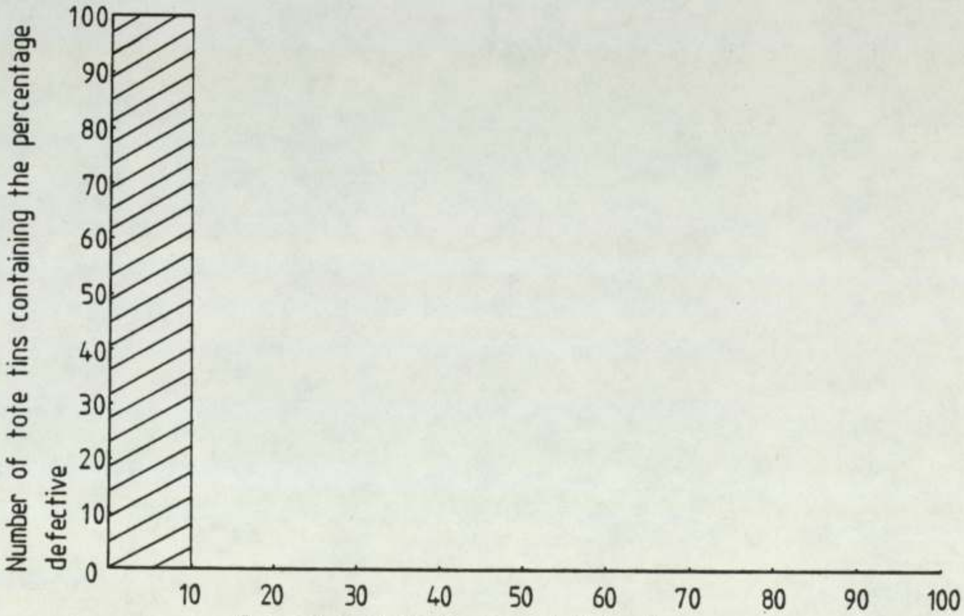


Figure 5.26 Production of defective phosphate coatings on the manual plant when using Bonderite 181X

TABLE 5.15 RESISTANCE TO THE SALT SPRAY TEST OF THE FINISHES BASED ON A WORKS BONDERITE 181X PHOSPHATE COATING

Treatment	Salt spray* resistance (hours)	Rating at* failure	Time to the* failure of paint adhesion
Phosphate and stain	64	5.1	-
Phosphate and oil	144**	-	-
Phosphate and a thin coat of paint	48	4.3	24 (2) 40 (1)
Phosphate and a thick coat of paint	144**	-	144**

* Typical results representative of the panels tested

** These values are the times at which the test was stopped not times to failure.

(ii) Phosphate and oil

The phosphated panels were oiled (3.7.2), salt spray tested (3.8.1) and evaluated (3.8.1.2). The results in Table 5.15 show that the panels had not failed after 144 hours exposure. After 144 hours the test was stopped as the panels had exceeded the customers requirements listed in Table 1.2.

(iii) Phosphate and a thin coat of paint

The panels were painted (3.7.4.2), salt spray tested (3.8.1) and evaluated (3.8.1.2) (3.8.1.3). The results in Table 5.15 show that all the panels failed the appearance evaluation after 48 hours testing, with a rating of 4.3. Two panels failed the paint adhesion test after 24 hours and the third after 40 hours. These results are virtually identical with those exhibited by the panels that had received a laboratory coating of Bonderite 181X.

(iv) Phosphate and a thick coat of paint

The panels were painted (3.7.4.1), salt spray tested (3.8.1) and evaluated (3.8.1.2) (3.8.1.3). The results in Table 5.15 show that the panels had not failed either on appearance or paint adhesion after 144 hours testing. After 144 hours the test was stopped as the panels had achieved the customers requirements listed in Table 1.2.

5.8.4 Alterations to Design Data Sheet 38

The results show that the change to Bonderite 181X had achieved the desired improvement in the resistance to the salt spray test of the finishes phosphate and oil, and phosphate and stain, without any detrimental effect on the two paint finishes based on a phosphate coating. Therefore it was decided to alter the information on Design Data Sheet 38 which gives details of the finishes used at Metalastik. This design data sheet is used by the draughtsperson to decide which finish is required on a product at its design stage.

Table 5.16 shows the salt spray resistances claimed for the finishes prior to this work, and Table 5.17 shows the new values claimed.

The resistance claimed for the finish phosphate and stain was raised from 16 to 56 hours, but not 64 hours or more as had been achieved because 56 hours was sufficient to meet the majority of customers requirements and raising the salt spray resistance any higher could lead the draughtsperson to believe the finish was better than the thick paint finish or nearly equivalent to phosphate plus a thick paint finish.

The resistance claimed for the finish phosphate and oil was raised from 24 to 48 hours. This figure was chosen because it met the majority of the customer requirements listed in Table 1.2. A higher figure could have been chosen as the results for phosphate and oil coatings easily exceed 48 hours resistance. However as a higher figure could lead the draughtsperson to believe the phosphate and oil finish was better than a phosphate and heavy coat of paint finish the figure of 48 hours was chosen. This highlights a criticism of the salt spray test, that it does not duplicate in service conditions, and unless the results are used carefully misleading information can be generated.

The resistances claimed for the paint finishes were not altered as the objective had been to maintain them at their existing levels

TABLE 5.16 SALT SPRAY RESISTANCES CLAIMED FOR FINISHES PRIOR TO THIS WORK

Organic coating applied	Basic component preparation	
	None	Heavyweight phosphate
	(Hours)	
Nil	-	-
Black stain	-	16
Oil	16	24
Paint finish (thin)	16	36
Paint finish (thick)	48	96

TABLE 5.17 SALT SPRAY RESISTANCES CLAIMED FOR FINISHES AFTER THIS WORK

Organic coating applied	Basic component preparation	
	None	Heavyweight phosphate
	(Hours)	
Nil	-	-
Black stain	-	56
Oil	16	48
Paint finish (thin)	16	36
Paint finish (thick)	48	96

which were already capable of satisfying the majority of the requirements listed in Table 1.2. Also as this work had concentrated on improving the phosphate and oil or stain finishes further testing would be required before sufficient confidence was felt to change the salt spray resistances claimed for other finishes.

All the salt spray resistances claimed in the data sheet carried the important rider that the values had been determined using test panels and that allowance would have to be made for any configurations such as crevices, joints or other corrosion traps that might lower the ability of the product to withstand the test.

The new Design Data Sheet 38 is shown in appendix 4 where a supplementary table that was attached to Design Data Sheet 38 can be seen. This table recommends the Metalastik finishes that should be applied to meet the various customer specifications. Where a finish could not be recommended, a note was entered to discuss the requirement with a Technical Authority. The table had the aim of making it easier for the draughtsperson to select the correct finish for a product. This should prevent the use of the wrong type of finish to meet a particular salt spray resistance as happened on numerous occasions during this work.

5.8.5 Testing of products to ensure that the finishes based on a phosphate coating, produced under normal shopfloor conditions, are capable of achieving the salt spray resistances claimed in DDS 38

On a random basis, samples of products that had received the four finishes based on a phosphate coating under unsupervised shopfloor conditions were obtained (3.2). These were salt spray tested

(3.8.1) and evaluated (3.8.1.2). After making allowance for corrosion that resulted from the products configuration (see 5.8.4) lowering the ability of the finish to withstand the salt spray test, the four types of finish were all found to be capable of meeting the salt spray resistances claimed in Table 5.17.

5.8.6 Evaluation by atmospheric corrosion testing of the improvement to the finishes resulting from the change to Bonderite 181X

If resistance to the salt spray test was used to rank the finishes based on a phosphate coating, the order would be as shown in Table 5.18.

TABLE 5.18 RANKING OF FINISHES BASED ON A PHOSPHATE COATING USING THE SALT SPRAY TEST AS A MEASURE OF THEIR CORROSION RESISTANCE

Resistance to the salt spray test (hours)	Finish	Ranking
192	Phosphate and oil	Best ↓
192	Phosphate and a thick coat of paint	
72	Phosphate and stain	
48	Phosphate and a thin coat of paint	Worst

However under the various types of corrosion conditions in service a phosphate and oil finish would not often be expected to give equivalent service life to a phosphate and thick coat of paint finish. Similarly a phosphate and stain finish would not often be expected to give better service life than a phosphate and thin coat of paint finish. Again this highlights a criticism often made of the salt spray test, that its results bear little correlation with the results that can be expected in service (2.2.2).

Therefore it was decided to ascertain the ranking of the finishes based on a works Bonderite 181X phosphate coating under atmospheric corrosion conditions. At the same time it was decided to investigate whether the improvement in the resistance to the salt spray test of the finishes based on a works phosphate coating that resulted from changing to Bonderite 181X was apparent under atmospheric corrosion conditions.

Sixteen test panels phosphated (3.4) using a works Bonderite 181X (3.4.3.2) phosphating solution were compared with sixteen that had already been phosphated using a works Parco 95 (3.4.3.1) phosphating solution. Four of each phosphate coating were stained (3.7.1) four oiled (3.7.2), four painted with a thin coat of paint (3.7.4.2) and four painted with a thick coat of paint (3.7.4.1). Two panels from each set of four were then scribed and all the panels were then exposed (3.8.2) on the roof of the factory from August 1980.

After four weeks the phosphate and stain coatings based on a works Parco 95 phosphate coating began to fail with the surfaces exhibiting a rating of 4.1. After six weeks the phosphate and oil coatings based on a works Parco 95 phosphate coating began to fail the surfaces exhibiting a rating of 4.1. Figure 5.27 shows the rack after three months exposure. The figure shows that the phosphate and stain and phosphate and oil finishes based on a works Parco 95 phosphating coating had failed completely, while no other finish shows any notable signs of corrosion.

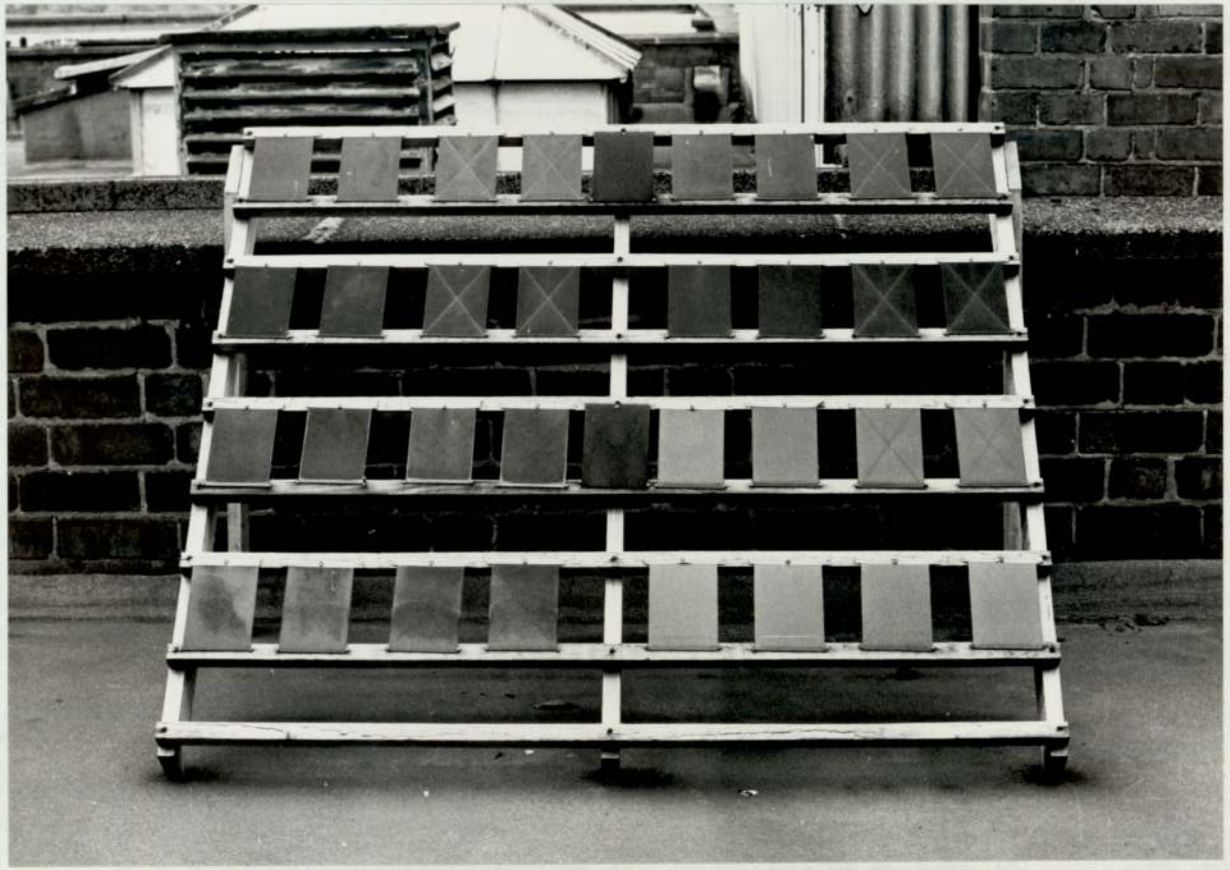


Figure 5.27 Test panels exposed in an atmospheric corrosion test, after three months

These results confirm that an improvement in the corrosion resistance of the phosphate and oil, and phosphate and stain finishes had been achieved by changing from Parco 95 to Bonderite 181X. To date they also show that the change to Bonderite 181X had not detrimentally affected the corrosion resistance of the paint finishes based on a phosphate coating. To complete the latter assessment and also to rank the finishes based on a phosphate coating the test was continued.

CHAPTER 6

THE NEW PHOSPHATING PLANT

At Metalastik phosphating is carried out using two tipping basket plants, one mechanically activated referred to here as the automatic plant and one manually operated referred to here as the manual plant. The plants consist of a series of tanks containing solutions. In each tank baskets are fixed sequentially down the length such that on tipping a basket the load contained is transferred into the next basket. The baskets are tipped in a sequence that passes a load through each basket in turn. The time products spend in each solution is determined by the number of baskets in a tank multiplied by the average time spent in a basket.

In 1967 a case was made out for replacing the manual phosphating plant, which criticised the plant on the grounds of its age and technical deficiencies and recommended its replacement with an automatic plant. However, when the automatic plant was installed, in that year, it was found to be incapable of processing certain product sizes because the sharpness of the mechanical tipping action caused very small products to be ejected from the plant and larger products to damage the plant. The manual plant therefore had to be retained for processing these products. Attempts were periodically made to obtain further money to purchase another phosphating plant to replace the manual phosphating plant, but without success. At the start of this project in 1977 the same manual plant was still in use, and the automatic plant was 10 years old, fully depreciated and in a poor state of repair.

Shortly after the start of this project the new Works Manager began to press the Production Engineering Manager to identify a replacement for the manual phosphating plant because of the number of defective phosphate coatings it was producing. At that time this project had identified that both the manual and automatic phosphating plants were producing defective phosphate coatings. This showed that the poor condition of the manual plant was not the cause of the defective phosphate coatings and it was suggested to the Production Engineering Manager that work to identify a new plant should be delayed until the cause of the problems with phosphating was found. If solving the cause of the production of defective phosphate coatings required any fundamental changes to the phosphating process, these changes could then be designed into the new phosphating plant. However, although a delay to the work was agreed, further pressure from the Works Manager caused early resumption of the work.

A project team consisting of a methods engineer, a senior methods engineer and the author was assigned to the work. At the outset it was intended to purchase the new plant in 1979, however the purchase was deferred because the Division had overspent its capital expenditure budget for that year. Sanction to purchase the new plant was seriously sought in June 1980, by which time the problem of producing defective phosphate coatings had been solved by a change of phosphating solution (see Chapter 5) and the design of the new plant had been altered to take this into account.

During the work to identify a new phosphating plant its specification was gradually refined. In this chapter an overall view of how the final specification was arrived at is presented.

The personnel making up the project team changed several times. Early in 1978 the methods engineer assigned to the project team left the company and was not replaced until late 1978. Shortly after the replacement methods engineer joined the team the senior methods engineer changed jobs within the Division and left the project team. Late in 1979 the replacement methods engineer left the company and the project team consisted solely of the author until early in 1980 when a replacement senior methods engineer joined the team. Because of the number of personnel changes in the project team the author enjoyed a greater involvement in the shaping of the new plant's specification than might otherwise have been allowed. Therefore except where certain areas of work are acknowledged to others the author claims a major involvement in the work presented.

6.1 Options

There were two options regarding identifying a new phosphating plant for purchase. The first option was to replace only the manual phosphating plant with a plant that would have to be capable of the following:-

(i) supplementing the capacity of the automatic phosphating plant.

(ii) processing all product types,both those types compatible with the automatic phosphating plant, (in order to supplement its capacity during periods of peak demand)and also those types not compatible with the automatic plant.

and (iii) providing the basic phosphating processes common to both of the existing phosphating plants plus the chlorinating of the rubber sections, and staining and oiling facilities which were only available on the manual plant.

The second option was to purchase a plant to replace both the manual and automatic phosphating plants which would have to be capable of the following:-

(i) providing the entire phosphating capacity

(ii) processing all the product types

and (iii) providing the basic phosphating processes common to both of the existing phosphating plants plus the chlorinating of the rubber sections, and staining and oiling facilities which were only available on the manual plant.

The second option of identifying a plant to replace both the automatic and manual phosphating plants was chosen for the following two reasons. Firstly, there would not be a great difference in the price of a plant bought to meet the first option and a plant bought to meet the second. The basic plant required would be the same, the only difference being requirement(i) the capacity of the plant. An increase in the capacity of the plant would not cause a large increase in its price as it would only require small increases in the sizes of the tanks and work holders. Therefore, the amount of labour and materials required to make the plant would not be substantially altered.

Secondly both the manual and automatic phosphating plants are old, fully depreciated and unsatisfactory in many respects. Their age and condition can be appreciated by examining figures 6.1 and 6.2 which show the manual and automatic phosphating plants respectively. Although as a result of the work reported some improvements were made to the plants, the remaining major defects are summarised in the following section.

6.1.1 Major defects of the phosphating plants

(i) The low level of automation allows the operators to interfere with the phosphating process. Neither the sequence of solutions used or the immersion times in solution, which are both critical to the quality of the phosphate finish produced, can be guaranteed.

(ii) The tipping action of the plants causes difficulties with the types of products that can be processed, and also causes products to strike each other sharply damaging the phosphate coating. After immersion in the post phosphating rinses, the damaged areas rust to give small rust scars.

(iii) The design, layout, age and poor state of repair of the plants results in difficulties maintaining the processing solutions in their optimum condition.

(iv) The low level of automation and open construction of the plants exposes operators to the risk of chemical splashes and necessitates their wearing protective clothing. Although such clothing is provided it is seldom worn. In addition on one plant there is exposed moving machinery in which an unwary operator could become trapped. These facts have caused the health and safety inspectorate

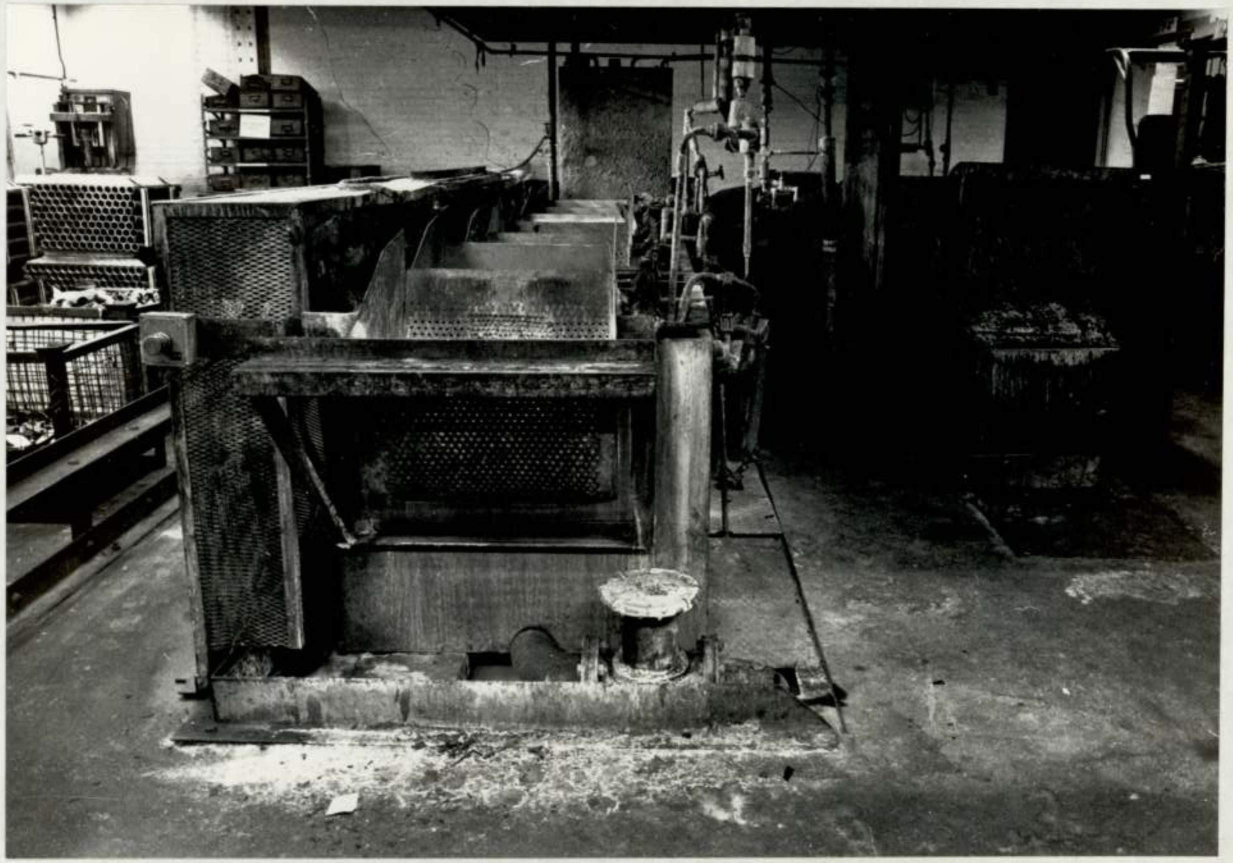


Figure 6.1 The automatic phosphating plant

Figure 6.2 The manual phosphating plant

to comment adversely on the plants.

6.2 Type of plant required

A heavyweight phosphate coating is normally applied by an immersion process, which limits the type of plant that can be used to

(i) A tipping basket plant

The type already in use.

(ii) An overhead track plant

The products are suspended on jigs, which are attached to a continuous overhead track. The track runs over the tanks containing the processing solutions, falling at the appropriate point to immerse the jigs in each tank of solution, and rising at the appropriate point to lift the jigs clear of the tank and carry them on to the next tank. The time products are immersed in a solution is determined by the speed of the overhead conveyor multiplied by the length of the tank containing the solution.

(iii) A transporter plant

The products are suspended on jigs or loaded into rotatable barrels, which are attached to a work carrier. A transporter, running on rails over the processing tanks, picks up the work carrier and takes it to the required tank of solution. The work carrier is deposited into holding lugs on the tank, immersing the jigs or barrel, and the transporter moves off to service other work carriers. After the appropriate immersion time the transporter returns and takes the work carrier on to the next required tank.

Experience with the tipping basket type of plant has already shown the tipping action causes problems (6 and 6.1.1). The disadvantage of an overhead track type of plant is the labour cost of having to load products on to and off jigs. Therefore the overhead transporter type of plant was chosen, as it offered the low labour costs of a barrelling operation for the majority of products, combined with the ability to deal with large awkward parts by a jigging process.

6.3 Processes required

As the new plant would be replacing both the manual and automatic plants it would have to be capable of the processes already in existence on both plants. The manual phosphating plant contains the basic phosphating process common to both plants plus the rubber chlorination process and the staining and oiling facilities. Therefore the layout of the manual phosphating plant was examined as a possible basis for the layout of the new plant. Figure 6.3 shows that the manual phosphating plant consists of 13 stages which can be considered as serving the following six functions.

6.3.1 Cleaning and rinsing

Although the Vaqua D machine had been installed to prepare the metal surfaces for phosphating (see Chapter Four) it was not linked directly to the phosphating plant, as not every product processed through it was phosphated. Therefore the products for phosphating that are processed through the Vaqua D machine are at risk of becoming contaminated with handling soils during their transit in tote tins from the Vaqua D machine to the phosphating plant. In addition products for phosphating in surface condition category 1

Stage No.	Description
1	Alkali cleaner
2	Cold rinse
3	Cold rinse
4	Chlorination
5	Cold rinse
6	Condioning rinse
7	Phosphate
8	Cold rinse
9	Cold rinse
10	Conditioning rinse
11	Warm air dry
12	Stain
13	Oil

Figure 6.3 The sequence of solutions in the manual phosphating plant

(see 4.3) are not cleaned on the Vaqua D machine and therefore do not receive any surface preparation prior to arrival at the phosphating plant.

Therefore a cleaning stage would be required on the new plant which would be accompanied by a double stage rinse, as on the existing plants, to prevent alkali cleaning chemicals being "dragged over" into the subsequent solutions.

6.3.2 Chlorination and rinsing

Chlorination is carried out on products on which the rubber sections have to be painted. Chlorination is carried out by immersing the product in a dilute solution of chlorine in water, and is usually (60) followed by a water rinse to remove any excess chlorine. The chlorination process was originally built into the manual phosphating plant because the majority of products that were chlorinated were also phosphated. The manufacturing records of the products that required chlorination were checked and it was found that the majority were still subsequently phosphated. Therefore a chlorination and rinse stage would be required on the new phosphating plant.

Work within Metalastik has shown that chlorination of a phosphated product, adversely affects the phosphate coating, therefore the chlorinating stage would have to be prior to the phosphating stage. As on the existing manual plant the rinse included in the chlorinating process would not be used for any other work to minimise the possibility of carrying over chlorine into any subsequent solutions.

6.3.3 Conditioning rinse

This rinse was originally built into the manual phosphating plant to promote a fine dense phosphate coating (see 2.1.7.2). It is generally not used by the plant operators in order to increase the output they achieve , and finish their work quota quickly. However, it was decided to keep a conditioning rinse in the design of the new phosphating plant and ensure that the operators could not prevent products being immersed in it.

6.3.4 Post phosphating rinses

Metalastik supplies products with a phosphate finish to the Ministry of Defence therefore the phosphating process has to meet the relevant MOD standard DEF 03-11. This requires that an accelerated phosphating solution is followed by 3 rinsing stages, one cold running water, one warm running water and one hot static water containing chromic acid (see 2.1.8.1).

Therefore the new phosphating plant would require 3 post phosphating rinses, of the type described, in order to meet this standard. Metalastik did not normally use chromic acid in the final rinse because of the health and safety problems (see 2.1.8.1) associated with using chromic acid. However during the course of this project Pyrene Chemical Services Ltd marketed an additive for the final rinse, based on chromic acid, called Parcolene 86, which they claim is formulated to avoid the problems normally associated with using chromic acid. Therefore it is recommended that this formulation should be assessed for use with the new phosphating plant.

6.3.5 Drying

The drying stage on the manual plant is simply a warm air blower designed to assist drying off rinse water on the products. The new phosphating plant would require a similar stage, however, in the light of the improvement in corrosion resistance that it is suggested (see 2.1.8.3)occurs when a chromic acid conditioned phosphate coating is heated to 100°C, it was decided to ensure the drying stage was capable of achieving temperatures of that order.

6.3.6 Oil and stain

Although the oiling and staining stages are shown at the end of the existing manual phosphating plant, the two operations are not carried out as part of the phosphating process.

The options for the new phosphating plant were either to have separate oiling and staining facilities or to build them into the new plant so that the operations would be carried out as part of the phosphating process. To avoid the labour costs involved in carrying out the staining and oiling operations separately it was decided to include the operations into the sequence of the new plant.

6.3.7 Process routes required

The processes required would be:-

(i) clean, rinse, phosphate, rinse, dry and stain, oil or no finish.

(ii) clean, rinse, chlorinate and rinse, phosphate, rinse, dry and stain, oil or no finish.

(iii) clean, rinse, chlorinate and rinse, dry.

6.4 Phosphating capacity required

Production engineering carried out the following analysis:

Volume of work phosphated January 1978 to September 1978

Manual Plant

Number of baskets phosphated = 7,782

Number of baskets per week = 222

Taking 68lbs as the average weight per basket the workload produced per week = 6.74 tons

Automatic Plant

Number of baskets phosphated = 10,970

Number of baskets per week = 314

Taking 68lbs as the average weight per basket the workload produced per week = 9.53 tons

The capacity required would be 16.27 tons per week provided the product mix and sales volume remained constant. Marketing had already indicated that the latter would be the case, provided Metalastik retained its position with respect to its competitors (see 1.4.2.1).

6.5 Companies asked to tender

The three companies asked to submit proposals for a new phosphating plant that met the requirements detailed here, were Process Plant and Chemicals Ltd., M and T Chemicals Ltd., and Cannings Engineering Ltd. Both M and T Chemicals and Process Plant and Chemicals offered an automatic or manual transporter plant.

Cannings Engineering did not submit any proposals despite being contacted several times.

6.6 Assessment of proposed plants

The quality criteria ranking technique was used to compare the proposed plants. The following list of the desirable features for a new phosphating plant was drawn up. In this comparison attention was paid to the defects of the present plants (6.1.1) that had not already been overcome by choosing a transporter type plant.

Letter	Description
A	Minimum possibility of operator interference.
B	Good control over solution temperatures.
C	Automatic control over solution strengths.
D	Automatic control of rinse cleanliness.
E	Ease of day to day maintenance.
F	Adaptability w.r.t. capacity changes.
G	Adaptability w.r.t. process changes.
H	Compactness.
I	Ease of handling.
J	Resistance to corrosion.
K	Emergency procedures.
L	Correct operation of oil and stain stages.
M	Safe in operation.

These were then ranked against each other, as shown in the matrix presented as Table 6.1. Each of the criteria along the top row of the matrix was compared with each criteria down the first

TABLE 6.1 QUALITY CRITERIA RANKING

	A	B	C	D	E	F	G	H	I	J	K	L	M
A	2	1	1	1	1	1	1	1	1	1	1	1	2
B	3	2	2	2	2	1	1	1	1	1	2	1	2
C	3	2	2	2	2	1	1	1	1	2	1	2	2
D	3	2	2	2	2	1	1	1	1	2	1	2	2
E	3	2	2	2	2	1	1	1	2	3	1	2	2
F	3	3	3	3	3	2	3	3	3	3	3	3	3
G	3	3	3	3	3	1	2	3	3	3	3	3	3
H	3	3	3	3	3	1	1	2	2	3	3	3	2
I	3	3	3	3	2	1	1	2	2	3	2	2	2
J	3	3	2	2	1	1	1	1	1	2	2	2	2
K	3	2	3	3	3	1	1	1	2	2	2	2	2
L	3	3	2	2	2	1	1	1	2	2	2	2	2
M	2	2	2	2	2	1	1	2	2	2	2	2	2
Totals													
	37	31	30	30	28	14	16	20	23	29	25	27	28

Key 1 of less importance

2 of equal importance

3 of greater importance

left hand column of the matrix, and rated 1 if it was less important, 2 if it was of equal importance and 3 if it was more important. The totals for each criteria, shown at the bottom of the matrix, give the following order of importance.

Ranking	Description
1	Minimum possibility of operator interference.
2	Good control over solution temperatures.
3	Automatic control over solution strengths.
3	Automatic control of rinse cleanliness.
4	Resistance to corrosion.
5	Ease of day to day maintenance.
5	Safe in operation.
6	Correct operation of stain and oil stages.
7	Emergency procedures.
8	Ease of handling.
9	Compactness.
10	Adaptability w.r.t. capacity changes.
11	Adaptability w.r.t. process changes.

The ranking indicates that ensuring the products received the optimum processing was generally ranked higher than the ease with which the plant could be operated. Each of the plants offered was compared against these criteria in order of their importance. Under a criteria each proposal is awarded one point if it meets the criteria or no points if it does not. The results in Table 6.2 show that the automatic transporter plant proposed by Process Plant and Chemicals achieved the highest rating of 10 points. No weighting of the criteria was required as its nearest rival achieved a

TABLE 6.2 QUALITY MATRIX

Plant	Quality criteria	A	B	C	D	J	E	M	L	K	I	H	G	F	TOTAL
Process Plant and Chemicals	Manual		1			1	1		1				1		5
	Automatic	1	1			1	1	1	1	1	1	1	1		10
M and T Chemicals	Manual		1			1	1		1						4
	Automatic	1	1			1	1		1				1		6

significantly lower rating of 6 points, with the major differences being in the lower ranked criteria.

6.7 Further work with the highest ranked plant

Having identified the automatic transporter plant proposed by Process Plant and Chemicals to be the most suitable, further discussions were held with that company to improve features F, C and D of the plant. At this stage a report recommending the plant for purchase was distributed within Metalastik, but no response to the report was received. The project lay dormant for several months because the capital to purchase the plant was not available. Then interest in the plant was renewed and several more meetings were held with Process Plant and Chemicals to refine further the plant's specification. A further report was drawn up recommending the plant for purchase.

In this report, attached as appendix 5, the cost of the three alternative ways of continuing to phosphate products were presented.

	Running costs per year	
	1980	1981
(i) Existing costs of phosphating	£49,500 (4.7 p/lb)	£56,925
(ii) Cost of phosphating using new plant	£34,800 (3.32 p/lb)	£40,020
(iii) Cost of having the products phosphated by a subcontractor if for health and safety reasons the use of the existing plant was prohibited	£116,000	£133,400

These comparisons relate to a weekly phosphating requirement of 9 to 10 tons. This requirement is lower than the 16.25 tons estimated in section 6.4 due to production engineering carrying out a revision of the work on the capacity required. A brief description of the plant was included in the report, which is used as the basis for the following description.

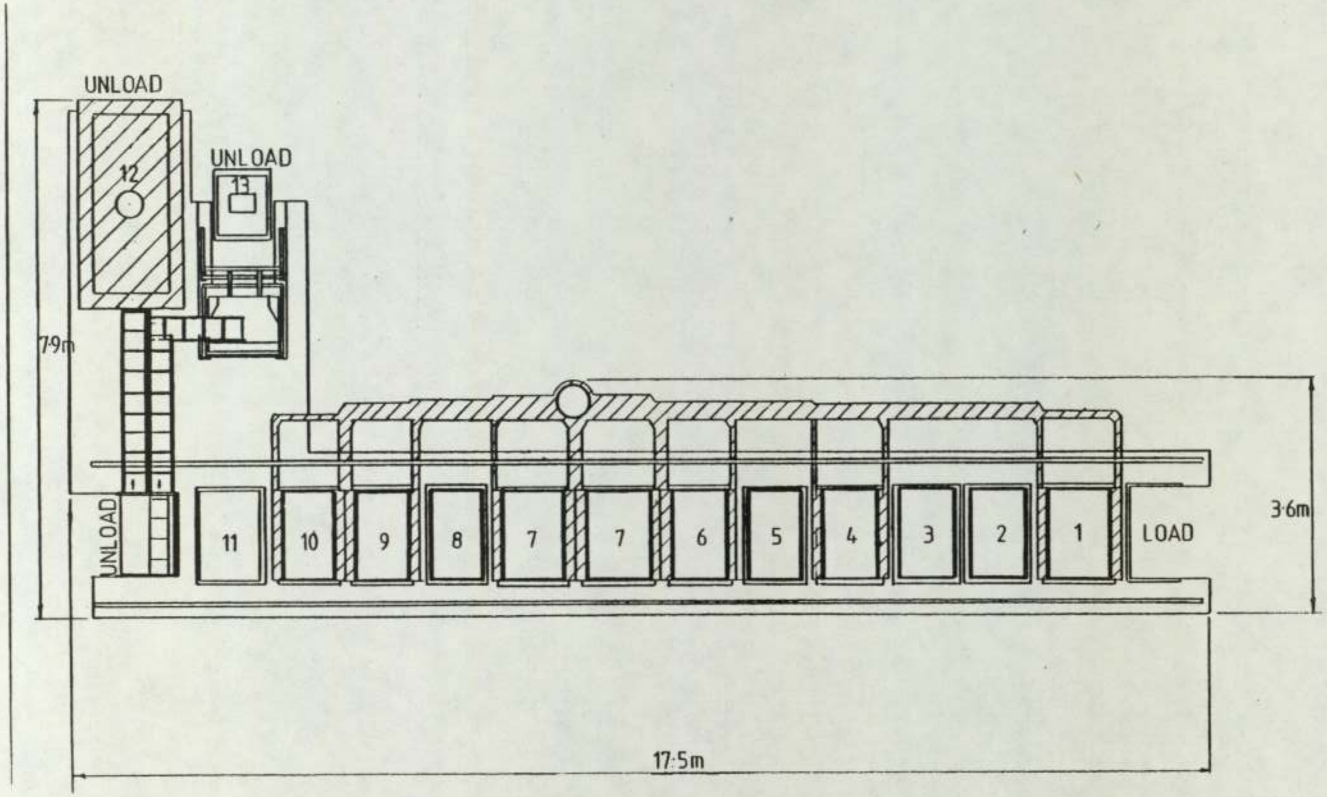
The proposed new plant consists of 14 inline process tank stations and would be approximately 19.5 metres in length, 3.6 metres wide and 2.97 metres high. An oiling station and staining station would be situated at right angles at the end of the plant. The products would be manually loaded and unloaded from the plant, but the complete phosphating process would be carried out automatically(63).

Movement between stations would be by means of a single bridge gantry transporter travelling on rails over the top of the tanks. It would be capable of carrying either a self powered rotating barrel with two compartments, or jigs for large products; very small products would be processed in a miniature barrel placed in one of the main barrels. At full production the plant would be capable of 7 1/4 loads per hour at approximately 120 lbs per load.

The replenishment chemicals for the phosphating solution would be added automatically using a metering pump, and a record would be produced of the concentration of chemicals in the phosphating solution using a conductivity probe (64). The automatic addition of chemicals to the plant would ensure that the nitrite content was maintained at its optimum level (see 2.1.5.1) and that large fluctuations in the concentration of the other chemicals in the solution would be avoided (see 5.8.2.2.).

The conductivity probe could be connected to the metering pumps to ensure they would only deliver chemicals to the solution when the concentration of chemicals dropped below a set level. The rinse water would be kept below a set level of contamination by the use of conductivity probes to control the fresh water inlet. The level of automation of the plant would allow it to be surrounded by interlocked guarding to keep the operators a reasonable distance from the solutions and moving machinery. Figure 6.4 shows an overall plan of the proposed layout of the plant.

The report was accepted and senior management within Metalastik have applied for permission to purchase the plant. However because the total capital expenditure involved is in excess of £100,000 the purchase requires the approval of the Dunlop Group. At the time of writing this chapter permission to purchase the plant was still being actively sought.



Key

Stage No.	Description
1	Alkali cleaner
2	Cold rinse
3	Cold rinse
4	Chlorination
5	Cold rinse
6	Condioning rinse
7	Phosphate
8	Cold rinse
9	Cold rinse
10	Conditioning rinse
11	Warm air dry
12	Stain
13	Oil

Figure 6.4 Layout of the proposed phosphating plant

CHAPTER 7

DISCUSSION

7.1 Attitude within Metalastik towards anti-corrosion finishing

For some years prior to this project Metalastik had been processing poorly prepared metal surfaces through an unsuitable phosphating solution. This caused the production of poor quality phosphate coatings which resulted in certain of the finishes based on a phosphate coating being of inadequate corrosion resistance. It is suggested that the reasons for these problems being tolerated for some years can be explained by referring to the following two behavioural assumptions that McCrae (65) makes about an organisation.

> "(i) Organisations are coalitions of individual participants. Strictly speaking the organisation itself which is 'mindless' cannot have goals - only individuals have goals.
>
> (ii) Those objectives which are usually viewed as organisational goals are in fact the objectives of the dominant members of the coalition, subject to whatever constraints are imposed by the other participants and by the external environment of the organisation."

The coalition responsible for the running of Metalastik's production facilities consists of the managers of the following departments, Quality Assurance, Quality Control, Production Engineering, Works Engineering, Production Management, Production Control, Technical and the Works Manager. Within this coalition the dominant members are the Works Manager and the Production Managers whose primary short term aim is to meet production targets rather than standards of quality. As a result, problems with abnormally large and unpredictable reject rates at the moulding stage of production causing shortages of products ready for despatch to the customer tended to cause any problems with anti-corrosion finishing that would cause further shortages due to products being rejected by internal Quality Control to be ignored.

It is suggested that this attitude of ranking the problems with anti-corrosion finishing below the problems with moulding and the need to despatch the products was further reinforced by the following:-

Firstly, Metalastik considers its expertise is in producing the optimum design of product for each particular use, and then manufacturing the best rubber formulation for that product. Anti-corrosion finishing is considered to be the last and least important stage in the design and manufacture of the products.

Secondly, the large number of specifications imposed by the 4 major automotive customers causes difficulty in assessing whether anti-corrosion finishing is acceptable overall. To ensure Metalastik finishes meet all the quality assurance requirements of these specifications would require a wide range of specialised testing equipment, a range that it is suggested would be more compatible with the facilities of a paint manufacturer's laboratory. The large number of specifications is due to each automotive customer writing their own set of specifications. The reasons for a large company producing its own specifications have been documented elsewhere (66). However, it is suggested that many of the specifications produced by the automotive companies are only slight variations of National Standards. This wasteful and confusing duplication could be avoided if as R.Sagesser (67) suggests the large companies used the National Standards rather than altering them and in addition co-operated through such a body as the Society of Motor Manufacturers and Traders to draw up a common set of specifications. At first this seems unlikely in the increasingly competitive business of selling vehicles. However, as most major components of a particular type such as these products, are bought in by automotive companies from a relatively small number of suppliers it is suggested that as at Metalastik, the same finish is being applied to meet a variety of specifications, which negates the value of slight differences between the specifications.

An attempt has already been made by the British Rubber Manufacturers Association (68) to produce a common set of anti-corrosion finishing specifications to which the rubber-to-metal bonded products manufacturers will supply products. However, it is more difficult for relatively small suppliers to impose radical changes on large customers, and this is reflected by the fact that these specifications are little used.

7.1.1 Change in the external environment

Considering the external environment McCrae refers to, it is suggested that this was changing for Metalastik. Firstly, there was the possibility that the European Economic Community would introduce Product Liability Regulation. Although the following is an over-simplification, basically such legislation would shift the emphasis from a person injured as a result of an accident with a product, having to prove the manufacturer guilty of some form of negligence in the design or manufacture of the product, to the manufacturer having to prove they were innocent of such negligence (69).

Secondly, the automotive manufacturers have become increasingly aware of the anti-corrosion performance of their vehicles. This awareness has been accelerated by the fact that several countries have been considering whether to introduce legislation regarding the in service life that should be expected from a vehicle (70). The lead was set by Canada who issued an Anti-Corrosion Code for Motor Vehicles, (appendix 6). It is not legally enforceable but the federal government have indicated that enforcement will be considered if it is not met. The code required for the 1978 model year:-

(a) no surface corrosion for one year or 40,000 km.

(b) no perforation corrosion for 3 years or 120,000 km.

(c) no structural corrosion for 6 years or 240,000 km.

and by the 1981 model year:-

(a) no surface corrosion for 1½ years or 60,000 km.

(b) no perforation corrosion for 5 years or 200,000 km.

(c) as before.

However the vehicle owner has to follow the vehicle maintenance guide included in the code in order to benefit from the legislation.

These two changes impinged directly on Metalastik because in 1977 it was already supplying some products to the automotive customers with anti-corrosion finishes which did not meet the requirements of these customers specifications. Therefore should any claim arise due to poor corrosion performance causing premature failure, Metalastik would be in a poor position to defend itself. It is suggested that these factors combined with the reasons given in section (1.4.2), for Metalastik proposing this project to cause the company to take a more serious approach to anti-corrosion finishing. This change in approach combined with the positive results of cost benefit analyses for changes to the phosphating process to ease their introduction.

7.2 Aim of the Project

As has been reported for other projects of this type (2) the sponsor misinterpreted its problem. In this case the misinterpretation took two forms. Firstly, the project's original aim was to identify a range of finishes for the products that would meet the customers specifications. However,as the work has shown what was required was not new finishes but improvements to the existing finishes in order to meet the specifications. Secondly, at an early stage in the work it was believed within Metalastik that the problems with phosphating were due to the poor condition of the manual phosphating plant and could be solved by purchasing a new phosphating plant. Whereas the work has shown that there were three key areas of work involved in improving the anti-corrosion finishes applied to Metalastik products, and solving the problems associated with phosphating. These are discussed in the following three sections.

7.2.1 Cleaning of the products prior to phosphating

The cleaning that products received prior to phosphating required improving, because no allowance had been made for the effects of the metal manipulation operations and the presence of adhesive residues on the surfaces to be phosphated. The importance of a clean substrate for all anti-corrosion finishing processes has been reported elsewhere (71).

After Metalastik had purchased and installed (see Chapter 4) a machine from Abrasive Departments to improve the cleaning products received prior to phosphating, it was learnt that two major competitors, Avon Industrial Polymers Division and Perradin Ltd were considering purchasing identical machines for the same purpose. Therefore it is suggested that the problems of preparing the metal surfaces of rubber-to-metal bonded products for phosphating were not peculiar to Metalastik.

7.2.2 Phosphating solution used

Although the phosphating chemical suppliers, Pyrene, were aware that rubber-to-metal bonded products had a reputation for being difficult to phosphate, they were not attempting to solve the problem. It was not until work at Metalastik identified that the Parco 95 phosphating solution was producing defective phosphate coatings that Pyrene offered an alternative phosphating solution. Although at that stage several other phosphating chemical suppliers were contacted, none had carried out detailed research into solving the problems of phosphating rubber-to-metal bonded products. Therefore it was decided to subject the Bonderite 181X phosphating solution to trials.

At approximately the same time as Metalastik were commencing works trials with Bonderite 181X, Pyrene suggested to Avon Industrial Polymers Division, who were also using Parco 95 and experiencing problems with the phosphating process, that a change to Bonderite 181X might prove beneficial.

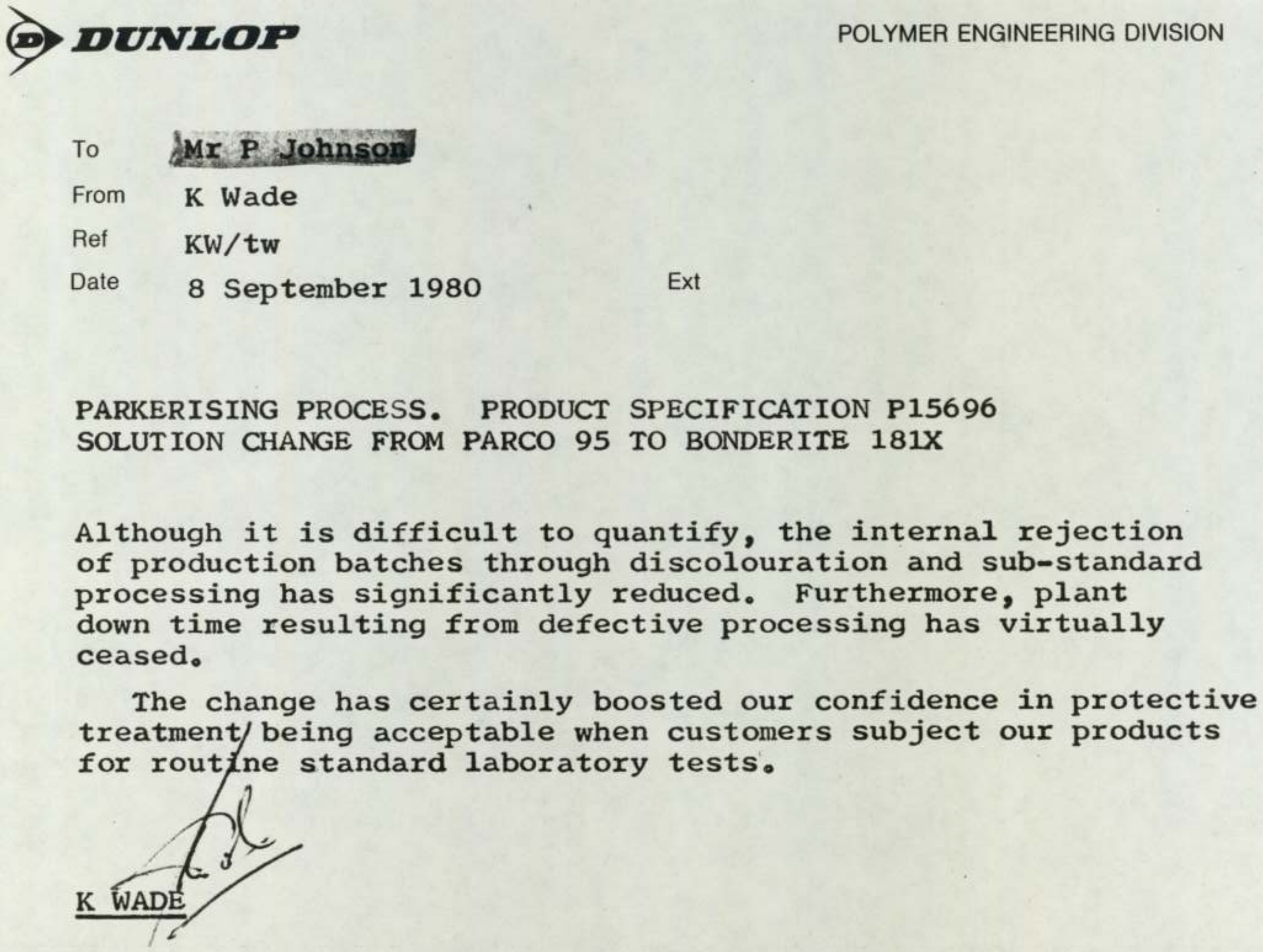
At Metalastik the change to Bonderite 181X substantially reduced problems with the phosphating process and improved the corrosion resistance of the phosphate and oil and phosphate and stain finishes produced under shopfloor conditions. It is believed that Avon changed to Bonderite 181X at approximately the same time, and achieved similar improvements with the phosphating process. At the start of this section of work Process Plant and Chemicals Ltd who phosphate rubber-to-metal bonded products on a sub contract basis, claimed that they had solved the problems associated with the phosphating of these products by using an I.C.I. phosphating solution. However, after noting the success of the Bonderite 181X solution at Metalastik, in 1980 they also changed to using Bonderite 181X.

7.2.3 New phosphating plant

When the changeover to Bonderite 181X and the improvement in the cleaning of products were completed on the shopfloor, the Quality Control Manager was asked to comment on the results. In a memo presented as figure 7.1, he indicated that there had been a significant reduction in the problems experienced with the phosphating process, and that there was increased confidence in the ability of products to meet customers anti-corrosion finishing requirements. This shows that a new phosphating plant was not required to solve the problems with phosphating. However, it is recommended that to ensure that a good quality phosphate coating is consistently produced the new phosphating plant described in Chapter 6 should be purchased to overcome the problems associated with the design and age of the present plants.

7.3 Result of the changes

As a result of this project the situation at Metalastik has improved to the stage where the salt spray resistance claimed for the phosphate and oil finish meets all but one of the salt spray requirements listed against it in Table 1.2. Similarly, the salt



DUNLOP
POLYMER ENGINEERING DIVISION

To Mr P Johnson
From K Wade
Ref KW/tw
Date 8 September 1980 Ext

PARKERISING PROCESS. PRODUCT SPECIFICATION P15696
SOLUTION CHANGE FROM PARCO 95 TO BONDERITE 181X

Although it is difficult to quantify, the internal rejection of production batches through discolouration and sub-standard processing has significantly reduced. Furthermore, plant down time resulting from defective processing has virtually ceased.

The change has certainly boosted our confidence in protective treatment being acceptable when customers subject our products for routine standard laboratory tests.

K WADE

Figure 7.1 Memorandum from the manager of the quality control department spray resistance claimed for the phosphate and stain finish meets all but one of the salt spray requirements listed against it in Table 1.2. The requirement that the two finishes are not able to meet is the 72 hours required by Talbot. When applied to test panels both the finishes did exceed 72 hours resistance to the salt spray test but this level of resistance was not claimed for the finishes for the reasons stated in section 5.8.4. When Talbot were invited to discuss their specifications they indicated that none of their suppliers could meet these particular specifications. It is suggested that this indicates that Talbot have set the level of resistance required unrealistically high for the finishes on actual products. Therefore it is suggested that the phosphate and oil and phosphate and stain finishes have been improved sufficiently to meet all the realistic requirements in Table 1.2. Hence Metalastik products meet all but one specification that it supplies products to. That specification is the Vauxhall specification that requires 144 hours resistance for a paint finish (see 1.4.2). However, as the results in section 5.8.1.3 and 5.8.3.1 show, the phosphate and a heavy coat of paint finish exceeded 144 hours resistance to the salt spray test on several occasions. As stated in that section further testing of this finish would be required before sufficient confidence was felt to increase the claimed salt spray resistance. In particular, the effect of varying the thickness of the paint film on the salt spray resistance of the finish would require investigation as the thickness of paint applied is under operator control, with no subsequent Quality Control check.

7.4 Future options for improving the resistance to the salt spray test of the phosphate and stain finish

The phosphate and oil finish now substantially exceeds the highest salt spray resistance imposed on it. Therefore it is the phosphate and stain finish which is most likely to require improving if, in the future, the automotive customers increase their salt spray resistance requirements. There would be 3 possible ways of achieving an improvement:-

(i) treating the phosphate coating with a process such as Endurion (see 2.1.8.2) before applying the black stain. However, this process is expensive and difficult to operate.

(ii) dipping the phosphated product in black stain, allowing it to dry and then dipping the product in an oil finish that would increase the salt spray resistance, without redissolving the stain coating.

(iii) buying in the process that Oxy Metal Industries Corporation of Detroit are developing to meet the General Motors specification G.M.6174-M (see appendix 7). This specification has increased the salt spray resistance requirement for a phosphate and stain finish on fasteners from 72 hours to 240 hours. To meet this requirement a finish consisting of heavyweight phosphate, coloured organic finish and oil is being developed.

7.5 Relationship between this work and corrosion prevention and control in general

Ideally (72) the prevention and control of corrosion begins at the design stage of a product. In this work an improvement in the corrosion resistance of existing products was required. This improvement was achieved by the application of existing knowledge and techniques in new ways. It is suggested that this work confirms the statement in the 1971 Report of the Committee on Corrosion that estimated £310m of the £1365m (1971 costs) lost annually through corrosion could be saved by the application of the existing knowledge and techniques of corrosion control and prevention (73).

CHAPTER 8

CONCLUSIONS, RECOMMENDATIONS AND FURTHER WORK

8.1 Conclusions

1. The cleaning methods used to prepare the metal surfaces of rubber-to-metal bonded products for phosphating, must counteract the unique combination of soils on the metal surfaces, that result from the method of manufacture.

2. The solution used for phosphating rubber-to-metal bonded products must deposit a phosphate coating by chemical reactions that are not subject to interference by any contaminants leached from the rubber sections of the products.

3. At the sponsors factory, improving the cleaning methods used to prepare the metal surfaces for phosphating, combined with changing the phosphating solution for one compatible with rubber-to-metal bonded products produced a large improvement in the quality of the phosphate coating. The improvement resulted in some of the anti-corrosion finishes being capable of meeting the customers salt spray resistance requirements that they had previously failed to meet.

4. This work shows that the salt spray test is a useful tool for detecting large changes in the quality of the phosphate coating used as part of a phosphate and stain finish.

8.2 Recommendations

1. In order to produce a consistently good phosphate coating (which will form the base of five of Metalastik's eight standard finishes) the phosphating plant described in Chapter 6 should be

purchased. The high level of automation of this plant should ensure that abuse of the phosphating process is prevented, and also improve the safety of the working conditions for the operators.

2. Metalastik should initiate a system to check regularly the performance of the anti-corrosion finishes applied to the products.

3. Metalastik should send its full range of finishes to an independent laboratory to be subjected to the full range of tests that the automotive customers require. From these results it could be judged whether further improvements are required to the existing finishes.

8.3 Further Work

1. The effect on the protective value of the Bonderite 181X phosphate coating of the use of an oxalic acid based conditioning rinse prior to phosphating (see 2.1.7.2) and a chromic acid based conditioning rinse after phosphating (see 2.1.8.1) should be investigated. This work has not been carried out here for the reasons stated in section (3.4). However, the work needs to be carried out prior to the installation of the new phosphating plant to ascertain whether the plant should be programmed to process all or only certain products through these two conditioners.

2. The atmospheric corrosion test (see 5.8.6) could be continued to assess fully the improvement resulting from the change to the Bonderite 181X phosphating solution, and also to rank the finishes based on a works phosphate coating in order of their resistance to atmospheric corrosion conditions. This work could usefully be extended to ranking the finishes by in service testing.

This could be restricted to automotive service conditions, as the largest proportion of products go for that use, and it represents the worst corrosion conditions that the standard finishes will be exposed to.

3. From the firm base of using anti-corrosion finishes capable of meeting the customers salt spray resistance requirements Metalastik could try to anticipate the future finishes that will be required by surveying its customers.

4. The mechanism by which organic materials interfere with the deposition of a phosphate coating could be investigated. Such an investigation might give further information on the processes occurring at the metal/solution interface, during phosphating.

APPENDIX 1

A reprint of the standard ASTM B117-73 Salt Spray (Fog) Testing.

AMERICAN NATIONAL STANDARD
ANSI/ASTM B 117 - 73
(Reapproved 1979)

Endorsed by American Electroplaters' Society
Endorsed by National Association of Metal Finishers

Standard Method of
SALT SPRAY (FOG) TESTING[1]

This Standard is issued under the fixed designation B 117; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval.

This method has been approved for use by agencies of the Department of Defense to replace Method 811.1 of Federal Test Method Standard No. 151b and for listing in DoD Index of Specifications and Standards.

1. Scope

1.1 This method sets forth the conditions required in salt spray (fog) testing for specification purposes. Suitable apparatus which may be used to obtain these conditions is described in Appendix A1. The method does *not* prescribe the type of test specimen or exposure periods to be used for a specific product, nor the interpretation to be given to the results. Comments on the use of the test in research will be found in Appendix A2.

NOTE 1—This method is applicable to salt spray (fog) testing of ferrous and non-ferrous metals, and is also used to test inorganic and organic coatings, etc., especially where such tests are the basis for material or product specifications.

2. Apparatus

2.1 The apparatus required for salt spray (fog) testing consists of a fog chamber, a salt solution reservoir, a supply of suitably conditioned compressed air, one or more atomizing nozzles, specimen supports, provision for heating the chamber, and necessary means of control. The size and detailed construction of the apparatus are optional, provided the conditions obtained meet the requirements of this method.

2.2 Drops of solution which accumulate on the ceiling or cover of the chamber shall not be permitted to fall on the specimens being tested.

2.3 Drops of solution which fall from the specimens shall not be returned to the solution reservoir for respraying.

2.4 Material of construction shall be such that it will not affect the corrosiveness of the fog.

3. Test Specimens

3.1 The type and number of test specimens to be used, as well as the criteria for the evaluation of the test results, shall be defined in the specifications covering the material or product being tested or shall be mutually agreed upon by the purchaser and the seller.

4. Preparation of Test Specimens

4.1 Metallic and metallic-coated specimens shall be suitably cleaned. The cleaning method shall be optional depending on the nature of the surface and the contaminants, except that it shall not include the use of abrasives other than a paste of pure magnesium oxide nor of solvents which are corrosive or will deposit either corrosive or protective films. The use of a nitric acid solution for the chemical cleaning, or passivation, of stainless steel specimens is permissible when agreed upon by the purchaser and the seller. Care shall be taken that specimens are not recontaminated after cleaning by excessive or careless handling.

4.2 Specimens for evaluation of paints and other organic coatings shall be prepared in accordance with applicable specification(s) for the material(s) being tested, or as agreed upon by the purchaser and supplier. Otherwise, the test specimens shall consist of steel meeting the requirements of ASTM Methods D 609 for Preparation of Steel Panels for Testing

---

[1] This method is under the jurisdiction of ASTM Committee G-1 on Corrosion of Metals, and is the direct responsibility of Subcommittee G01.05 on Laboratory Corrosion Tests.

Current edition approved March 29, 1973. Published June 1973. Originally published as B 117 – 39 T. Last previous edition B 117 – 64.

Paint, Varnish, Lacquer, and Related Products,[2] and shall be cleaned and prepared for coating in accordance with applicable procedure of Method D 609.

4.3 Specimens coated with paints or nonmetallic coatings shall not be cleaned or handled excessively prior to test.

4.4 Whenever it is desired to determine the development of corrosion from an abraded area in the paint or organic coating, a scratch or scribed line shall be made through the coating with a sharp instrument so as to expose the underlying metal before testing. The conditions of making the scratch shall be as defined in ASTM Method D 1654, Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments,[2] unless otherwise agreed upon between the purchaser and seller.

4.5 Unless otherwise specified, the cut edges of plated, coated, or duplex materials and areas containing identification marks or in contact with the racks or supports shall be protected with a suitable coating stable under the conditions of the test, such as ceresin wax.

NOTE 2—Should it be desirable to cut test specimens from parts or from preplated, painted, or otherwise coated steel sheet, the cut edges shall be protected by coating them with paint, wax, tape, or other effective media so that the development of a galvanic effect between such edges and the adjacent plated or otherwise coated metal surfaces, is prevented.

5. Position of Specimens During Test

5.1 The position of the specimens in the salt spray chamber during the test shall be such that the following conditions are met:

5.1.1 Unless otherwise specified, the specimens shall be supported or suspended between 15 and 30 deg from the vertical and preferably parallel to the principal direction of horizontal flow of fog through the chamber, based upon the dominant surface being tested.

5.1.2 The specimens shall not contact each other or any metallic material or any material capable of acting as a wick.

5.1.3 Each specimen shall be so placed as to permit free settling of fog on all specimens.

5.1.4 Salt solution from one specimen shall not drip on any other specimen.

NOTE 3 Suitable materials for the construction or coating of racks and supports are glass, rubber, plastic, or suitably coated wood. Bare metal shall not be used. Specimens shall preferably be supported from the bottom or the side. Slotted wooden strips are suitable for the support of flat panels. Suspension from glass hooks or waxed string may be used as long as the specified position of the specimens is obtained, if necessary by means of secondary support at the bottom of the specimens.

6. Salt Solution

6.1 The salt solution shall be prepared by dissolving 5 ± 1 parts by weight of sodium chloride in 95 parts of distilled water or water containing not more than 200 ppm of total solids. The salt used shall be sodium chloride substantially free of nickel and copper and containing on the dry basis not more than 0.1 percent of sodium iodide and not more than 0.3 percent of total impurities. Some salts contain additives that may act as corrosion inhibitors; careful attention should be given to the chemical content of the salt. By agreement between purchaser and seller, analysis may be required and limits established for elements or compounds not specified in the chemical composition given above.

6.2 The pH of the salt solution shall be such that when atomized at 35 C (95 F) the collected solution will be in the pH range of 6.5 to 7.2 (Note 4). Before the solution is atomized it shall be free of suspended solids (Note 5). The pH measurement shall be made electrometrically at 25 C (77 F) using a glass electrode with a saturated potassium chloride bridge in accordance with Method E 70, Test for pH of Aqueous Solutions with the Glass Electrode[3]; or colorimetrically using bromothymol blue as indicator, or short range pH paper which reads in 0.2 or 0.3 of a pH unit (Note 6).

NOTE 4—Temperature affects the pH of a salt solution prepared from water saturated with carbon dioxide at room temperature and pH adjustment may be made by the following three methods:

(*1*) When the pH of a salt solution is adjusted at room temperature, and atomized at 35 C (95 F), the pH of the collected solution will be higher than the original solution due to the loss of carbon dioxide at the higher temperature. When the pH of the salt solution is adjusted at room temperature, it is therefore necessary to adjust it below 6.5 so the collected solution after atomizing at 35 C (95 F) will meet the pH limits of 6.5 to 7.2. Take about a 50-ml sample of the salt solution as prepared at room temperature, boil gently for 30 s, cool, and determine the pH. When the pH of the salt solution is adjusted to 6.5 to 7.2 by this procedure, the pH of the atomized and collected solution at 35 C (95 F) will come within this range.

---

[2] *Annual Book of ASTM Standards*, Part 27.

[3] *Annual Book of ASTM Standards*, Parts 22, 30, and 41.

(*2*) Heating the salt solution to boiling and cooling to 95 F or maintaining it at 95 F for approximately 48 h before adjusting the pH produces a solution the pH of which does not materially change when atomized at 35 C (95 F).

(*3*) Heating the water from which the salt solution is prepared to 35 C (95 F) or above, to expel carbon dioxide, and adjusting the pH of the salt solution within the limits of 6.5 to 7.2 produces a solution the pH of which does not materially change when atomized at 35 C (95 F).

NOTE 5—The freshly prepared salt solution may be filtered or decanted before it is placed in the reservoir, or the end of the tube leading from the solution to the atomizer may be covered with a double layer of cheesecloth to prevent plugging of the nozzle.

NOTE 6—The pH can be adjusted by additions of dilute cp hydrochloric acid or cp sodium hydroxide solutions.

7. Air Supply

7.1 The compressed air supply to the nozzle or nozzles for atomizing the salt solution shall be free of oil and dirt (Note 7) and maintained between 69 and 172 kN/m^2 (10 and 25 psi) (Note 8).

NOTE 7—The air supply may be freed from oil and dirt by passing it through a water scrubber or at least 610 mm (2 ft) of suitable cleaning material such as asbestos, sheep's wool, excelsior, slag wool, or activated[4] alumina.

NOTE 8—Atomizing nozzles may have a "critical pressure" at which an abnormal increase in the corrosiveness of the salt fog occurs. If the "critical pressure" of a nozzle has not been established with certainty, control of fluctuation in the air pressure within plus or minus 0.7 kN/m^2 (0.1 psi), by installation of a suitable pressure regulator valve[5] minimizes the possibility that the nozzle will be operated at its "critical pressure."[6]

8. Conditions in the Salt Spray Chamber

8.1 *Temperature*—The exposure zone of the salt spray chamber shall be maintained at 35 + 1.1 - 1.7 C (95 + 2 - 3 F). The temperature within the exposure zone of the closed cabinet shall be recorded at least twice a day at least 7 h apart (except on Saturdays, Sundays, and holidays when the salt spray test is not interrupted for exposing, rearranging, or removing test specimens or to check and replenish the solution in the reservoir).

NOTE 9—A suitable method to record the temperature is by a continuous recording device or by a thermometer which can be read from outside the closed cabinet. The recorded temperature must be obtained with the salt spray chamber closed to avoid a false low reading because of wet-bulb effect when the chamber is open.

8.2 *Atomization and Quantity of Fog*—At least two clean fog collectors shall be so placed within the exposure zone that no drops of solution from the test specimens or any other source shall be collected. The collectors shall be placed in the proximity of the test specimens, one nearest to any nozzle and the other farthest from all nozzles. The fog shall be such that for each 80 cm^2 of horizontal collecting area there will be collected in each collector from 1.0 to 2.0 ml of solution per hour based on an average run of at least 16 h (Note 10). The sodium chloride concentration of the collected solution shall be 5 ± 1 weight percent (Note 11). The pH of the collected solution shall be 6.5 to 7.2. The pH measurement shall be made electrometrically or colorimetrically using bromothymol blue as the indicator.

NOTE 10—Suitable collecting devices are glass funnels with the stems inserted through stoppers into graduated cylinders, or crystallizing dishes. Funnels and dishes with a diameter of 10 cm have an area of about 80 cm^2.

NOTE 11—A solution having a specific gravity of 1.0255 to 1.0400 at 25 C (77 F) will meet the concentration requirement. The concentration may also be determined as follows: Dilute 5 ml of the collected solution to 100 ml with distilled water and mix thoroughly; pipet a 10-ml aliquot into an evaporating dish or casserole; add 40 ml of distilled water and 1 ml of 1 percent potassium chromate solution (chloride-free) and titrate with 0.1 *N* silver nitrate solution to the first appearance of a permanent red coloration. A solution that requires between 3.4 and 5.1 ml of 0.1 *N* silver nitrate solution will meet the concentration requirements.

8.3 The nozzle or nozzles shall be so directed or baffled that none of the spray can impinge directly on the test specimens.

9. Continuity of Test

9.1 Unless otherwise specified in the specifications covering the material or product being tested, the test shall be continuous for the duration of the entire test period. Continuous operation implies that the chamber be

---

[4] Registered U. S. Patent Office.

[5] The Nullmatic pressure regulator (or equivalent) manufactured by Moore Products Co., H and Lycoming Sts., Philadelphia, Pa. 19124, is suitable for this purpose.

[6] It has been observed that periodic fluctuations in air pressure of ±3.4 kN/m^2 (0.5 psi) resulted in about a twofold increase in the corrosivity of the fog from a nozzle which was being operated at an average pressure of 110 kN/m^2 (16 psi). Controlling the fluctuations within ±0.7 kN/m^2 (0.1 psi), however, avoided any increase in the corrosivity of the salt fog. See Darsey, V. M. and Cavanagh, W. R., "Apparatus and Factors in Salt Fog Testing," *Proceedings*, ASTEA, Am. Soc. Testing Mats., Vol. 48, 1948, p. 153.

closed and the spray operating continuously except for the short daily interruptions necessary to inspect, rearrange, or remove test specimens; to check and replenish the solution in the reservoir, and to make necessary recordings as described in Section 8. Operations shall be so scheduled that these interruptions are held to a minimum.

10. Period of Test

10.1 The period of test shall be as designated by the specifications covering the material or product being tested or as mutually agreed upon by the purchaser and the seller.

NOTE 12 Recommended exposure periods are to be as agreed upon by the purchaser and seller, but exposure periods of multiples of 24 h are suggested.

11. Cleaning of Tested Specimens

11.1 Unless otherwise specified in the specifications covering the material or product being tested, specimens shall be treated as follows at the end of the test:

11.1.1 The specimens shall be carefully removed.

11.1.2 Specimens may be gently washed or dipped in clean running water not warmer than 38 C (100 F) to remove salt deposits from their surface, and then immediately dried. Drying shall be accomplished with a stream of clean, compressed air.

12. Evaluation of Results

12.1 A careful and immediate examination shall be made for the extent of corrosion of the dry test specimens or for other failure as required by the specifications covering the material or product being tested or by agreement between the purchaser and the seller.

13. Records and Reports

13.1 The following information shall be recorded, unless otherwise prescribed in the specifications covering the material or product being tested:

13.1.1 Type of salt and water used in preparing the salt solution,

13.1.2 All readings of temperature within the exposure zone of the chamber,

13.1.3 Daily records of data obtained from each fog-collecting device including the following:

13.1.3.1 Volume of salt solution collected in milliliters per hour per 80 cm^2,

13.1.3.2 Concentration or specific gravity at 35 C (95 F) of solution collected, and

13.1.3.3 pH of collected solution.

13.4 Type of specimen and its dimensions, or number or description of part,

13.5 Method of cleaning specimens before and after testing,

13.6 Method of supporting or suspending article in the salt spray chamber,

13.7 Description of protection used as required in 4.5,

13.8 Exposure period,

13.9 Interruptions in test, cause and length of time, and

13.10 Results of all inspections.

NOTE 13—If any of the atomized salt solution which has not contacted the test specimens is returned to the reservoir, it is advisable to record the concentration or specific gravity of this solution also.

APPENDIXES

A1. CONSTRUCTION OF APPARATUS

A1.1 Cabinets

A1.1.1 Standard salt-spray cabinets are available from several suppliers, but certain pertinent accessories are required before they will function according to this method and provide consistent control for duplication of results.

A1.1.2 The salt spray cabinet consists of the basic chamber, an air-saturator tower, a salt solution reservoir, atomizing nozzles, specimen supports, provisions for heating the chamber, and suitable controls for maintaining the desired temperature.

A1.1.3 Accessories such as a suitable adjustable baffle or central fog tower, automatic level control for the salt reservoir, and automatic level control for the air-saturator tower are pertinent parts of the apparatus.

A1.1.4 The cabinet should be of sufficient size to test adequately the desired number of parts without overcrowding. Small cabinets have been found difficult to control and those of less than 0.43-m^3 (15-ft^3) capacity should be avoided.

A1.1.5 The chamber may be made of inert materials such as plastic, glass, or stone, but most preferably is constructed of metal and lined with impervious plastics, rubber, or epoxy-type materials or equivalent.

A1.2 Temperature Control

A1.2.1 The maintenance of temperature within the salt chamber can be accomplished by several methods. It is generally desirable to control the temperature of the surroundings of the salt spray chamber and to maintain it as stable as possible. This may be accomplished by placing the apparatus in a constant-temperature room, but may also be achieved by surrounding the basic chamber of a jacket containing water or air at a controlled temperature.

A1.2.2 The use of immersion heaters in an internal salt-solution reservoir or of heaters within the chamber is detrimental where heat losses are appreciable, because of solution evaporation and radiant heat on the specimens.

A1.2.3 All piping which contacts the salt solution or spray should be of inert materials such as plastic. Vent piping should be of sufficient size so that a minimum of back pressure exists and should be installed so that no solution is trapped. The exposed end of the vent pipe should be shielded from extreme air currents that may cause fluctuation of pressure or vacuum in the cabinet.

A1.3 Spray Nozzles

A1.3.1 Satisfactory nozzles may be made of hard rubber, plastic, or other inert materials. The most commonly used type is made of plastic. Nozzles calibrated for air consumption and solution atomized are available. The operating characteristics of a typical nozzle are given in Table A1.

A1.3.2 It can readily be seen that air consumption is relatively stable at the pressures normally used, but a marked reduction in solution sprayed occurs if the level of the solution is allowed to drop appreciably during the test. Thus, the level of the solution in the salt reservoir must be maintained automatically to ensure uniform fog delivery during the test.[7]

A1.3.3 If the nozzle selected does not atomize the salt solution into uniform droplets, it will be necessary to direct the spray at a baffle or wall to pick up the larger drops and prevent them from impinging on the test specimens. Pending a complete understanding of air-pressure effects, etc., it is important that the nozzle selected shall produce the desired condition when operated at the air pressure selected. Nozzles are not necessarily located at one end, but may be placed in the center and can also be directed vertically up through a suitable tower.

A1.4 Air for Atomization

A1.4.1 The air used for atomization must be free of grease, oil, and dirt before use by passing through well-maintained filters. Room air may be compressed, heated, humidified, and washed in a water-sealed rotary pump, if the temperature of the water is suitably controlled. Otherwise cleaned air may be introduced into the bottom of a tower filled with water, through a porous stone or multiple nozzles. The level of the water must be maintained automatically to ensure adequate humidification. A chamber operated according to this method and Appendix will have a relative humidity between 95 and 98 percent. Since salt solutions from 2 to 6 percent will give the same results (though for uniformity the limits are set at 4 to 6 percent), it is preferable to saturate the air at temperatures well above the chamber temperature as insurance of a wet fog. Table A2 shows the temperatures, at different pressures, that are required to offset the cooling effect of expansion to atmospheric pressure.

A1.4.2 Experience has shown that most uniform spray chamber atmospheres are obtained by increasing the atomizing air temperature sufficiently to offset heat losses, except those that can be replaced otherwise at very low-temperature gradients.

A1.5 Types of Construction

A1.5.1 A modern laboratory cabinet is shown in Fig. A1. Walk-in chambers are not usually constructed with a sloping ceiling due to their size and location. Suitably located and directed spray nozzles avoid ceiling accumulation and drip. Nozzles may be located at the ceiling, or 0.91 m (3 ft) from the floor directed upward at 30 to 60 deg over a passageway. The number of nozzles depends on type and capacity and is related to the area of the test space. A 11 to 19-dm^3 (3 to 5-gal) reservoir is required within the chamber, with the level controlled. The major features of a walk-in type cabinet, which differs significantly from the laboratory type, are illustrated in Fig. A2. Construction of a plastic nozzle, such as is furnished by several suppliers, is shown in Fig. A3.

A2. Use of the Salt Spray (Fog) Test in Research

A2.1 The detailed requirements of this method are primarily for quality acceptance and should not be construed as the optimum conditions for research studies. The test has been used to a considerable extent for the purpose of comparing different materials or finishes with an acceptable standard. The recent elimination of many cabinet variables and the improvement in controls have made the three ASTM Salt Spray Tests: Method B 117, Method B 287, Acetic Acid-Salt Spray (Fog) Testing,[8] and Method B 368, for Copper-Accelerated Acetic Acid-Salt Spray (Fog) Testing (CASS),[9] into useful tools for many industrial and military production

---

[7] A suitable device for maintaining the level of liquid in, either the saturator tower, or reservoir of test solution may be designed by a local engineering group, or may be purchased from manufacturers of test cabinets as an accessory.

[8] *Annual Book of ASTM Standards*, Parts 9, 10, and 27.

[9] *Annual Book of ASTM Standards*, Parts 9 and 27.

and qualification programs.

A2.2 The test has been used to a considerable extent for the purpose of comparing different materials or finishes. It should be noted that there is seldom a direct relation between salt spray (fog) resistance and resistance to corrosion in other media, because the chemistry of the reactions, including the formation of films and their protective value, frequently varies greatly with the precise conditions encountered. Informed personnel are aware of the erratic composition of basic alloys, the possibility of wide variations in quality and thickness of plated items produced on the same racks at the same time, and the consequent need for a mathematical determination of the number of specimens required to constitute an adequate sample for test purposes. In this connection it is well to point out that Method B 117 is not applicable to the study or testing of decorative chromium plate (nickel-chromium or copper-nickel-chromium) on steel or on zinc-base die castings or of cadmium plate on steel. For this purpose Methods B 287 and B 368 are available, which are also considered by some to be superior for comparison of chemically-treated aluminum (chromated, phosphated, or anodized), although final conclusions regarding the validity of test results related to service experience have not been reached. Method B 117 is considered to be most useful in estimating the relative behavior of closely related materials in marine atmospheres, since it simulates the basic conditions with some acceleration due to either wetness or temperature or both.

A2.3 When a test is used for research, it may prove advantageous to operate with a different solution composition or concentration or at a different temperature. In all cases, however, it is desirable to control the temperature and humidity in the manner specified, and to make certain that the composition of the settled fog and that of the solution in the reservoir are substantially the same. Where differences develop, it is necessary to control conditions so that the characteristics of the settled fog meet the specified requirements for the atmosphere.

A2.4 Material specifications should always be written in terms of the standard requirements of the appropriate salt-spray method, thereby making it possible to test a variety of materials from different sources in the same equipment.

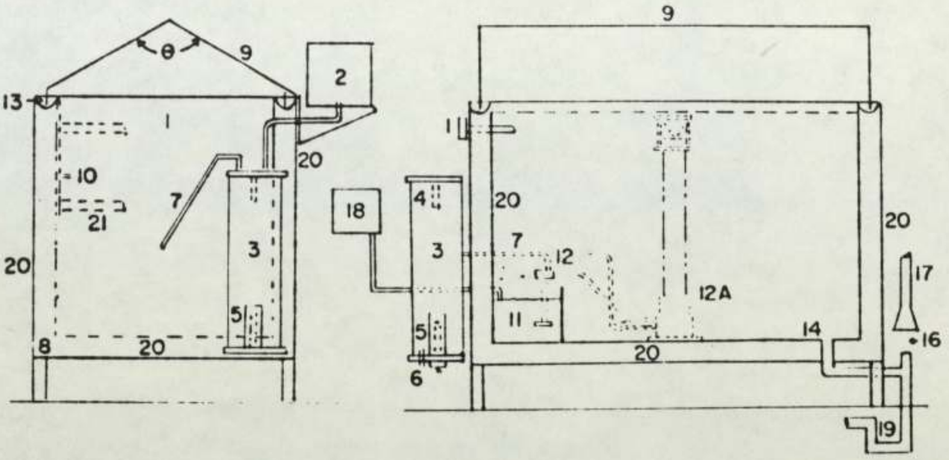
TABLE A1 Operating Characteristics of Typical Spray Nozzle

Siphon Height, in.	Air Flow, liters/min				Solution Consumption, ml/h			
	Air Pressure, psi				Air Pressure, psi			
	5	10	15	20	5	10	15	20
4	19	26.5	31.5	36	2100	3840	4584	5256
8	19	26.5	31.5	36	636	2760	3720	4320
12	19	26.5	31.5	36	0	1380	3000	3710
16	19	26.6	31.5	36	0	780	2124	2904

Siphon Height cm	Air Flow, dm^3/min				Solution Consumption, cm^3/h			
	Air Pressure, kN/m^2				Air Pressure, kN/m^2			
	34	69	103	138	34	69	103	138
10	19	26.5	31.5	36	2100	3840	4584	5256
20	19	26.5	31.5	36	636	2760	3720	4320
30	19	26.5	31.5	36	0	1380	3000	3710
40	19	26.6	31.5	36	0	780	2124	2904

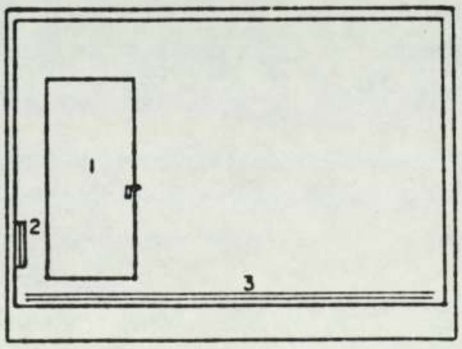
TABLE A2 Temperature and Pressure Requirements for Operation of Test at 95 F

	Air Pressure, psi			
	12	14	16	18
Temperature, deg F	114	117	119	121
	Air Pressure, kN/m^2			
	83	96	110	124
Temperature, deg C	46	47	48	49



θ — Angle of lid, 90 to 125 deg
1 — Thermometer and thermostat for controlling heater (Item No. 8) in base
2 — Automatic water levelling device
3 — Humidifying tower
4 — Automatic temperature regulator for controlling heater (Item No. 5)
5 — Immersion heater, non-rusting
6 — Air inlet, multiple openings
7 — Air tube to spray nozzle
8 — Strip heater in base
9 — Hinged top, hydraulically operated, or counterbalanced
10 — Brackets for rods supporting specimens, or test table
11 — Internal reservoir
12 — Spray nozzle above reservoir, suitably designed, located, and baffled
12A — Spray nozzle housed in dispersion tower located preferably in center of cabinet
13 — Water Seal
14 — Combination drain and exhaust. Exhaust at opposite side of test space from spray nozzle (Item 12), but preferably in combination with drain, waste trap, and forced draft waste pipe (Items 16, 17, and 19).
16 — Complete separation between forced draft waste pipe (Item 17) and combination drain and exhuast (Items 14 and 19) to avoid undesirable suction or back pressure.
17 — Forced draft waste pipe.
18 — Automatic levelling device for reservoir
19 — Waste trap
20 — Air space or water jacket
21 — Test table or rack, well below roof area

FIG. A1 Typical Salt Spray Cabinet.



NOTE The controls are the same, in general as for the laboratory cabinet (Fig. A1), but are sized to care for the larger cube. The chamber has the following features:

(*1*) Heavy insulation,

(*2*) Refrigeration door with drip rail, or pressure door with drip rail, inward-sloping sill,

(*3*) Low-temperature auxiliary heater, and

(*4*) Duck boards on floor, with floor sloped to combination drain and air exhaust.

FIG. A2 Walk-in Chamber, 1.5 by 2.4 m (5 by 8 ft) and Upward in Over-all Size.

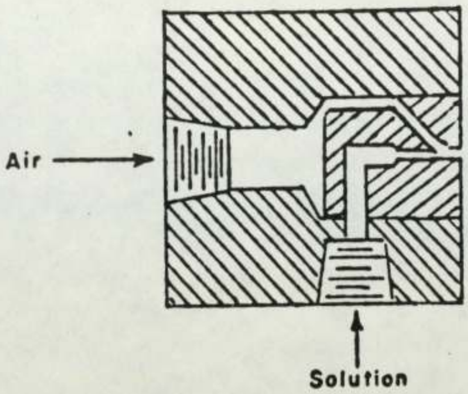


FIG. A3 Typical Spray Nozzle.

The American Society for Testing and Materials takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, is entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 1916 Race St., Philadelphia, Pa. 19103, which will schedule a further hearing regarding your comments. Failing satisfaction there, you may appeal to the ASTM Board of Directors.

APPENDIX 2

Internal company documentation raised for the Vulcan Vaqua D plant

a - The General Manufacturing Specification document, which describes the machine and how it should be operated.

b - The Solution Specification Sheet, which describes how the solutions used in the machine should be made up and maintained during use.

c - The Daily Additions Sheet, which describes how to carry out the daily checks on the solutions in the machine.

2A

Product Specification Dept.
General Manufacturing Specification
Vulcan VaquaD Plant

Spec.No.P18032
Sheet 1 of 6

Index

1. General Description

This machine is designed for wet blast cleaning bonded components, and is capable of dealing with rusty surfaces, bonding agent residues and lubricant contamination.

The unit consists of a cabinet incorporating two automatic barrelling positions and one manual work position.

1.1. Automatic barrelling positions

The automatic barrelling positions are accessed via. the left and right hand doors of the cabinet. A processing barrel, driven by an externally mounted drive unit, is fitted to each door. When a barrel is loaded and the door closed, the barrel slowly rotates while media (Aluminium oxide DSFA/11A is a degreasing solution of DEFM/84A in water) is blasted at the parts through guns, using compressed air. This is followed by a rinsing cycle. Both the blasting and the rinsing cycles are timer controlled.

1.1. Associated equipment

a. Sump - The base of each work area is covered with sections of perforated steel sheet, through which used media drains into a sump for recycling.

Capacity-65 gallons

Heating - 9Kw immersion.

b. Klarti Klarifier unit- a tank, linked by pipework to the sump, which continuously removes oil and grease from the media.

Capacity - 26 gallons.

c. Settling tank - a small weiring tank designed to accept broken down DSFA/11A filtered out of the media.

d. Portable wet cyclone - for the removal of DSFA/11a from the media.

e. Conveyors - Two conveyors for loading parts into the barrels.

2. Solution used

Solution S658 (Hazard 81A)

Temperature 55 - 65°C

The amount of DEFM/84A the part required is calculated on the combined capacities of the sump and Klarti Tank.

The amount of DSFA/11A the plant requires is calculated on the capacity of the sump.

ISSUE	1	PJ															
DATE	25.2.80																

3.Operating Instructions

3.1. Start up procedure

Switch on

a. Water supply

b. Compressed air supply

c. Electricity at isolator

d. Sump heater

e. Klarti pump

f. Machine lighting

g. Check that manual gun is secured to support arm.

h. Switch on steam supply to conveyor cleaning tank.

Media pump i. If the plant is to be in continuous use press low then high buttons ,and turn off pump only during breaks in working.

If only one station is to be used start pump as part of the loading sequence of station and stop pump as part of the unloading sequence.

To start pump press low then high buttons.

The solution in the plant should be brought up to operating tmeperature before processing is begun.

3.2. Automatic Barrel Processing

Either the left or right hand or both barrels can be used as required. Each barrel has separate control panels located by the door. The automatic barreling position are not designed to cope with large parts. The load per barrel should not exceed 120lbs and should ideally consist of 60 to 70lbs to ensure parts are cleaned sufficiently .

The following sequence is applicable to both stations.

3.2.1 Loading (Automatic barrel processing)

a. Open clips securing door.

b. Operate lever hand valve to pneumatically open barrel door.

c. Check that unload flap is closed and secured.

d. Check that the gantry mounted process guns are positioned to give coverage to barrel contents.

e. Push delivery chute into barrel opening.

f. Push Tote tin containing parts into cradle above conveyor.

g. Invert cradle.

h. After conveyor has finished delivering parts into barrel lower delivery chute.

i. Operate hand lever valve to pneumatically close barrel door.

j. Close clips securing door.

k. Set process timer.

l. Set wash(rinse)timer.

m. Press Auto start button.

3.2.2. Unloading (Automatic barrel processing)

The sequence has completed when the orange lights in both the process and the wash timers have gone out.

a. Open clips securing door.

b. Operate lever hand valve to pneumatically open barrel door.

c. Wheel a tote tin under the barrel.

d. Use the inch button to rotate the barrel until the unload flap is positioned over the tote tin.

e. Open unload flap.

f. Ensure all parts have emptied from the barrel.

g. Close and secure unload flap.

h. Wheel tote tin from under the barrel.

j. For continuous running return to e. of 3.2.1 Loading (Automatic barrel processing.

k. If finished with the barrel,operate hand lever valve to pneumatically close doo

l. Close clips securing door .

3.3. Manual work station.

3.3.1. Loading (Manual work station)

a. Ensure media to gun and air to gun buttons are off.

b. Open clips securing door.

c. Manually open door.

d. Detach hand gun from its mounting.

e. Load component .

f. Close door.

g. Close clips securing door.

h. Switch on window wash.

i. Switch on window wiper.

j. Insert hands into work gloves pick up gun and hold firmly.

k. With knee press media to gun then air to gun buttons.

N.B. To prevent damage to the viewing window ensure that the window wash is always switched on before the wipe.

As an alternative to hand holding,the gun can be left fixed in its mounting and the part manipulated in the gun blast . However in this mode care must be taken to ensure the gun is not pointed such that damage is done to the cabinet.

ISSUE	1	PJ			
DATE	25.2.80				

3.3.2 Unloading (Manual work station)

a. Press air to gun and media to gun stop buttons with knee.
b. Attach gun to mounting or put down component.
c. Withdraw hands from gloves.
d. Switch off window wiper
e. Switch off window wash.
f. Release clips holding door
g. Open door
h. Rinse component with water if necessary.
i. Unload component
j. For continuous use return to d. of 3.3.1 loading (Manual work station)
k. If finished with the manual work station close door.
l. Close clips securing door.

3.4. Shut down procedure for plant

a. Close and secure all doors.
b. Switch off sump heater.
c. Switch off Klarti pump.
d. Switch off media pump.
e. Switch off machine lighting.
f. Switch off electricity at isolator.
g. Turn off compressed air.
h. Turn off water.
i. Turn off steam supply to conveyor wash tank

4. Emergency stop buttons and interlocks.

4.1. Emergency Stop buttons

An emergency stop button is fitted to each barrel control panel, which will stop the machine immediately when pressed. To restart the machine pull back the button to its original position.

An emergency stop button is fitted to each conveyor system, which will stop the conveyor immediately when pressed. To restart the conveyor it will be necessary to first pull back the button to its original position.

4.2. Interlocks

Limit switches are fitted to the doors at each work position. Each switch prevents the gun in that work position from operating while the door is open.

5. Maintenance

5.1. Machine maintenance

5.1.1 Daily

a. Check wiper arm and blades. Replace as necessary.

b. Check operation of window wash jet. Clean/replace, as necessary.

c. Check abrasive and air hose fastenings.

d. Check that work grids are undamaged, fitting correctly and are free of foreign matter.

5.1.2. Weekly or every 40 hours

a. As daily

b. When Klarti tank has been drained as part of solution maintenance procedure dismantle tee piece on Klarti tank and check condition and positioning of Venturi jet.

Note: The correct positioning of the jet is vital to the correct operation of the filtration tank. The end of the jet should protrude about 1/8" 3mm) over the centre line of the tee piece.

c. Check interlocks on doors.

d. Check air abrasive and by-pass hoses for wear or damage .Replace as necessary.

e. Check gun nozzles,air jets and non return valve balls and seatings for wear or damage.replace as necessary.

f. Check gun and by-pass adaptors for wear or damage.Replace as necessary.

g. Check gloves of manual station for wear and damage.

5.1.3. Three monthly or every 500 hours.

a. As monthly

b. Remove media pump from cabinet and check top and bottom casings,impellor, extension shaft,gland housing and flow back hose for wear and damage.

c. Check all electrical fastenings.Lubricate door hinges and catches.

d. Check barrel lining for wear or damage.

5.1.4. Six monthly or every 1000 hours.

a. As every three months.Dismantle pump motors and check bearingsfor wear or damage.Clean and lubricate bearings with Shell Alvania 2 Grease or similar.

b. Remove Tornado assembly from pipework.Dismantle and check top ,central tube and orifices to bottom chamber for excessive wear.Replace parts,as necessary.

Caution:
If using a very coarse abrasive continuously,the Tornado assembly should be checked every 500 working hours.

5.2. Solution Maintenance

5.2.1. Daily maintenance.procedures are contained in solution specification.
Solution S658 (Hazard Code 81A)

5.2.2:Weekly or every 40 hours

5.2.2.1.Media solution S658

Change solution S658/81A completely by the following procedure:-
To remove DSFA/11A from solution.

a.Stop media pump and switch off compressed air
b.Open doors and thoroughly wash down cabinet interior.
c.Close and secure all doors.
d.Place a suitable container below cyclone hopper.
e.Check hand valve at base of hopper is closed.
f.Open lower hand valve on branch piece to the media pump.
g.Close upper hand valve in media delivery line from pump to cabinet.
h.Ensure cyclone unit is stable and will not tip.

ISSUE	1	TJ																
DATE	25.2.80																	

5.2.2.1 cont. i. Press media pump low and high buttons,allow pump to run in high speed for a few moments.This will remove DSFA/11A from the sump to the cyclone hopper.

j. Press pump stop button.

k. Open hand valve at base of hopper and drain hopper contents into a container.

l. Repeat operation until cabinet sump is totally clear of old media.

N.B. The wet cyclone unit becomes less effective at separating DSFA/11A finer than 200 mesh.

m. When the sump is empty of old media close hand valve in branch piece to sump.

n. Open hand valve in pump delivery line to cabinet.

To remove old Solution.

o. Turn off water supply

p. remove emptying out bung from tee piece.

q. Drain solution from sump.

r. Open drain valve on Klarti tank.

s. Drain solution from Klarti tank

t. Clean sump and Klarti tank.

u. Decant solution from settling tank.

v. Clear out settling tank

x. Make up a new solution of S658/81A.

y. Turn on water supply.

z. Turn on compressed air supply.

5.2.2.2. Conveyor cleaning tank.

a. Drain water from conveyor cleaning tank.

b, Replace with fresh water.

ISSUE	1	TJ
DATE	25.2.80	

2B

HAZARD 81A	**SPECIFICATION FOR SOLUTION No. S** 658
INITIAL MAKE-UP	**USE** Vulcan Vaqua D Solution

INGREDIENTS	**HAZARD**	**WEIGHT**	**VOLUME**	**WEIGHT**	**VOLUME**
DEFM	84 A	9 lbs			
DSFA	11 A	130 lbs			
WATER			90 gallons		
BATCH SIZE					

Instructions to Production Dept. shown within heavy lines

Solution prepared in suppliers/ working/ separate container on batch / continuous basis.

MIXING PROCEDURE* Fill sump ½ full with water. Add DSFA/11A and DEFM/84A. Then add water until solution runs through overflow pipe and fills adjacent klarti tank. Wear eye protection, non absorbent gloves, protective clothing and face mask.

DEPT./PLANT INVOLVED
Make-up: Vulcan Vaqua D

Using: " " "

Identification

Col.code

TESTS REQUIRED BEFORE USE
BY PRODUCTION: TEST: LIMITS:
BY Q.C./Lab.: CONTROL TESTS Nos. 1 (see below)

SOLUTION MAINTENANCE	**Level** Water to working level
Agitation None	**Additions*** To raise strength by one point add 10 ozs DEFM/84A. Add 44 lbs DSFA/11A after each shift the plant is used
Pot-life -	
P. Spec. ref. P18032	

DISPOSAL* After forty hours use remove DSFA/11A from solution. Discard solution from sump and klarti tank then clean both. Decant and discard solution from settling tank, remove sludge and clean. Do not neutralize any solution with acid. Wear eye protection, non absorbent gloves and protective clothing. Make up a fresh solution of S658/81A protection as above.

	CONTROL TESTS	**Method**	**Limits**	**Frequency QCA**	**Frequency Lab.**
1	Pointage	101	10–16		2
2					
3					
4					

FREQUENCY CODE
0 = no tests required
1 = on make-up
2 = once per shift
3 = once per day
4 = twice per week
5 = once per week
6 = once per month
Any other to be specified

ISSUE No	1	PJ									
DATE	14/2/80										

DISTRIBUTION CODE

* Including safety precautions

2C

VULCAN VAQUA 'D' PLANT

DAILY ADDITIONS

DEFM/84A.

AT THE START OF EACH SHIFT THE PLANT IS TO BE USED ADD 2 LBS OF DEFM/84A (WHITE POWDER).
WEAR EYE PROTECTION, PROTECTIVE CLOTHING, NON ABSORBENT GLOVES AND A FACE MASK.

DSFA/11A

AT THE START OF EACH SHIFT CHECK THE DSFA/11A PINK ALUMINA CONTENT OF THE SOLUTION AS FOLLOWS.

1. Place a plastic measuring cylinder in the manual work position.
2. Switch on the media supply to the gun. DO NOT switch on the air supply to the gun.
3. Fill the measuring cylinder by holding it in the edge of the blast of media.
4. Allow the contents of the measuring cylinder to settle then read off the level of DSFA/11A (pink alumina) at the bottom of the cylinder.

THE DSFA/11A CONTENT MUST BE MAINTAINED BETWEEN THE MARKINGS 15 AND 25.

TO MAINTAIN THE DSFA/11A CONTENT ADD AMOUNTS ACCORDING TO THE FOLLOWING TABLE.

INCREASE IN READING REQUIRED	ADD
1	4 lbs
2	8 "
3	12 "
4	16 "
5	20 "
6	24 "
7	28 "
8	32 "
9	36 "
10	40 "

P. JOHNSON

APPENDIX 3

The memoranda issued in connection with the works trial of the Bonderite 181X phosphating solution

These documents are referred to individually in Chapter 6.

3A

DUNLOP POLYMER ENGINEERING DIVISION

To Mr A R Nutt. Manager Envirómental Health Research Centre.
From J F Powell. Technical Adviser P.E.D.
Ref JFP/LS
Date 21st March 1979 Ext 229

Use of Nitrites.

I attach copies of three documents relating to the use of nitrites, in particular sodium nitrite, and would be glad to have your comments.

In brief, the documents are as follows:-

1/ Letter from Alfa Chemicals to our Mr Hopkins, indicating the possibility of sodium nitrite reacting with secondary amines to form nitrosamines, which are carcinogenic.

2/ Memo. from myself to colleagues, drawing attention to this letter, and indicating the advisability of eliminating sodium nitrite from our processes - as a reaction to the disclosure of the hazard rather than on any positive risk basis.

3/ Memo. from our Mr Johnson to colleagues, indicating the need for sodium nitrite in a (new) process, and suggesting that the risk is so small, if indeed present at all, that it can be discounted.

I have, of course, discussed this matter with our Mr Johnson, and we are in agreement that our present "ban" on nitrites would be difficult, if not impossible, to substantiate on a chemical basis. It was, in fact, a calculated, over-reaction to Alfa's letter, on the assumption that it would be fairly easy to dispense with sodium nitrite. This has proved not to be the case and we need to take a more realistic view of the situation, which is why your advice would be invaluable.

JFP

J F Powell

3B

RESEARCH CENTRE

To Mr J F Powell Technical Advisor Polymer Engineering Division Leicester
From A R Nutt Manager - Environmental Health
Date 10 May 1979 Ref ARN/JS/60 Ext 2168

Use of Nitrites

Thank you for your letter on the above topic, and for the information from Alfa Chemicals.

The reaction between nitrites and secondary (and in some cases tertiary) amines to give nitrosamines has received considerable attention in the literature in recent years, particularly because nitrites find widespread use as food additives, for instance as preservatives in cooked meat and fish. There have been a number of attempts to detect and measure traces of nitrosamines in such foods, sometimes with positive (though very low) results.

Animal experiments indicate that the low molecular weight di-alkyl nitrosamines (particularly dimethynitrosamine and diethylnitrosamine) are potent carcinogens. The di-aryl nitrosamines are either very much less potent carcinogens or are non-carcinogens. Diphenyl nitrosamine, used as a retarder in the rubber industry, has been tested for carcinogenicity with negative results.

Secondary amines have been detected in the vulcanisation products of compounded rubber, though usually in very small amounts. I note your comments on the improbability that significant quantities of nitrosamines would be generated by contact of silicone emulsions containing nitrites with compounded rubber and I agree with this.

Although the possibility of any hazard arising from use of materials containing nitrites is extremely remote, it is as you suggest prudent that where alternative materials are easily available, these should be used. However, where nitrites form part of a system in which they cannot easily be replaced, I do not think that we would be justified in seeking to ban them in the absence of positive evidence that dialkyl-nitrosamines are produced under practical working conditions.

I understand from Mr Johnson's letter that the most important of your current uses of sodium nitrite is as an addition to the new phosphating system (181x) used to treat metal parts prior to metal-to-rubber bonding. It may be worth investigating whether there is sufficient nitrite remaining on the treated parts to cause further reactions, and whether there are any routes by which this nitrite could come into contact with relevant secondary amines. Analytical Section at Research Centre could no doubt help in investigating this aspect of the process.

It is my view that the proposed process should be regarded as acceptable unless and until it can be shown that the theoretical chemical pathways leading to the production of nitrosamines have some basis in the practical situation.

A R Nutt

cc Mr K D Iliffe

3C

DUNLOP
POLYMER ENGINEERING DIVISION

Copies to : Mr. A.J. Reed
Mr. M.R. Horton
Mr. G. Hopkins
Mr. M. Booth
Mr. R.G. Iliffe
Mr. C.D. Keen
Mr. T. Taylor

To Mr. S. Hall
From P. Johnson
Ref PJ/MAR
Date 11th April, 1979
Ext 493

Works Trial of a new phosphating solution

Technical Laboratory has been investigating the abysmally poor corrosion resistance of phosphate coatings produced by Metalastik.

Although a report will be available on completion of the work, an interim summary of key facts is : -

1) Phosphate coatings produced on the automatic and manual phosphating plants exhibit markedly inferior corrosion resistance compared to a coating produced in the laboratory.

   Works phosphate and laboratory stain - less than 16 hours resistance to ASTM B117
   Laboratory " " " " - 72 hours resistance to ASTM B117.

2) When examined by Scanning Electron Microscopy there are clearly evident 'bald' patches in the works phosphate coating compared to the laboratory coating. One type of phosphate crystal is missing from the works phosphate coating causing incomplete surface coverage of poor corrosion resistance.

3) The presence of organic contaminants has been detected in the works phosphating solutions. Anti-oxidants and anti-ozonants have been identified that must have been leached from the rubber.

4) These contaminants are believed to prevent the formation of a satisfactory phosphate coating in a Parco 95 solution. It is therefore proposed to try another solution, 181X, that is claimed to be more tolerant to the presence of organic contaminants.

5) A small scale comparison of Parco 95 and 181X indicates that any difference between the phosphate coatings produced should not adversely affect subsequent painting, staining or oiling operations.

Work required for a trial of 181X

Assuming no objections on health and safety grounds, a trial of 181X is planned to commence on May 21st using the automatic phosphating plant.

This requires the following : -

1) Completion of the repairs requested to the phosphating plants by May 21st.
2) A complete clean out of both phosphating plants on or just before May 21st.
3) Make up a Parco 95 solution in the manual plant as normal.
4) Make up a 181X solution in the automatic plant.

Cont'd..............2

Effect of Production

No changes will be required to production methods or processing times. However, the 181X solution does need closer control over operating conditions and chemical additions than a Parco 95 solution. The closer control over operating conditions can be achieved by completing the repairs required on the phosphating plants and Technical Laboratory will liaise with Process Control regarding the closer control required over the chemical additions.

In order to react quickly to any problem and minimise interference with production, I will be working in the vicinity of the plants for most of the 6 - 2 and 2 - 10 shifts for the initial period of the trial. As the situation normalises, I will work as much of the two shifts as is required.

In addition, Pyrene, the chemical suppliers, are expected to send a representative to the initial period of the trial.

To ensure the integrity of the trial, it is requested that I should be able to give instructions directly to plant operators.

ACTION

Mr. S. Hall

To reply whether these arrangements are acceptable. A reply by April 20th would be appreciated, as I shall be away from then until May 14th.

Meeting

It is suggested that a meeting to finalise details should be arranged for 2 p.m. on Wednesday, 16t May.

P. Johnson

3D

DUNLOP

POLYMER ENGINEERING DIVISION

To	Mr P Johnson ✓	
From	M R Horton	
Ref	MRH/IEH	
Date	20th April 1979	Ext 232

PHOSPHATING

Ref your memo of 18.4.79, please expedite introduction of solution to replace Parco 95.

Report to me weekly on progress.

Thank you.

M R Horton

3E

PURCHASE REQUISITION

№ 35864

FROM TECHNICAL LABS DEPT.

DATE 19/4/79

QUANTITY	DESCRIPTION	£ :
195 Kg	PHOSPHATING CHEMICAL 181X 1MU @61p/kg	118 — 95
1040 Kg	PHOSPHATING CHEMICAL 181X R @61p/kg	634 — 40
100 Kg	ADDITIVE 3 @ 80p/kg	80 —
55 Kg	COMPENSATING SOLUTION 2 @ 31p/kg	17 — 05

SUGGESTED SUPPLIERS	SUPPLIER
~~PYRENE CHEMICAL SERVICES LTD~~	PYRENE CHEMICAL SERVICES LTD
~~RIDGE~~	RIDGEWAY
	IVER
	BUCKS.
DELIVERY TO R.M.S.	ORDER No. 012220 18 APR 79
SANCTION No.	CHARGE TO
AUTHORISED BY G Hopkins A.A. Freeman	DATE

REF. 4JD

3F

DUNLOP

POLYMER ENGINEERING DIVISION

To Mr. S. Hall, Mr. G. Hopkins, Mr. R.G. Iliffe, Mr. T. Taylor
Mr. C.D. Keen.
From P. Johnson
Ref PJ/MAR
Date 14th May, 1979 Ext 483

Works Trial of phosphating solution 181X.

In order to finalise details and discuss any problems regarding this trial, would you please attend a meeting in Mr. S. Hall's Office at 11 a.m. on Wednesday, 16th May, 1979.

P. Johnson.

3G

DUNLOP POLYMER ENGINEERING DIVISION

To Mr. S. Hall, Mr. G. Hopkins, Mr. R. Pearson, Mr. J. Powell, Mr. T. Taylor, Mr. C.D. Keen, Mr. L. Airey

From P. Johnson

Ref PJ/MAR

Date 17th May, 1979 Ext 483

PHOSPHATING - Works Trial of anew phosphating solution - 181X

This trial requires the use of materials new to Metalastik, for which provisional Hazard Warning Cards are attached.

If it is decided to adopt these materials, they will replace Parco 95 1MU (DOMU) and Parco 95 R (DRCO) and the Hazard Warning Cards will be issued at the appropriate time.

P. Johnson

3H

DUNLOP POLYMER ENGINEERING DIVISION

To Mr G Hopkins cc Mr J Marsh Mr P Johnson

From D B Kenyon

Ref DBK/EHS

Date 29 June 1979 Ext

PRODUCT FINISHING STANDARDS

I have heard a number of encouraging but un-official reports relating to the improved performance of our phosphating plant; does this mean that we can increase the levels quoted for Salt Spray performance in DDS 38, which are generally low in relation to customer expectation for this class of finish ?

D Kenyon

3J

DUNLOP LIMITED POLYMER ENGINEERING DIVISION

To Mr. M.R. Horton
Mr. G.J. Midgley
Mr. A.J.Reed
Mr. G. Hopkins
Mr. S. Hall
Mr. D. Kenyon
Mr. K. Wade
Mr. S. Wheeler
Mr. R.G. Iliffe
Mr. C.D. Keen
Mr. D.A.R. Stevenson
Mr. T. Taylor

From P. Johnson

TECHNICAL NOTE NO. BD 97

Works trial of phosphating solution 181X

Object

The Parco 95 phosphating solution currently used has been identified as producing an unsatisfactory phosphate coating when used for processing rubber-to-metal bonded products. A works trial was carried out to assess whether an alternative phosphating solution 181X alleviated the problem.

Summary

For a trial period the manual phosphating plant has been using Parco 95 and the automatic plant 181X. Comparison of the performance of the two solutions using test panels has revealed that the phosphating solution 181X produces a better quality phosphate coating under shop floor conditions than the Parco 95 solution.

Although the 181X solution chemicals cost more and the usage rate may increase, the savings on both heating and labour more than offset the increase. In addition, there should be a decrease in production problems and an improvement in product quality resulting from the change to 181X.

Conclusion

Subject to Health and Safety approval by Central Research, Metalastik should change to using 181X in the automatic and manual phosphating plants.

P. Johnson

3K

DUNLOP POLYMER ENGINEERING DIVISION

To Mr H R Horton Mr A J Reed Mr G J Midgley Mr K Wade
Mr G Hopkins
Mr R G Iliffe
From Quality Assurance Manager
Ref JFP/tw
cc:Mr P Johnson ✓
Date 30 July 1979 Ext

PHOSPHATING SOLUTION

I have had sight of Mr Johnson's Technical Note BD97 on the use of 181X phosphating solution.

In view of the problems we have from time to time with meeting customer corrosion resistance requirements (and it is welcome to observe the "quality awareness" content of the Technical Note) I would urge that we convert to this system without delay. The Note draws attention to the need for close control of process and plant maintenance: it would seem to me that nothing beyond reasonably good chemical and engineering practice is required, and we ought therefore to be able to set our stall out to meet these needs.

So far as Health and Safety approval by CR & DD is involved, my own recollection of the situation is that no-one could see any good reason for regarding the process as hazardous, but CR & DD was carrying out checks aimed at inducing the formation of hazardous nitrosamines. Whilst no-one would condone the pursuance of a risky process, I would suggest we be sure that CR & DD is aware of the need for some promptness in coming to a decision.

J F POWELL

3L

DUNLOP POLYMER ENGINEERING DIVISION

To Mr P Johnson ✓
From M R Horton
Ref MRH/IEH
Date 1st August 1979 Ext 232

cc Mr S Hall
Mr R P Freeman
Mr G J Midgley
Mr F Cowles
File

PHOSPHATING SOLUTION 181X

Thank you for your report and memo of 26.7.79.

I agree that we should proceed with the change from our present Parco 95 solution to 181X as soon as possible on both the automatic and hand phosphating plants.

Will you please arrange with Mr R Freeman for the provisioning of the correct quantities of the chemicals required (at the right price!)

Will you please ensure that all safety, maintainance and control procedures are implemented to ensure a proper operation of the plants.

Thank you.

M R Horton

DUNLOP POLYMER ENGINEERING DIVISION

To Mr. R.P. Freeman
From P. Johnson
Ref PJ/MAR
Date 2nd August, 1979

Copies to Mr. M.R. Horton
Mr. G.J. Midgley
Mr. G. Hopkins

Ext 493

CHANGE OF PHOSPHATING CHEMICALS

Attached is a report recommending that Metalastik changes from using Pyrene's Parco 95 chemicals to Pyrene's 181X chemicals and additives in our phosphating plants.

As the automatic phosphating plant is already using the 181X phosphating solution, I propose the changeover be done by : -

1. Ordering sufficient chemicals to continue running 181X in the automatic plant.

   3 x 65 kg. drums of 181XIMU @ 61p/kg.

   3 x 275 kg. drums of 181XR @ 61p/kg.

   3 x 50 kg. drums of Additive 3 @ 80p/kg.

   2 x 50 kg. drums of Compensating Solution @ 31p/kg.

2. Ceasing to order Parco 95 chemicals, and using the remaining stocks in the Manual phosphating plant.

3. When the Parco 95 chemicals have been used, ordering 181X chemicals for use on both plants,

I think a meeting would be useful to discuss -

a) Stocking level and ordering levels of the new chemicals

b) The possibility of a meeting between Pyrene and Metalastik to negotiate lower prices for the 181XIMU and 181XR chemicals which, prima facia, are too high.

P. Johnson

3N

DUNLOP POLYMER ENGINEERING DIVISION

To Mr. R.P. Freeman
Mr. R.W. Johnson
Copies to Mr. G.J. Midgley
Mr. G. Hopkins
From P. Johnson
Ref RP/MAR
Date 3rd August, 1979. Ext 493

Strength of 181X chemicals.

Although the price of 181X chemicals is 61p/kg it appears to have a lower level of phosphating chemical per unit volume than Parco 95 which is only 57p/kg.

This is true both for the IMU subscript chemicals which are only used to make up a new solution after a clean out and for the R chemicals which are used for the daily additions.

	Total Acid points	Free Acid points	Price per kg.
1 ml 181 X IMU	67	15	61p
1 ml 95 IMU	83	21	57p
1 ml 181 X R	85	18	61p
1 ml 95R	95	20	57p

Points: a generally recognised measure of the strength of a phosphating chemical.

Total Acid: is when the free and combined phosphate chemical content is measured (i.e., phosphoric acid and zinc phosphates).

Free Acid: is when only phosphoric acid content is measured.

From the above results it can be seen that the 181X IMU chemicals give a lower strength reading for both the Total Acid and Free Acid when compared with Parco 95 IMU. This means 181X IMU contains less phosphating chemicals per unit volume, yet it costs more than Parco 95 IMU.

Similarly, 181X R chemicals give a lower strength reading for both Total Acid and Free Acid than Parco 95R yet 181X R costs more.

Unless Pyrene can quote a significant difference in the cost of manufacturing 181X and Parco 95, we would be justified in pressing for the price of 181X to be reduced to the price of Parco 95, if not lower.

181X Usage rate

The following represents a more recent estimation of the usage of 181X chemicals than that present in Technical Note BD97.

Compensating solution 2 - 2 x 50 kg drums every 8 weeks
Additive 3 - 2 x 50 kg drums every 8 weeks
181X IMU - 2 x 65 kg drums every 6 weeks
181XR as for Parco 95.

I would recommend that, until we have more experience of running 181X, the stocks of the above chemicals should not fall below : -

Compensating solution 2 - 2 x 50 kg drums
Additive 3 - 2 x 50 kg drums
181X IMU - 3 x 65 kg drums
181XR - as for Parco 95.

P. Johnson

3P

DUNLOP

POLYMER ENGINEERING DIVISION

To Mr. F. Cowles
From P. Johnson
Ref PJ/MAR
Date 2nd August, 1979

Copies to Mr. M.R. Horton
Mr. G.J. Midgley
Mr. S. Hall
Mr. G. Hopkins

Ext 493.

Maintenance of phosphating plants

Please find attached Technical Note BD97 which recommends we change to using the 181X phosphating solution.

The report refers to the better maintenance required on the phosphating plants to assure successful use of the new solution.

In particular: -

1. Thermostats - need to be checked regularly to ensure they are maintaining temperatures in the correct limits.
2. Ballcocks controlling water inlets - need to be checked regularly for damage and efficient operation.

(The ballcock on the alkali cleaning tank F150 needs replacing with a shorter version, as it is useless at the moment - (automatic plant))

Alterations to manual phosphating plant for conversion to 181X.

The manual plant requires the following work done before 181X can be used in it.

Fitting of thermostats

Bath	No.	Temperature limits
Alkali Cleaning bath	F105	85 - 90°C
Phosphating bath	F111	65 - 70°C
Post phosphating rinse 2	F112	65 - 70°C
Post phosphating rinse 3	F113	65 - 70°C

Fitting of ballcocks

The phosphating tank requires a ballcock fitting to the water inlet.

Water rinses - automatic and manual plants

Rinses affected

Manual		Automatic	
Post phosphating rinse 1	F125	Rinse 1 after alkali cleaner	F151
		Rinse 1 after phosphating	F154

Cont'd..........2

Cont'd ......

Currently the fresh water inlets to these tanks are as shown in the attached Figure 1 (spray bars or top pipes). As shown in the diagram, the clean water largely flows straight to drains leading to these rinses being badly contaminated.

I would appreciate your opinion on the feasibility and cost of changing the rinse water inlets to the type shown in Figure 2.

P. Johnson

APPENDIX 4

The altered Design Data Sheet 38, showing the supplementary table.

DUNLOP LIMITED	POLYMER ENGINEERING DIVISION [METALASTIK]	DESIGN DATA SHEET	No. 38
		SHEET No.	1
		No. OF SHEETS	7

CONFIDENTIAL MUST NOT BE COPIED OR COMMUNICATED

DESCRIPTION

FINISHES FOR METALASTIK COMPONENTS.

General

Current Metalastik finishes are designed to provide a limited range of anti-corrosion coatings that will satisfy the majority of customer requirements.

Finishes are designated 'Preferred' or 'Non-Preferred'.

Preferred Finishes will generally be available without restriction, although certain exceptions may apply; for example, on large items restrictions may be imposed by virtue of plant capacity.

'Non-Preferred' Finishes referred to in this data sheet should be severely restricted to those component applications where a Preferred Finish would be totally unacceptable and the use of a non-preferred finish is considered to be commercially viable.

Salt Spray Resistance Data

Salt spray resistance data should, strictly speaking, refer to the performance of the finishing system applied uniformly to a test panel and judged against a particular set of failure criteria. In practice, performance of the finish has to be judged on production components against failure criteria which can vary from customer to customer. The geometry of the component can affect the thickness of the finish and its behaviour on salt spray. Whilst the quoted data can be applied as it stands in most cases, it may be advisable to check out the salt spray resistance on production components having a typical standard finish, and tested in accordance with the customer's specification.

....

DATE	[illegible]	18 11 80		DRAWN		DESIGN DATA SHEET
ISSUE	2	3		CH'KD		

DUNLOP LIMITED	POLYMER ENGINEERING DIVISION [METALASTIK]	DESIGN DATA SHEET	No. 38
		SHEET No.	2
		No. OF SHEETS	7

CONFIDENTIAL MUST NOT BE COPIED OR COMMUNICATED

DESCRIPTION

PREFERRED FINISHES

Class 1

S33 - Temporary Protective

Based on Shell Ensis 256 Fluid diluted with an approved thinner to render it suitable for the application method, which is normally dipping.

This finish is similar to BS 1133 Section 6 Type TP2b.

On Salt Spray Test to ASTM B-117 - should withstand 16 hours without rusting.

The finish is normally fairly soft when first applied but has a tendency to harden with age. It will afford a reasonable degree of protection for a period of approximately 6 montns under normal indoor storage conditions.

Should a permanent finish subsequently need to be applied, removal of S33 would be necessary and this could be achieved using aqueous alkali degreasers.

Class 2

Etch Primer Finish (E.P.F.)

Comprises a solution of special resins together with a black pigment and a small amount of phosphoric acid, produces a semi-black matt finish approximately 0.0004" thick.

On salt spray test to ASTM B-117 should withstand 16 hours without rusting.

Application is normally by dipping individually jigged parts but spray application is also feasible.

The finish can be applied over metal surfaces previously coated with adhesive; also there is no undue interference with threads. However, due to 'runs', painting of accurately machined faces should be avoided.

Class 3

Phosphate and Stain

Consists of a heavy-weight phosphate conversion coating which is then sealed with a black resin based finish.

The phosphate coating will normally conform to BS 3189 Class 1B.

After 56 hours salt spray testing to ASTM B117 the finish should exhibit no significant corrosion.

Components for treatment should be free from adhesive, rubber residues and significant amounts of rust and are subject to a preliminary degreasing operation.

DATE	17.12.76	18 11 80		DRAWN		DESIGN DATA SHEET	38
ISSUE	2	3		CH'KD			

DUNLOP LIMITED	POLYMER ENGINEERING DIVISION [METALASTIK]	DESIGN DATA SHEET	No. 38
		SHEET No.	3
		No. OF SHEETS	7

CONFIDENTIAL MUST NOT BE COPIED OR COMMUNICATED

DESCRIPTION

Phosphate and Stain (Contd.)

Processing is normally carried out in bulk on automated equipment although larger parts may require individual handling.

NON-PREFERRED FINISHES

Class 4

Heavy E.P.F.

Similar in composition to a standard E.P.F. but with the thickness increased to provide 0.001" minimum coating thickness.

On Salt Spray Test to ASTM B-117 should withstand 48 hours without rusting.

Owing to 'runs' considerable interference with threads can be expected.

Class 5

Phosphate and E.P.F.

Consists of E P F applied over a heavy-weight phosphate coating.

On salt spray test to ASTM B-117 should withstand 36 hours without rusting.

Conditions for phosphating are as before but for maximum protection abrasive cleaning before phosphating is recommended.

Class 6

Phosphate and Heavy E.P.F.

Consists of heavy E.P.F. applied over a heavy-weight phosphate coating.

On salt spray tests to ASTM B-117 should withstand 96 hours without rusting.

Owing to 'runs' considerable interference with threads can be expected.

Class 7

Phosphate Only

Comprises a heavy-weight phosphate coating applied over properly cleaned metal surfaces.

No supplementary finish is applied and thus salt-spray resistance is poor.

This finish is normally limited to specific automotive applications.

DATE	17·12·75	18 11 80		DRAWN		DESIGN DATA SHEET	38
ISSUE	2	3		CH'KD			

DUNLOP LIMITED	POLYMER ENGINEERING DIVISION [METALASTIK]	DESIGN DATA SHEET	38
		SHEET No.	4
		No. OF SHEETS	7

CONFIDENTIAL MUST NOT BE COPIED OR COMMUNICATED

DESCRIPTION

Class 8

Phosphate and Oil

Comprises the S33 type finish applied over a heavy-weight phosphate coating. After 48 hours salt spray testing to ASTM B117 the finish should exhibit no significant corrosion.
Finish provides minimum interference with dimensions.

Class 9

Zinc Plating

A zinc coating applied by electro-plating processes to parts normally pre-treated by grit blasting.

A relevant British Standard is BS 1706 which specifies alternative thickness standards.

The coating may be subsequently passivated to further improve corrosion resistance.

The standard of corrosion protection is relatively high and will depend on coating thickness.

We no longer have internal facilities for applying this finish and consequently it must be carried out on a sub-contract basis.

It should be noted that components having a significant degree of tension at the bond edge are liable to bond failure on zinc plating.

Class 10

Anti-Ozonant Paint P E.D Ref. S652

Comprises a blend of liquid anti-ozonants which is painted on to the rubber surface and absorbed by the rubber.

The treatment is designed to provide additional protection by minimising the effects of ozone cracking, thereby extending the fatigue life of critical components where the surface rubber may be subject to tension stresses.

DATE	17.12.76	22 3 78	18 11 80	DRAWN		DESIGN DATA SHEET	38
ISSUE	2	3	4	CH KD	APPR		

DUNLOP LIMITED	POLYMER ENGINEERING DIVISION [METALASTIK]	DESIGN DATA SHEET	38
		SHEET No.	5
		No. OF SHEETS	7

CONFIDENTIAL MUST NOT BE COPIED OR COMMUNICATED

DESCRIPTION

SUMMARY OF METALASTIK FINISHES

The following table shows the relationship between a limited range of finishes in terms of the degree of corrosion protection offered. The first number refers to the process number and the second to the number of hours salt spray resistance.

Organic coating type	Basic component preparation	
	None	Heavyweight Phosphate
Nil		⑦
Black stain		③ - 56
Soft film	① - 16	⑧ - 48
Paint finish (thin)	② - 16	⑤ - 36
Paint finish (thick)	④ - 48	⑥ - 96

Miscellaneous Paints

Various single or multi-coat paint finishes may be specified for specific applications, e.g. Ministry of Defence. Materials are normally to Customer Specifications.

Technical advice should be sought before agreeing the use of any paint finish.

Flexible Paints

These paints, available in a strictly limited range of colours, provide a measure of protection against oil and similar fluids when applied to rubber, and limited protection against corrosion when applied to metal.

Rubber surfaces require pre-treatment to ensure good adhesion whilst metals are usually phosphated.

Flexible paints do not give adequate protection against continuous contact with oil, for which application oil-resisting rubber compounds should be used.

Vapour Phase Inhibitors (V P I)

Materials capable of inhibiting corrosion by their presence in the air surrounding the component.

Normally supplied in sachets or pellets which are placed in the package which must be reasonably air-tight.

Protection ceases as soon as parts are removed from the package or by excessive ventilation of same.

DATE	21 1 75	22 3 78	18 11 80	DRAWN	DESIGN DATA SHEET	38
	1	2	3			

DUNLOP LIMITED	POLYMER ENGINEERING DIVISION [METALASTIK]	DESIGN DATA SHEET	38
		SHEET No.	6
		No. OF SHEETS	7

CONFIDENTIAL MUST NOT BE COPIED OR COMMUNICATED

DESCRIPTION.

The following table shows which of Metalastik's finishes should meet both the type of finish (e.g. paint or phosphate and oil/stain sealant) and the salt spray resistance requirements of the automotive customers specifications. If the finish indicated in the table is unsuitable the possibility of changing to an alternative finish should be discussed with the Customer.

Guide to which Metalastik finish meets
<u>the Automotive Customer's specifications</u>.

Customer	Specification Number	Metalastik finish Class Number
<u>LEYLAND</u>	BLS22 MS02 Type B	6
	BLS22 MS02 Type C	3
	BLS21 PS01 Stain	3
	BLS21 PS01 Oil	8
	BLS22 OF02	*
	BLS22 OF03	6
	BLS22 OF04	5
	BLS22 OF05	5
(Truck and Bus)	PP 1	*
(Austin Morris)	FP/1	6
(Triumph)	PP222	*
	PP223	6
	PP224	6
(Jaguar)	JCF 103	6
	JCF 103/1	*
<u>FORD</u>	ESEA M2P 1005	4
	PS M3 (old code ESF M3) P6 - A	8
	" " P7 - A	6
	" " P8 - A	7
	SLM2 P1014 A	2
	SLM2 P1014 B	4
	SLM2 P9101 A	6
	SN2 P1015 A	5

Contd. on Sheet 7

DATE	18 11 80	DRAWN		DESIGN DATA SHEET	38
ISSUE	1	CH'KD			

DUNLOP LIMITED	POLYMER ENGINEERING DIVISION [METALASTIK]	DESIGN DATA SHEET	38
		SHEET No.	7
		No. OF SHEETS	7

CONFIDENTIAL MUST NOT BE COPIED OR COMMUNICATED

DESCRIPTION.

Customer	Specification Number	Metalastik finish Class Number
VAUXHALL	P1/1	4
	P2/1	4
	P4/1	6
	P20	4
	P25	6
	P45	•
	R10 Class I and II oil	8
	R10 Class I and II stain	3

• **N.B.** Consult Technical Laboratory regarding a finish to meet these specifications.

DATE	18·11 80	DRAWN		DESIGN DATA SHEET	38
ISSUE	1	CH'KD			

APPENDIX 5

Report recommending that the new phosphating plant should be purchased

PROPOSALS OF NEW PHOSPHATING PLANT

CONTENTS

PROPOSAL FOR A NEW PHOSPHATING PLANT

1. INTRODUCTION

Current Metalastik finishes are designed to provide a limited range of anti-corrosion coatings that will satisfy the majority of customer requirements. There are eight standard finishes for Metalastik components. Five of these finishes require parts to be phosphated. It is estimated that 60% of Metalastik parts by volume require phosphating.

Presently there are two phosphating plants in operation one is manually operated, the other is an automatic tipping basket unit. The plants have been in existence for 33 and 13 years respectively and have no book value.

Present methods are labour intensive and the poor condition of the equipment with inadequate control produces work of inferior quality. No modernisation of these units is possible since their design and construction provides no opportunity to reduce the labour intensity or to provide the strict programmed control of immersion times and temperatures that are necessary to meet present customer standards of protective finishes for Metalastik components.

Recent reports from Quality Control and Technical Laboratory have indicated increasing customer concern with regard to the quality achieved by the existing finishing processes. The equipment has also been severely criticised in their failure to meet present Health & Safety standards. References made by the Factory Inspectorate indicate imminent possibility of Improvement/Prohibition notices being applied.

Upon carrying out an extensive review of a number of suppliers, it is considered that the most appropriate Automatic Phosphate Plant can best be provided by Process Plant & Chemical Ltd. A quality analysis has been carried out on the various equipment available and has shown that the recommended machine satisfies the quality criteria required.

An analysis of present phosphating requirements indicates that an average of 9-10 tons of various types of Bonded units require to be phosphated per week. This will be accommodated by the proposed plant in single shift operating.

2. COST COMPARISON OF THE ALTERNATIVES

The alternatives available are to replace the equipment within 12 months or to arrange to contract the requisite amount of work requiring phosphating to outside suppliers within the next 12 months.

		1980	1981
2.1	EXISTING RUNNING COSTS	£49,500 (4.700p/lb.)	£56,925
2.2	ALTERNATIVE 1.		
	PROPOSED NEW PLANT RUNNING COSTS	£34,800 (3.315p/lb.)	£40,020
2.3	ALTERNATIVE 2.		
	CONTRACT WORK OUTSIDE	£116,000 (11p/lb.)	£133,400

The above comparisons are related to 10 tons of bonded work requiring phosphating.

The additional cost of contracting out work during 1981 would be £ 76,475 over existing running costs.

DESCRIPTION OF PROPOSED PLANT

The Phosphate Plant consists of a series of inline process tank stations covering 14 stages and is approx. 19.5 metres in length, approx: 3.6 metres wide and 2.970 metres high together with a Lanolin oil station and a spirit stain station situated at right angles to the main plant, unload end.

The components loaded and unloaded manually only, with the complete phosphating process being carried out automatically, including movement, sequence and time aspects, the control system being micro-processor based.

The movement between stages, hoist and lower operations is by means of a single bridge gantry transporter travelling on rails over the top of the tanks. It is capable of carrying either a self powered rotating process barrel with two compartments or alternatively a basket for large components, very small components would be processed in a miniature barrel and placed in the main barrels.

At full production the plant is capable of up to 6 barrels in process, with a capacity of 7¼ loads per hour at approx. 120 lbs per load maximum.

The proposed plant will provide for the following types of finish requirements.

1. Phosphate only
2. Phosphate and Spirit Stain
3. Phosphate and Lanolin oil
4. Chlorinate and Phosphate
5. Chlorinate only

COST OF PROPOSED PLANT

-	DESIGN AND MANUFACTURE OF PLANT DELIVERY, INSTALLATION AND COMMISSIONING	£ 93,000
-	ADDITIONAL MOTORISED PROCESS BARREL	2,200
-	MTE MICRO PROCESSOR CONTROL SYSTEM	5,200
-	OVERHEAD EXHAUST CANOPY	2,750
-	PHOSPHATE STRENGTH RECORDING SYSTEM	2,450
-	CO_2 FIRE PROTECTION EQUIPMENT	1,000
-	PHOSPHATE METERING PUMP SYSTEM	1,450
-	OTHER ITEMS DETAILED IN PLANT SPECIFICATION	3,950
-	CONTINGENCY FOR MODIFICATIONS	10,000
-	PROVISION OF SERVICES & FOUNDATIONS	£ 11,000
	CAPITAL TOTAL	£133,000
-	ADDITIONAL REVENUE EXPENSE RE RE-PAINTING AND MODERNISING THE SPECIFIC SITE FOR THE PLANT	£ 11,000
-	REMOVAL OF OBSOLETE PLANT	£ 2,000
	REVENUE TOTAL	£ 13,000

SUMMARY OF COST SAVINGS

	PROPOSED METHOD	EXISTING METHOD
	2 MEN 1 - SHIFT	2 MEN 2 - SHIFTS
DIRECT LABOUR	£ 9,200	£19,500
INDIRECT LABOUR	1,600	4,000
MAINTENANCE	1,000	2,000
INDIRECT MATERIALS (Chemicals etc.)	7,000	7,000
POWER	1,500	2,500
WATER	1,500	1,500
STEAM	10,000	10,000
ANCILLARY COSTS	3,000	3,000
TOTAL OPERATING COSTS	£34,800	£49,500

SAVINGS IN OPERATING COSTS = £14,700

+ 10% for Saving MID 1980 = £16,170

RUNNING COSTS - Weekly Output 10 Tons

EXISTING PLANT RUNNING COST £49,500 = 4.700 pence per lb.
(2 x 8 Hour Shifts/Day)

PROPOSED PLANT RUNNING COST £34,800 = 3.315 pence per lb.

REDUCTION IN RUNNING COST = 1.385 pence.
= 29% REDUCTION

SECTION A PLANT STRUCTURE AND BASEFRAME

The process stages would be mounted on a channel section baseframe. Transporter rails would be supported by means of vertical rail posts, these being bolted to the baseframe and braced from the adjacent tank.

SECTION B TANKS, FITTINGS, CONVEYORS, TIPPERS AND HOPPERS

All tanks would be manufactured from mild steel plate (unless specified otherwise) fully seam welded and provided with rim angle and fitted with base mounted fixing brackets. Harness location saddles and couch blocks are included. An electrical pick up box for barrel drive would be provided.

Individual stage specifications are as follows:-

Stage Load

This would be manufactured from rolled steel sections to form an open fronted framework to support the work carriers, it would be provided with location saddles and couch blocks, barrel drive pick ups and inching button.

Stage Holding Frame

This stage would be manufactured from steel channel and angle section to form a framework to support a spare basket or barrel. It would be provided with location saddles and couch blocks.

This stage would allow one extra work carrier to be contained within the plant over and above the full compliment of 6.

Stage Alkali Clean

This tank would be fitted with:-

a. Drain outlet and valve
b. Weir and downpipe
c. Four side insulated with mineral wool steel faced for protection
d. Thermostatically controlled mild steel heating coil complete with condensate fittings
e. 100mm (4" dia.) vapour pressure thermometer and pocket

Stage Cold Water Rinse

This tank would be fitted with:-

a. Drain outlet and valve
b. Weir and downpipe
c. Water make-up tundish

Stage Cold Water rinse

This tank would be fitted with:-

a. Drain outlet and valve
b. Weir and downpipe
c. Water make-up tundish

/cont....

Stage Chlorinating Rinse

This tank would be fitted with:-

a. Flanged drain outlet and valve
b. Weir overflow, flanged outlet and downpipe
c. Water make-up tundish
d. $\frac{1}{8}$" (3mm) thick rigid P.V.C. lining on internal surfaces extending through all outlets and over flange faces

Stage Cold Water Rinse

This tank would be fitted with:-

a. Drain outlet and valve
b. Weir and downpipe
c. Water make-up tundish

Stage Conditioning Rinse

This tank would be fitted with:-

a. Tank would be constructed from stainless steel Grade 316
b. Four side insulated with mineral wool steel faced for protection
c. Thermostatically controlled stainless steel heating coil complete with condensate fittings
d. Drain outlet and valve
e. Water make-up tundish

Stage Phosphate

These tanks would be fitted with:-

a. Flanged outlet and valve
b. Four side insulated with mineral wool steel faced for protection
c. Thermostatically controlled stainless steel heating coil complete with condensate fittings
d. 100mm (4" dia.) vapour pressure thermometer and stainless steel pocket
e. $\frac{1}{8}$" (3mm) thick rubber lining on internal surfaces extending through all outlets and over flange faces

Stage Cold Water Rinse

This tank would be fitted with:-

a. Drain outlet and valve
b. Weir and downpipe
c. Water make-up tundish

/cont....

Stage Warm Water Rinse

This tank would be fitted with:-

a. Drain outlet and valve
b. Weir overflow, outlet and valved downpipe
c. Four side insulated with mineral wool steel faced for protection
d. Water make-up tundish
e. Thermostatically controlled mild steel heating coil complete with condensate fittings
f. 4" (100mm) dial vapour pressure thermometer and pocket

Stage Chromate Rinse

This tank would be fitted with:-

a. Drain outlet and valve
b. Weir overflow, outlet and valved downpipe
c. Four sides insulated with mineral wool steel faced for protection
d. Water make-up tundish
e. Thermostatically controlled mild steel heating coil complete with condensate fittings
f. 4" (100mm) dial vapour pressure thermometer and pocket

Stage Warm Air Drying Tank

The unit would be constructed in the form of a framework into which would be fitted a galvanised steel liner. The liner would be provided with specially formed perforations to direct air flow into the work carrier and be fitted with rim level recovery slots.

The unit would be fitted with:-

a. Outer frame insulated with Monolux
b. Interconnecting galvanised ductwork to link inner liner and outer frame
c. Heat exchanger
d. Recirculating fan
e. 4" (100mm) dial type vapour pressure thermometer
f. Fresh air intake damper

Stage Unload

This would be manufactured from rolled steel section to form an open fronted framework to support the work carriers, it would be provided with location saddles and couch blocks, barrel drive pick ups and inching button. Positioned within the frame would be a hopper to allow discharge into tote bins or to pass to a lower portion fitted with deflector to allow transfer by conveyor

Stage Lanolin Oil

The basic tank would be constructed from mild steel fully seam welded and fitted with top surround together with base mounted fixing brackets. The tank would be fitted with a drain valve and light gauge lid.

/cont....

Stage Spirit Stain Tank

The basic tank would be constructed from mild steel fully seam welded and fitted with top surround together with base mounted fixing brackets. The tank would be fitted with a drain valve and light gauge lid.

At this stage we have included as an optional extra Co2 fire fighting equipment which could be fitted to the rim of the tank. Furthermore, we have included for an exhaust hood and discharge stack. Due to the nature of this solution, we would require discussion with your fire and safety officer to ascertain whether our proposal as shown on the attached drawing is acceptable, both for the siting of the tank and the optional extra.

Component Transfer System

At stage , unload, components would be unloaded into tote bins or into a hopper. The hopper would be fitted with a two way back plate which would direct the components onto either of two conveyor belts

The components would then be conveyed into a perforated mild steel bin attached to the Lodematic tipper.

A hydraulic system attached to the bin would be ulitised to immerse this in the solution. The bin would then be raised to allow the components to drain, and then raised further and tipped to unload the components via a hopper into tote bins.

The Lodematic tipper would be manually controlled by a single hand held lever complete with 20ft. of flexible hose, or electrically interlocked into the overall control system.

SECTION C. DRIP SHIELDS

Sloping covers would be provided between stages where appropriate to protect floor from solution carry-over during transfer of work.

SECTION D. STEAM HEATING

Where specified heating would be in the form of coils mounted on hangers from the side walls of the tank. The feed to coil would be provided with isolating valve, strainer and control valve complete with adjustable control thermostat and pocket. A by-pass complete with isolating valve would be fitted around the control valve. The condensate return pipe would be fitted with strainer, trap, sightglass and check valve. The coil and hangers would be manufactured from materials specified.

SECTION E. SERVICES

Each of the following services would be connected with suitable piping terminating with an isolating valve.

a. Mains water with individual isolating valves for all aqueous stages

b. Steam

c. Condense

/Cont....

SECTION F. FUME EXHAUST SYSTEM

Tank top fumes and vapour would be removed by an exhaust system provided for stages 2,5,7,8, 9, 11 & 12. A lip exhaust duct fitted with damper control would be located near the rim of each tank.

The ducts would be positioned between the tanks and would extend to the rear of the plant to connect into an exhaust manifold.

The manifold would terminate in a single outlet to which would be fitted an exhaust fan complete with drive motor. A locally positioned starter for the fan unit would be provided.

Stage 16 would have a galvanised exhaust canopy and framework above the tank with a separate fan unit and locally positioned starter.

SECTION G. WORK CARRIERS

The components would be processed in horizontally immersed barrels, five would be provided.

The barrels would be constructed from perforated stainless steel to form a cylinder 457mm dia. (18") x 610mm long (24")

The cylinder would be supported on stub shafts mounted in side members welded to a support harness. The harness would be constructed from box section fitted with horns to provide support from the tank rim and to locate with the transporter flight beam.

A geared motor unit fitted with polypropylene drive pinion would be mounted on the harness. A polypropylene idler gear would be fitted between the drive pinion and a polypropylene ring gear bolted to the side of the barrel to achieve rotation.

The barrel cylinder would be provided with a centre division plate to offer two compartments, each compartment being capable of containing a standard tote bin of work. Each section of the barrel would be fitted with a spring loaded lid which would be fully removable.

To meet the output suggested the machine will require a total of six work carriers, therefore in addition to the five barrels we would provide 4 top harnesses, 1 to be used in conjunction with the barrels and 3 available as spares. This will allow interchangeability of types of carriers according to component requirements. The top harness will be designed to allow you to fit either jigs or work baskets of your own design.

SECTION H. TRANSPORTER UNIT

The transporter would be constructed from steel channels and box sections in the form of side frames supported and braced by cross beams to form a robust and rigid structure.

A captive flight beam constructed from box section would be supported within the unit by chains and guided by rollers in the side frames. The beam would be fitted with pick up angles to engage with the work carrier horns on the top harness.

/cont....

SECTION H. TRANSPORTER UNIT (cont)

Power for hoist and traverse would be provided by two separate twin output shaft motoriced gearboxes, each with fitted brake. The hoist movements would be transmitted via. half-shafts and chains, the traverse via direct drive half-shafts.

The transporter would run on tyres wheels, one pair would be fitted with double flanges to guide the unit along the rails.

An electrical pick up box would be provided to rotate the barrel during transfer between stages.

Manual operation can be achieved by the use of a ' pendant ' control.

Flight beam travel and stage positioning would be controlled by limit switches.

The transporter would be fitted with monitoring switches to detect the following conditions:-

a. Displacement from the rails
b. Flight beam overtravel
c. Presence of a carrier in a stage before lowering

The occurence of any of the above conditions will revert the machine to its manual state.

SECTION I. CATENARY CABLE SYSTEM

Power and signals would be fed to the transporter via a flatform catenary cable. The cable would be supported by trolleys which run in a formed track mounted from the plant structure. A cable towing trolley would be provided on the transporter.

SECTION J. PROGRAMME CONTROL EQUIPMENT

A reprogrammable logic system would be provided to control transporter movements, the programme of which would be formed by diode pins inserted in matrix boards. The machine will be equipped with 3 such boards to provide 3 alternative programmes operated by means of a key selection switch. The sequence for each programme would be as follows:-

a. Cleaning, phosphate dry
b. Cleaning, chlorinate, phosphate, dry
c. Cleaning and chlorinate

All gates and logic functions are designed for industrial applications and are of the high voltage, high noise immunity type with L.E.D. indication facilities on indputs and outputs.

All components would be mounted in a cubicle situated close to the load stage of the machine.

All stages would be addressed individually by means of solid state proximity switches which allow monitoring of the following stage to that being addressed, to detect transporter overtravel.

/cont....

SECTION J. PROGRAMME CONTROL EQUIPMENT (cont)

The fascia of the control cubicle would carry the necessary controls to operate the system together with fault indicators and a number display which would show the instruction being followed at any instant.

The system would be protected against any incorrect movement of the transporter which would revert the machine to a manual state with the appropriate fault light illuminated.

SECTION K. ELECTRICAL ANCILLARIES

All ancillary electrical items would be wired to local starters to which the client would be responsible for connecting power.

SECTION L. SAFETY SYSTEMS

Emergency stop buttons would be located at convenient positions along the plant, the load and unload stages and the control cubicle. The operation of any of these buttons would stop all moving parts and cause the machine to revert to its manual state.

The front and rear elevations of the plant would be screened by mesh guards extending above the rail and below the tank rim. At the rear these guards would be permanently fixed and at the front they would be removable. The front guards would be pneumatically interlocked and connected via a pressure switch to the control system. The removal of any front guard would stop the transporter and would revert the machine to its manual state. Additional fixed guarding would be provided around both stages 15 and 16, this will include the conveyors.

Manual operation can be achieved by a pendant control located on the side of the transporter. To safeguard against obstruction, this control must be hung from the transporter for automatic operation.

The transporter is electrically interlocked so that traverse movements are only possible when the flight beam is in the top or bottom position and hoist movements are only possible when the transporter is positioned on stage.

We require you to acknowledge that the safety systems specified meets your approval, together with the arrangement of exhaust and possible inclusion of Co2 equipment as described previously. Any variation required should be advised, in writing, prior to acceptance of our tender.

SECTION M. PAINT SYSTEM

All untreated steelwork would be painted with a good quality primer followed by two coats of a chlorinated rubber paint to BSS 2660 colour reference 7-080 electric blue.

SECTION N. DELIVERY

We would be responsible for loading the equipment on to vehicles at our Works and transporting to your nominated site. You would be responsible for off-loading and conveying to its final site location.

/cont....

SECTION O. INSTALLATION AND COMMISSIONING

Following delivery we would provide the services of our installation personnel to connect all sections of equipment of our supply. Following this installation you would be responsible for making connections to the service points, supplying chemicals and charging the tanks with solutions.

The equipment would be fully tested and commissioned, following installation, by our Electrical and Mechanical Engineering Staff. This does not include chemical processing test which is not our responsibility. We would, of course, offer our assistance during wet commissioning in co-operation with your named chemical supplier.

Exclusions

Any items not mentioned in our quotation are excluded from our supply. In this category we list below some main items of equipment that are not included in our quotation but which should be borne in mind when considering the scheme as a whole.

a. Process chemicals
b. Fume discharge stack(s) from fan(s) to atmosphere
c. Connection of services
d. Foundations and Builders Work
e. Power to ancillary starters
f. Off-loading facilities and conveying local to site
g. Lagging of steam lines

APPENDIX 6

The anti-corrosion code for motor vehicles that was introduced in Canada in 1978

The *Federal/Provincial Anti-Corrosion Code for Motor Vehicles* and the *Owner Care Guide* were introduced by the federal and provincial Ministers of Consumers Affairs in January 1978.

They were developed by a Federal/Provincial Task Force in close cooperation with automobile nanufacturers and importers and with the full technical support and cooperation of Transport Canada and the National Research Council.

The Code and Guide have been endorsed by the Federation of Canadian Municipalities, and major consumer groups such as the *Consumers' Association of Canada*, the *Canadian Automobile Association*, and the *Automobile Protection Association*.

© Minister of Supply and Services Canada 1978

Catalogue No. RG23-42/1978

ANTI-CORROSION CODE FOR MOTOR VEHICLES

1. INTRODUCTION

Compliance with the Anti-Corrosion Code for Motor Vehicles by vehicle manufacturers and importers is voluntary, but it is in the long term interests of new car buyers to purchase only those vehicles which meet or exceed the minimum provisions of this Code.

The Code establishes minimum levels of corrosion protection which can and should be provided for all new vehicles sold in Canada. It is hoped that manufacturers will provide a higher level of corrosion protection for their customers than that specified in the Code. It is suggested that any warranty provisions relating to corrosion protection be examined carefully to ensure that they provide at least as much protection as suggested in the Code.

Vehicle owners must realize that maximum benefit from the corrosion resistance of their vehicles may be achieved only with proper care and maintenance. The Code includes Owner Care Guidelines which, when followed, would provide a reasonable standard of care for owners who demand durability. It is expected that these guidelines would form the basis of normal owner maintenance of any vehicle.

Owners who wish to further extend the durability of their vehicles *beyond* the terms set out in the Code, should consider the application of rust-inhibiting materials by recognized, professional firms whose reputation is known and which provide a comprehensive written warranty.

As stated in section 9 of the Code, the application of rust-inhibiting material by the owner is ***not required*** in order that the Code be valid.

Where, through defect in the construction, design or functioning of a motor vehicle, corrosion affects or is likely to affect its safe operation, the vehicle manufacturer or importer is obligated to give notice of the defect under the provisions of the Motor Vehicle Safety Act administered by Transport Canada. Nothing in this Code alters the provisions of that Act.

2. In this Code:

a) *Vehicle* means a motor vehicle which is a passenger car, bus, truck or multipurpose passenger vehicle, as defined in the Motor Vehicle Safety Act, having a gross vehicle weight rating of 4536 kg (10,000 pounds) or less;

b) *Model Year* means the year designated by the manufacturer or importer in the vehicle identification number;

c) *Normal Operating Conditions* means all usual and reasonable conditions of vehicle use anywhere in Canada; including operation, maintenance and repair in accordance with the reasonable recommendations and conditions of warranty of the vehicle manufacturer or importer; prompt repair to professional standards of any accident damage; and regular maintenance of the vehicle in accordance with the Owner Care Guidelines which form an integral part of this Code;

d) *Component of the vehicle body* means any moving or non-moving component of the vehicle, with the exception of those components which form part of the vehicle powertrain and of the steering, suspension, braking and exhaust systems;

e) *Corrosion* means the process whereby a metal is destroyed by chemical or electrochemical reaction with its environment;

f) *Surface Corrosion* means corrosion affecting any readily visible surface area of any component of the vehicle body, but not including the vehicle underbody;

g) *Perforation* means the corrosion of any metal component of the vehicle body from one surface through to another;

h) *Structural Damage* means the corrosion of any component of the vehicle body which results in a weakening of that component such that it may no longer fulfill its designed function.

3. The following requirements apply to vehicles of the 1978 and subsequent model years, as indicated;

   a) Every new vehicle sold or offered for sale in Canada shall remain free from surface corrosion resulting from defects in design, materials or manufacture for a period of 12 months or 40,000 km, whichever occurs first, from the date the vehicle is first put into service. For vehicles of the 1981 and subsequent model years, the periods shall be 18 months and 60,000 km respectively.

   b) Every new vehicle sold or offered for sale in Canada shall remain free from perforation, under normal operating conditions, during the first 36 months or 120,000 km, whichever occurs first, from the date the vehicle is first put into service. For vehicles of the 1981 and subsequent model years the periods shall be 60 months and 200,000 km respectively.

   c) Every new vehicle sold or offered for sale in Canada shall remain free from structural damage, under normal operating conditions, during the first 72 months or 240,000 km, whichever occurs first, from the date the vehicle is first put into service.

4. The provisions of this Code shall apply only to a vehicle which is presented to a dealer or other agent duly authorized by the manufacturer or importer, for inspection for corrosion at intervals of approximately 12 months from the date the vehicle is first put into service.

   a) Such inspections shall be performed at no cost to the vehicle owner.

   b) It shall be the obligation of the inspecting agent to provide a copy of a written evaluation of such inspection to the party presenting the vehicle, including reasonable repairs which the agent deems necessary to maintain the vehicle's resistance to corrosion.

5. If, following any inspection described in section 4, the vehicle owner fails to have the repairs referred to in subsection 4 (b) carried out to professional standards in accordance with the reasonable recommendations of the inspecting agent and within a reasonable period of time, the affected area or areas of the component of the vehicle body shall no longer be covered by the Code.

   a) Where the necessity for such repairs results from damage to the surface protection of any component of the vehicle body, the cost of such repairs shall be the responsibility of the vehicle owner.

   b) Where the necessity for such repairs results from a defect in or deterioration of the corrosion protection of the vehicle such that a minimum standard set out in section 3 is not attained, the cost of such repairs shall be the responsibility of the vehicle manufacturer or importer.

6. A vehicle manufacturer or importer may require that any repairs, the cost of which are his responsibility pursuant to subsection 5 (b), be performed by a dealer or other agent duly authorized by him.

7. It is the obligation of the vehicle owner to obtain and retain documentary evidence of all inspections and repairs carried out in accordance with sections 4, 5 and 6.

8. It is the responsibility of vehicle dealers, importers and manufacturers to supply to vehicle owners such information and reasonable recommendations as will enable them to obtain maximum effect from the corrosion resistance of their vehicles.

9. Notwithstanding section 8, no dealer, importer, or manufacturer shall require, as a condition of his obligations under this Code, that an owner take any further action at his own expense beyond his obligations described in sections 4 and 5 and those of normal owner maintenance as described in the Owner Care Guidelines.

10. The provisions of this Code remain applicable to a vehicle notwithstanding any transfer of its ownership.

11. In the case of any dispute arising between a vehicle manufacturer or importer and the vehicle owner regarding their respective rights and obligations in relation to a matter dealt with in this Code, consideration may be given to the condition of the owner's vehicle in comparison to other vehicles of the same model and model year used under normal operating conditions in the same geographical location.

OWNER CARE GUIDE

WHAT CAUSES RUST

The two most common causes of rust to your car are:

1. the accumulation of road dirt and moisture in hard-to-get-at cavities and other areas under the car;

2. the removal of paint and protective coatings on the outside of the car and underneath through damage by stones and gravel or minor accidents.

Several factors influence the speed at which corrosion will occur:

1. The length of time various parts of a car stay wet. Parts of the car filled with road dirt and water remain damp for long periods of time even when other parts are dry.

   Particular attention should be paid to the underside of the car and floor sections inside.

   The floor sections stay wet because moisture collects and remains under the floor matting.

   Drain holes located at the bottom of the doors get clogged with dirt, trapping water inside the door and causing the door to rust through at the bottom.

2. Corrosion will be accelerated in areas of higher relative humidity, especially where temperatures often stay above the freezing point and where the atmosphere is affected by industrial pollution, or where salt is used for de-icing the roads.

   Where parts of the car are covered with road dirt containing road salt, corrosion will be accelerated at a lower relative humidity than if the surface were clean.

3. Increased temperature will cause an accelerated rate of corrosion of those parts of the car which are not well ventilated to permit quick drying.

4. Industrial pollution and the presence of salt will also accelerate the deterioration of paint finishes.

The foregoing identifies the need for every car owner to keep the car and particularly the underside, as clean and dry as possible and to repair any minor damage to paint work and protective coating as soon as possible. The need is more important in those localities where road salt is used for de-icing, the relative humidity is higher, air pollution is present and temperatures regularly stay above freezing. Southern Ontario, Québec, the Atlantic provinces and the coast of British Columbia are areas where rust is more likely.

REGULAR WASHINGS

Wash your car at regular intervals, and to the extent that weather conditions permit and appropriate facilities are available, at least once a week

APPENDIX 7

The specification issued by General Motors which raised the salt spray resistance required for a phosphate and sealant finish to 240 hours.

CORROSION PROTECTIVE COATINGS
PHOSPHATE/ORGANIC/OIL TYPE; BLACK
GM 6174-M

1 SCOPE. This specification covers basic requirements for a black corrosion protective coating which is produced in a process consisting of zinc phosphate treatment, chromic acid rinse or seal, organic coating, oven bake, water and oil emulsion post treatment, and air dry.

1.1 This coating is especially suitable for bolts, nuts, clips and other small ferrous parts where above normal levels of corrosion protection, freedom from hydrogen embrittlement and decorative black color are desired.

2 APPEARANCE AND CURE. Coating shall have a uniform dense black appearance and shall be free from tears and thoroughly cured. It shall not be oily or tacky to the touch.

2.1 Where metric identification is specified separately on engineering drawing, per GM 9083-P, blue color takes precedence over black specified above.

3 THICKNESS. Coating in threads of threaded products shall not have an adverse effect on normal installation and removal practices.

NOTE: The maximum thickness of coating which may be applied to threads on threaded products is limited by the basic thread size. Where greater thickness is necessary to meet the requirements of this specification, threads may be produced undersize (before coating) to accommodate the greater thickness, providing the finished product (after coating) meets all specified mechanical properties. Where mechanical properties are not specified, undersizing is subject to approval of purchaser.

4 CORROSION RESISTANCE. Parts coated to this specification and subsequently subjected to a detergent wash (see 9.1.1) shall be capable of withstanding neutral salt spray testing for a minimum of 240 hours.

4.1 "Acceptable resistance" shall be as agreed between purchaser and supplier. Generally, however, there shall be no evidence of red rust or blistering and no change in color.

5 FLEXIBILITY AND CHIP RESISTANCE. Coating shall withstand the normal extension and compression of springs, and the normal flexing encountered by spring clips during assembly in the end product, without evidence of flaking or loss of adhesion to basis metal. Also, it shall withstand normal handling and storage conditions without chipping, flaking or other coating damage.

6 ADHESION CHARACTERISTICS. Parts coated to this specification shall show no evidence of blistering or other appearance changes after exposure to humidity testing for 96 hours, minimum, and shall show no more than 3.0 mm peel back from intersection of lines scribed and tape tested immediately after a 10-minute recovery period following exposure, and no other peeling in area under tape.

7 WEATHERING CHARACTERISTICS. Parts coated to this specification shall show no blistering, peeling, cracking, loss of adhesion, discoloration, or red rust after 1000 hours exposure to the weathering test.

8 TESTING.

8.1 Neutral salt spray testing shall be conducted according to GM 4298-P.

8.1.1 Prior to salt spray testing, parts shall be washed as follows in a room temperature solution of tap water and DuPont Rally Car Wash Concentrate or equivalent (5 mL/L):

(1) agitate parts in the solution for 30 seconds

(2) rinse in tap water

(3) air blow-off dry

8.1.2 When these coatings are specified for bolts and screws, the parts should be power driven into a nut or tapped hole in a manner simulating a production assembly condition in which the head of the fastener turns tight against a flat surface, then removed prior to salt spray testing. Rating of these parts should be done on the head and shoulder; not the threads.

8.2 Humidity testing shall be conducted according to GM 4465-P (100 percent RH at 38°C).

8.3 Tape testing shall be conducted according to GM 9071-P (C10M).

8.4 Weathering test shall be conducted according to ASTM G23, with Type EH apparatus. The daily schedule consists of twenty cyclic periods (20 hours). Each period consists of light only at 60 ± 3°C for 51 minutes and light with spray at 7 ± 3°C for 9 minutes.

9 INSPECTION AND REJECTION. Shipments of material against contracts or purchase order shall be equivalent in every respect to samples approved by the purchaser. While samples may be taken from incoming shipments and checked according to this specification, the supplier shall accept the responsibility for shipments meeting this specification without dependence upon the purchaser's inspection.

10 NEW SOURCES. No shipments shall be made by a new source until a sample of the material which it proposes to supply under this specification has been approved by the purchaser's laboratory (unless by special agreement the purchaser elects to temporarily accept shipments on the supplier's certification).

11 GENERAL INFORMATION. This specification first published August, 1976; last revised January, 1977.

These specifications were developed without considering whether patents may or may not be involved. In all cases, therefore, the supplier shall be required to assume patent liability.
PRINTED IN U.S.A.

REFERENCES

1. Use of rubber in engineering. P.W.Allen, P.B.Lindley, A.R. Payne, (1967) Maclaren and Sons Ltd, London.
2. R.W.Pearson. Journal of European Industrial Training 4, 1, 17, (1980).
3. D.J.Van Rest. Works Management 23, March, (1970).
4. D.R.Cox. Rubber Journal 151, 50, (1969).
5. G.Lorin. Phosphating of metals, Finishing Pub Ltd. (1974).
6. J.E.Salmon and H.Terrey. J.C.S. 10, 2815, (1950).
7. U.R.Evans. Metallic corrosion passivity and protection, Arnold (1948).
8. W. Machu. Korrosion und Metallschutz, 17, (1941).
9. L.O.Gilbert. Tech Proc. American Electroplaters Soc. 43, 195, (1956).
10. W.Machu. Cebelcor Technical Report No. 119 (1964).
11. P.Tyvaert. Protection des surfaces metalliques contre la corrosion, Estoup (1961).
12. J.Saison. Doctorate Thesis. Paris (1962).
13. V.Cupr and J.B.Pelikan Metalloberflache. July (1965).
14. V.Cupr and J.B.Pelikan Metalloberflache. June (1965).
15. M.J.Bigeon. Chimie et Industrie. January (1962).
16. D.James and D.B.Freeman T.I.M.F. 49, 79, (1971).
17. P.G.Chamberlain. Metal Finishing, 60, January, (1962).
18. W.Machu. Metalloberflache. June, (1967).
19. J.Cournot and G.Lorin. Galvano-Organo May, 575, (1977).
20. D.J.Mills. PERA Conference Protective and Decorative Finishes, Warwick, June, (1969).

21. G.W.Jernstedt Trans Electrochem Soc. 83, 361,(1943).

22. W.Machu. Metallwirtschaft, 22, 481, (1943).

23. D.L.C.Burgess T.I.M.F. 54, 138, (1976).

24. D.B.Freeman. Corrosion Prevention and Control. October, (1962).

25. W.A.Holden. Corrosion Prevention and Control. August, (1963).

26. L.F.Spencer. Metal Finishing, 57, 64, (1959).

27. R.F.Drysdale T.I.M.F. 47, 149 (1969).

28. W.R.Cavanagh, Society of Automotive Engineers Meeting, Detroit, May, (1970).

29. E.Bronder and D.Funke. Symposium Automotive and Other Industrial Finishing I.M.F. and O.C.C.A. Coventry, April, (1973).

30. D.M.Bishop and F.D.Timmins. T.I.M.F. 53, 188, (1975).

31. G.W.Walter. Corrosion Science, 17, 983, (1977).

32. J.B.Lakeman, D.R.Gabe and M.O.W. Richardson T.I.M.F. 55, 47, (1977).

33. J.A.Capp. Proceedings ASTM 14, 474, (1914).

34. H.S.Rawdon, A.I.Krynitsky and W.H.Finkedly. Proceedings A.S.T.M. 24, 717,(1924).

35. Report of Committee B-3. Proceedings A.S.T.M. 24, 281, (1924).

36. H.S.Rawdon and E.C.Groesback. National Bureau of Standards Technical Paper No. 367, March, (1928).

37. W.H.Mutchler, R.W.Buzzard and P.W.C.Strausser. National Bureau of Standards. Circular Letter No. 530, July, (1938).

38. L.J.Waldron. Proceedings A.S.T.M. 44, 654, (1944).

39. A.N.Finn, H.S.Rawdon and M.A.Grossman. National Bureau of Standards. Circular Letter No. 80, (1919).

40. C.E.Haussner. Proceedings (Educational Sessions) Am Electroplaters Soc. June, (1942).

41. T.P.May and A.A. Alexander. Proceedings A.S.T.M. 50, 1131, (1950).

42. W.D.McMaster. 1st International Congress on Metallic Corrosion, Butterworths (1961).

43. Report of Committee B-3 Proceedings A.S.T.M. 25, 150, (1925).

44. National Paint Varnish and Lacquer Assn.Inc.Circular No. 670 Scientific Section, February, (1944).

45. Report of Committee B-3 Proceedings A.S.T.M. 56, 154, (1956).

46. V.M.Darsey and W.R.Cavanagh. Proceedings A.S.T.M. 48, 153, (1948).

47. M.Pourbaix. Atlas d'Equilibries Electrochemiques a 25°C. Gauthiers Villas, Paris, (1963).

48. Report of Committee B-3 Proceedings A.S.T.M. 28, 223, (1928).

49. A.S.T.M. Book of Standards (1939).

50. Report of Committee B-3 Proceedings A.S.T.M. 43, 187, (1943).

51. K.Efer.Korrosion (Dresden) 1, 3, (1972).

52. F.L.La Que. Materials and Methods, February, (1952).

53. Published replies to F.La Que's Article, Materials and Methods, March, (1952).

54. T.R.Bullet and J.L.Prosser. Prod.Org.Coatings 1, 45, (1972).

55. R.J.Neville. International Automotive Engineering Congress and Exposition. Detroit, March, (1977).

56. J.B.Mohler. Metal Finishing, March, (1978).

57. J.L.Burbidge. The Introduction of Group Technology. Heineman, (1975).

58. I.H.A. Yearsley and P.D.Darlans. T.I.M.F. 51, 173, (1973).

59. L.A.Weinert. Anti-Corrosion, May (1978).

60. C.M. Blow. Rubber Technology and Manufacture, Butterworth (1971).

61. Anon. Chemical Engineering News. 54, 33, (1976).

62. Anon. Rubber World. February (1979).

63. W.Cannings. Product Finishing. April (1979).

64. R.D.Wyvil. Product Finishing. April (1978).

65. T.McCrae. Accounting and Business Research. Spring (1971).

66. W.L.Mercer. Metallurgist and Materials Technologist. 11, 575,(1979).

67. R.Sagesser. Sulzer Technical Review. 1, (1977).

68. B.R.M.A. Protective Finishes for Rubber-to-Metal Bonded Products. May (1975).

69. G.Janner. Metallurgist and Materials Technologist 12, 627, (1980).

70. Surface Treatments for the Motor Industry New Technologies and Market Forecasts 1977-1985. European Study. Battelle Institute (1978).

71. Anon. Metal Finishing Plant and Processes. June (1976).

72. G.H.Edwards. Br. Corros. J. 4, 236, (1969).

73. T.P.Hoar. The cost of corrosion. The Government Committee on Corrosion, London (1971).

BIBLIOGRAPHY

W.H.Ailor	Handbook on Corrosion Testing and Evaluation, John Wiley and Sons Inc. U.S.A. (1971).
F.A.Champion	Corrosion Testing Procedures, Pergammon Press Ltd. (1966).
S.Spring	Metal Cleaning, Reinhold Publishing (1963).
L.A.Tysall	Industrial Paints, Basic Principles, Pergammon Press Ltd. (1964).
G.P.A.Turner	Introduction to Paint Chemistry, Chapman and Hall Ltd. (1967).