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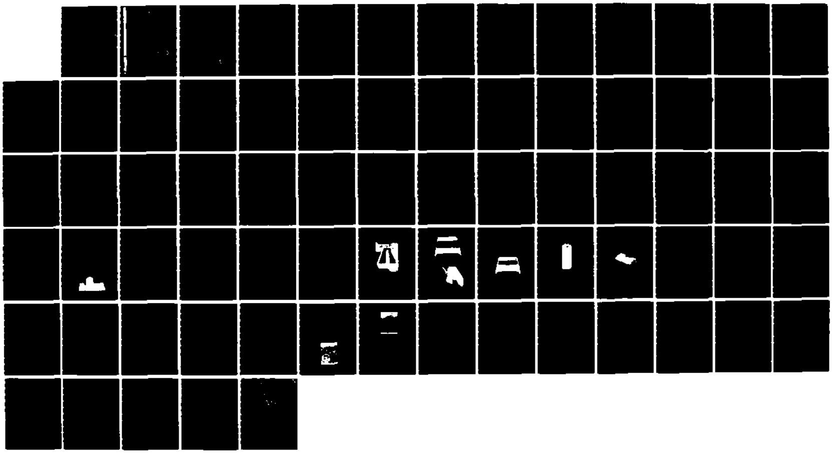

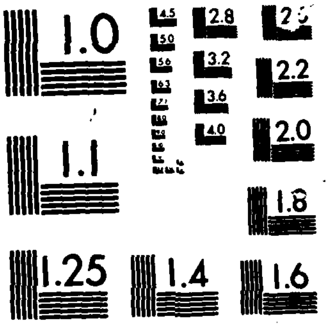

MICROCOPY RESOLUTION TEST CHART

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DEPARTMENT OF DEFENCE

DEFENCE SCIENCE AND TECHNOLOGY ORGANISATION

MATERIALS RESEARCH LABORATORIES

MELBOURNE, VICTORIA

REPORT

MRL-R-964

CONTROLLING CORROSION IN DEFENCE EQUIPMENT - TECHNICAL MEETING

Edited by D.A. Wright

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CONTROLLING CORROSION IN DEFENCE EQUIPMENT TECHNICAL MEETING

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ABSTRACT

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The meeting sought to expand and update the long established, and productive, liaison between MRL corrosion scientists and the Armed Services and Defence Factories in this important and costly area. Corrosion expertise immediately available to Defence personnel was highlighted, as were current developments in corrosion control areas in which MRL research and development is either presently active or could be deployed should Defence requirements so dictate. It was hoped, therefore, to show MRL's customers how to obtain advice on corrosion more effectively from present scientific resources and to direct their attention to developments in corrosion technology that might have future application in their work.

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Presentations at this Technical Meeting covered a wide range of corrosion theory and practical control measures. They were given by nine scientists currently working in the field and are here reported as either extended abstracts or complete papers. Topics range from protective measures such as electroplating, painting and surface modification, through ways of minimizing corrosion by suitable equipment design, to overviews of stress corrosion cracking and the monitoring of corrosion. Case histories of corrosion-induced failures in materiel that are typically representative of control problems, and estimates of the cost of corrosion to Defence are given in some detail.

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CONTROLLING CORROSION IN DEFENCE EQUIPMENT - TECHNICAL MEETING

Wednesday, 27 March 1985
Conference Room, John L. Farrands Building
Materials Research Laboratories
Maribyrnong, Vic.

Don Wright, Editor

Papers and extended abstracts of presentations given at this Technical Meeting sponsored by Metallurgy Division, MRL.

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CONTROLLING CORROSION IN DEFENCE EQUIPMENT

MRL TECHNICAL MEETING

WEDNESDAY, MARCH 27 1985

WELCOME TO THE LABORATORIES

Wynford Connick, Director, MRL

I would like to welcome you all to MRL and to this meeting on controlling corrosion in defence equipment. We are pleased at the overwhelming response that we have had for this meeting and I am sorry that we have had to limit the attendance somewhat. This has clearly touched a sensitive nerve in Defence.

In 1975 the cost of corrosion to the US community was estimated as $70,000 million US dollars, equivalent to 4% of the GNP. The equivalent figure for Australia is much the same. However we are unsure of the figure for the Australian Defence Department though in general terms we can take it to be very significant. As managers we are all responsible in one way or another to reduce unnecessary costs and in this context defining what is unnecessary will be a major objective for the meeting today.

Recently we have been celebrating 150th birthdays, and in a sense this is a 150th celebration. The science underpinning corrosion is electrochemistry and the foundation for this was put forward in a typically clear and concise fashion by Michael Faraday. His paper to the Philosophical Transactions of The Royal Society entitled "On electro-chemical decomposition" was presented 150 years ago, in 1834, the year that Edward Henty established a settlement at Portland!

If the foundations are not new, the application of the science to industry and the defence forces you will hear about today is and the speakers today will emphasize new developments in detection and monitoring, in failure investigations in the variety of modes and mechanisms of corrosion, and in ways of minimizing corrosion by protective coatings.

We have representatives from the entire range of defence functions here today. I trust you will find the meeting helpful and rewarding.

I declare the meeting open.

CONTROLLING CORROSION IN DEFENCE EQUIPMENT : INTRODUCTION

Maurice de Morton
Superintendent, Metallurgy Division

The Director has highlighted the objective for holding this meeting today. In essence we wish to see a reduction in defence costs related to maintenance, repair and overhaul caused by corrosion. With the evidence we see of corrosion each day, across the whole spectrum of defence equipment, we can draw the users' attention to the range and extent of these problems to ensure operational effectiveness and safety and to suggest means of reducing costs, for example through design, material selection, the use of inhibitors and the application of corrosion monitoring and protective coatings.

There is, however, another reason for organizing this meeting and this is frankly based on self-interest. Along with some other branches of Defence, we in Metallurgy Division have seen our resources seriously eroded in recent years - over 15% reduction in manpower over the last two years. To follow the effect of these cuts it is useful to look at the interactive way that consultants and researchers operate within the research groups. Here the type and incidence of corrosion problems are communicated to the research staff by the consultants for integrating into research tasks while the products of research are fed back to the consultants for implementation as shown in Fig. 1.

At the consulting level however we find similar problems reoccurring - we would like to believe that the deliberations from our consultants would be stored in the corporate memory of our customers so that we would not be called on to re-examine the past. Presently more than ten percent of our divisional resources are devoted to corrosion control. We would like to see more effort going into developing a better understanding of corrosion processes associated with newer materials and in improving detection and monitoring of corrosion.

There is also some urgency in achieving a better customer understanding of corrosion since some of our senior consultants are close to retiring and replacement of professionals with experience covering a full career is almost impossible.

We therefore hope that our advice on past problems will be heeded and that our services will be sought at the early design stage so that corrosion failures and subsequent investigations can be reduced to the minimum.

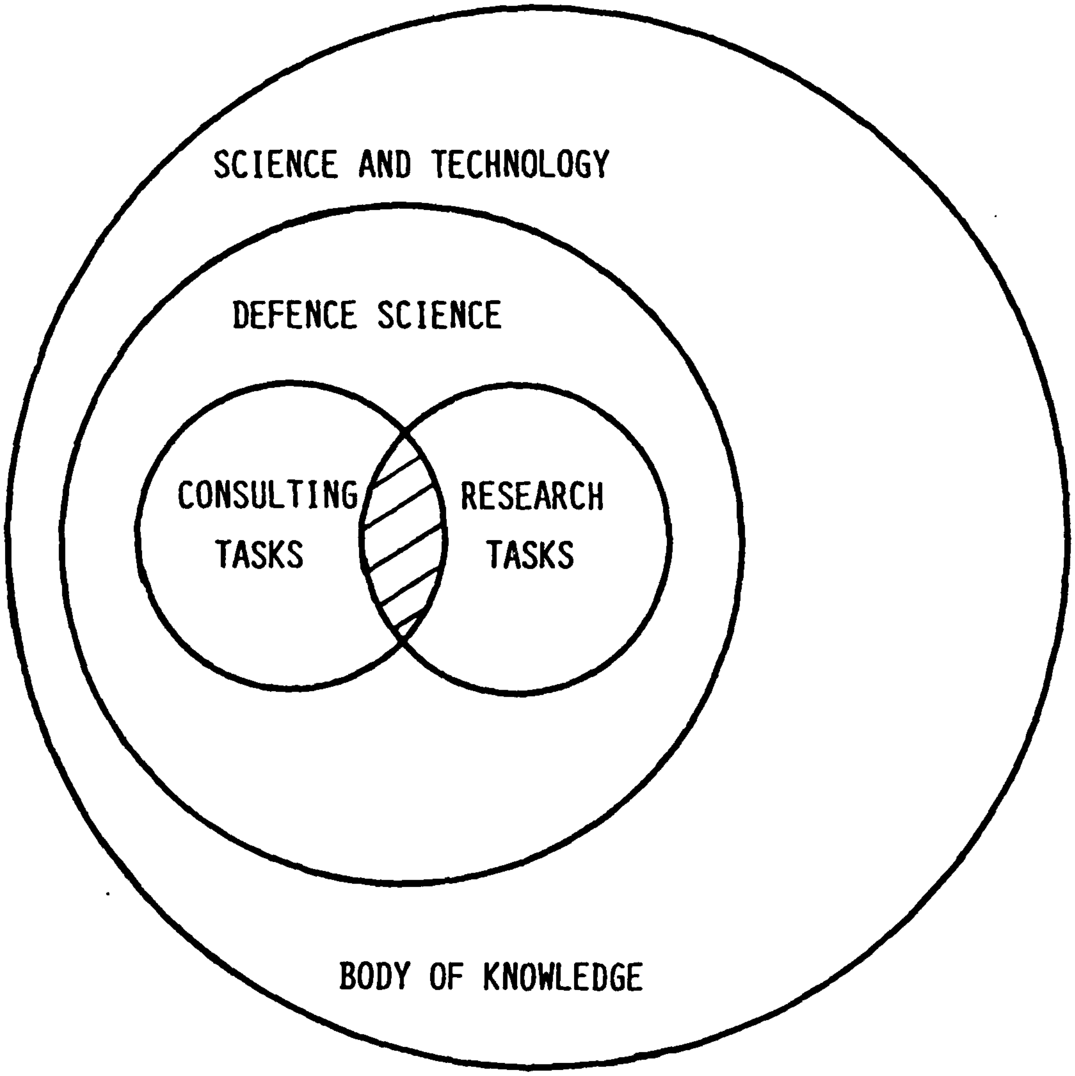

SCIENCE AND TECHNOLOGY
DEFENCE SCIENCE
CONSULTING TASKS
RESEARCH TASKS
BODY OF KNOWLEDGE

Figure 1

THE COST OF CORROSION TO DEFENCE

Jeff Batten

Head, Corrosion Control Group

1. INTRODUCTION

Let us examine the title of this lecture and see what we can learn from that

(i) To Defence. - This is quite clear, but in my opinion the factories must always be included in a technical meeting on corrosion whether or not they are actually in the Department of Defence.

(ii) Corrosion. - We all have had some experience with damage to our cars, etc. due to corrosion. But why is it that, say, a well known 10-year-old family sedan shows severe rust damage while a 20-year-old Wolsley shows no such damage. After all they are both made from similar steels and both have been exposed to the two essential ingredients required for corrosion, namely moisture and oxygen. This simple example introduces two concepts, namely the mechanism of corrosion and the term avoidable corrosion, i.e. corrosion where our technology knew how to avoid the corrosion. Conversely, unavoidable corrosion is that corrosion which occurs because our *technology is lacking*.

(iii) Cost. - Consider our motor car example again. Assume that in Australia there are one million of these sedans on the road, and make the further assumption that over their (average) 20-year life $500 will be spent repairing damage per car that can be directly attributed to corrosion. Then the cost of corrosion damage to these cars alone comes to $25 million per year. Admittedly this is all very rough, but it does give some idea of the magnitude of the problem.

(iv) The. - Placing a "the" before "cost" implies that there is one unique figure. This is certainly not the case, the best estimates that have been made to date can only be classed as educated guesses. Some of these we shall now discuss.

2. THE COST OF CORROSION TO AUSTRALIA IN THE CIVILIAN AREA

The direct annual loss to Australia caused by corrosion has been estimated (1-4) at $500 million (based on 1973 prices) or about 1.5% of our GNP. To arrive at this estimate, the cost of protection and prevention was added to the cost of deterioration due to corrosion.

The above figure does not include indirect losses such as

(a) cost of shut-down and loss of production,

(b) overdesign to take care of corrosive attack,

(c) loss of efficiency due to, for example, corroded heat exchangers,

(d) product contamination, for example to soap, dyes, food and beverages by corrosion products. These industries cannot tolerate the pick-up of even small quantities of metallic ions in their products,

(e) gas leaking from a corroded pipeline may enter a building, causing an explosion with consequent destruction of the building,

(f) food in corroded metal containers may become contaminated by bacteria resulting in serious sickness, and

(g) surface oxidation of an electrical contact could cause the failure of expensive and sophisticated equipment, and this could have serious consequences.

Thus it is quite clear that the total cost of corrosion can be considerably in excess of the figure normally called "the direct loss". This is even more so if the corrosion has resulted in loss of life (e.g. (e) above).

Earlier we introduced the concept of avoidable corrosion and we saw that it was possible to reduce the extent of corrosion simply by applying existing technology. Using this concept of avoidable corrosion, the 1982 figure for the potential economic saving to the Australian economy if optimum corrosion mitigation practice was to be applied universally has been calculated as $2,000 million, where the total cost of corrosion was calculated as $8,000 million.

Other countries have done similar calculations (1-7) and typical figures, for Australia, the UK and the US, are presented in the following table, which show that corrosion losses were estimated as about 2-5% of the country's GNP, and that between 15 and 25% of that loss could have been saved by the application of existing knowledge.

Table

THE COST OF CORROSION AND POTENTIAL SAVINGS

COUNTRY		DIRECT LOSS (M)	% GNP	POTENTIAL SAVINGS (M)
Australia	(1973)	$470	1.5	-
	(1982)	$8,000	5.2	$2,000
UK	(1970)	£1,365	3.5	£310
US	(1975)	$70,000	4.2	$10,000

Although there is a high degree of uncertainty with the figures in the Table the important consideration, germane to this meeting, is that the potentially recoverable costs of corrosion are large.

3. THE COST OF CORROSION TO THE DEFENCE FORCES OF THE USA

The figures that are available (5,6) for this are as follows:

(i) The annual maintenance cost for aircraft directly due to corrosion-control and repair for the Air Force, Navy and Coast Guard has been estimated as $990 million.

(ii) The annual cost for its ships due to corrosion control and repair has been estimated as $7.5 million for the Coast Guard and $392 million for the Navy.

Of the above figures it was estimated that about 15% could have been avoided by makin~ the most economical use of available technology.

4. THE COST OF CORROSION TO THE DEFENCE FORCES OF AUSTRALIA

No figures are available for this so an estimate will be made based on corrosion problems that have come to Corrosion Control Group for solution.

4.1 Estimated Losses Due to Corrosion for the Australian Navy

(i) Corrosion Loss Due to Repairs and Refits

For the financial year 1977/78, it was estimated (8,9) that the Royal Australian Navy spent $26 million on ship repairs and refits, and of that figure 40% (i.e. $10.4 million) was attributed directly to corrosion-related defects.

In order to emphasize the extent of the corrosion damage done to surface ships, a series of slides was shown that illustrated the amount of hull plating and decking that needed to be replaced due to corrosion damage during the modernization of HMAS Parramatta.

(ii) Corrosion Loss Due to Propeller Cavitation

A slide was shown of a propeller that had been fitted to the Navy's 33 ft GRP boats that was badly damaged by corrosion/erosion. Through a design fault, these propellers had had their lives reduced to about 3 months. There are 32 of these boats in service in Australia, each fitted with 2 propellers. It is estimated that each propeller would cost about $500, thus cost per annum of replacing the propellers is about $1.25 million.

(iii) Ikara Missile: Telesender Voltabloc Batteries

The slide showed major corrosion damage to these Ni-Cd batteries. This corrosion damage occurred to about 300 batteries during storage. At a cost of in excess of $100 each, total cost is about $0.05 million.

There is a more insidious aspect to this problem. Use of such a battery could cause an Ikara missile to malfunction, thus affecting the reliability of the missile with a possible concomitant loss of one of our destroyers. What then would be the cost of this corrosion damage?

(iv) Modernization of HMAS Parramatta - Liquid Metal Embrittlement of Steam Piping

After our investigation we recommended that the complete set of installed pipes should be rejected and that another set should be fabricated and installed. This action delayed the completion of the modernization by about 3 months and added an estimated $1 million to the cost of modernization.

(v) Corrosion of Bearings in Storage

The Navy is experiencing a problem of bearings corroding during storage at its Naval Stores at Zetland (NSW). It is estimated that there are more than 2 million bearings in store with an overall purchase price of $2.2 million. The age of much of the stock is in excess of that prescribed by RAN (i.e. > [illegible] years old), and when used the bearings fail prematurely.

It is estimated that the loss to Navy due to this corrosion problem would exceed $1 million per annum.

4.2 Estimated Losses Due to Corrosion for the Australian Army

(i) Magnesium Batteries Used in the Back-Pack Radio

The slide showed batteries that had corroded, with each the corrosion was located near the top of each cell. These batteries had been in storage for less than 12 months whereas the required storage life was five years.

The Australian Army orders about $1.5 million worth of these batteries each year, thus the estimated loss per annum due to corrosion could be $1 million.

(ii) 66 mm Rocket Motors and End Closures

The slide showed the above components with yellow corrosion products associated with inscribed marks on the surfaces of the anodised aluminium. About 10,000 components were in that condition, and if the components could not be refurbished, the loss due to corrosion would amount to about $0.5 million.

(iii) Corrosion Damage - Fuel Tanks - Armoured Personnel Carriers

The slide showed a hole through the fuel tank and the diesel fuel was being kept in the tank by a paint film on the outside of the tank. There are 750 APC's and if 50% were so affected the loss due to corrosion could amount to $2 million, where each tank could cost about $500.

4.3 Estimated Losses Due to Corrosion for the Australian Air Force

(i) Internal Corrosion in DEFA HE Ammunition

The slides showed the inside surfaces of DEFA cases that had corroded. This ammunition was considered to be in an unsafe condition and was destroyed. The estimated loss due to corrosion in this ammunition is put at $2 million.

(ii) External Corrosion of DEFA Practice Ammunition

The slide showed white corrosion products on the outside surfaces of this ammunition. Corrosion had occurred on more than 300 rounds of a consignment transported to Townsville for a RAAF exercise.

Estimated loss due to this corrosion damage $0.05 million.

(iii) Corrosion of C-12 Compass Amplifier Power Supply

The slide showed that the underneath surface of an electronics board was not corroded whereas the upper surface was. This electronics board forms part of the compass of an Hercules aircraft. Many of these boards have been similarly damaged, and the estimated loss due to this corrosion is put at $0.05 million.

(iv) Flexible Wave Guides

The slide showed that corrosion had occurred on the internal surfaces of the wave guide. Many similar examples exist, and the estimated loss due to this corrosion is estimated at $0.5 million.

4.4 Estimated Losses due to Corrosion for the Australian Defence Factories

(i) Premature Failure of BAMAG Pots

The slide showed a pot that had been perforated by corrosion above the concentrated acid outlet pipe. This pot had had a life of about 1 month rather than the expected life of 2 years. Each pot costs $16,000 and this fate was typical of several pots. Estimated loss due to corrosion is placed at $0.5 million p.a.

4.5 Summary

The total loss per annum due to corrosion damage outlined in the examples above comes to about $20 million. However, at most, these examples would represent not more than half the number of corrosion problems that come to Corrosion Control Group per annum for solution. If we assume that the above examples are representative of the whole, it would appear reasonable to double the above figure. Thus, from corrosion cases that come to Corrosion Control Group in a year, it can be estimated that the cost of corrosion damage to Defence amounts to at least $40 million per annum.

Our experience indicates, however, that the number of problems that come to Corrosion Control Group for solution is no more than "just the tip of the iceberg". If this is the case then the true cost of corrosion damage to Defence is probably close to $400 million per annum.

5. ESTIMATE OF COST SAVINGS TO DEFENCE THROUGH REFURBISHMENT OF COMPONENTS

5.1 Examples

(i) Storage of PDM 48 Fuze Bodies

Slides were shown of a corroded fuze, the package in which they had been stored, and the package in which they are now stored. There were 45,000 of these fuzes in storage and they were found to have corroded after only one year in storage. The required storage life was 20 years. The corroded fuzes were reclaimed and packaged in an MRL-designed container with another 45,000 fuzes.

These 90,000 fuzes have been in storage for 10 years and when last inspected (12 months ago) were still in pristine condition.

Estimated saving - $1 million.

(ii) Radio Terminal Set AN/MRL-127-FI

Slides were shown of imperfect silver plating on cast and wrought aluminium components from this radio. There were 100 sets all with defective silver plating, with a total value of $5 million. A method of refurbishment was suggested.

Estimated saving - $5 million.

(iii) Pontoon Foot Bridge

Slides were shown of corroded foot bridges. We were able to show that these foot bridges were still satisfactory for service and need not be replaced.

Estimated saving - $0.2 million.

(iv) Low Band Aluminium Heat Exchanger Assemblies from the F111C Aircraft

Slides of a corroded heat exchanger assembly were shown. A method of refurbishment was suggested.

Estimated saving - $0.5 million.

It should be mentioned that at the time it was not possible to buy replacement parts.

(v) DEFA Cartridge Cases

A slide was shown of corrosion occurring on the base of these cases. 210,000 cases were affected and subsequently reclaimed.

Estimated saving - $2 million.

5.2 Summary

The total saving per annum due to refurbishment of corroded components in the examples outlined above comes to about $9 million. Again, as was done previously, this figure can be doubled and then making allowance for "the tip of the iceberg", it is probably safe to estimate that, through refurbishment of corroded components, Corrosion Control Group could save Defence (say) $150 million per annum.

6. CONCLUDING REMARKS

Whether the above educated guesses are accepted or not, there is little doubt that the cost of corrosion to Defence runs into many millions of dollars per annum, and that groups such as Corrosion Control Group can achieve considerable savings not only by suggesting refurbishment procedures but also by ensuring that the same mistakes in the design that caused that corrosion are not repeated. Notwithstanding the above, although the cost of controlling corrosion is high, for the fighting soldier failures due to corrosion can have catastrophic effects. Reliability of equipment must take priority over the added cost to corrosion control measures.

7. REFERENCES

1. B.W. Cherry and B.S. Skerry, "Corrosion in Australia". The Report of the Australian National Centre for Corrosion Prevention and Control Feasibility Study, Department of Materials Engineering, Monash University, Australia, June 1983.

2. L.H. Keys, "Corrosion and its Effect on the Market Place", Conference of the Australasian Institute of Metals, 1978.

3. R.W. Revie and H.H. Uhlig, "The Cost of Corrosion to Australia", The Journal of The Institution of Engineers, Australia, March-April 1974, pp. 3-5, 11.

4. L.L. Shreir, "Corrosion", Newnes - Butterworths, London, 1976, Chapter 10.

5. L.H. Bennett, J. Kruger, R.L. Parker, E. Passaglia, C. Reimann, A.W. Ruff, H. Yakowitz, and E.B. Berman, "Economic Effects of Metallic Corrosion in the United States", NBS Special Publication, 511-1, 1978.

6. J.H. Payer, D.G. Dippold, W.K. Boyd, W.E. Berry, E.W. Brooman, A.R. Buhr and W.H. Fisher, "Economic Effects of Metallic Corrosion in the United States", NBS Special Publication, 511-2, 1978.

7. "The Cost of Corrosion" in EMD Anti Corrosion Review, Engineering Materials and Design, September 1971, pp. 765-767.

8. Rear Admiral M.P. Reed, "Corrosion Prevention is Everybody's Business", Fleet Maintenance Bulletin, Australia, November 1977, pp. 3-11.

9. P.G.V. Dechaineux and M. Mulligan, "Corrosion - Our Continuing Common Enemy", Lecture presented to the Commonwealth (Naval) Engineer Officers' Symposium at Nirimba, Australia, December 1978.

INVESTIGATING CORROSION FAILURES:

A SUMMARY

Peter Knuckey

Corrosion Control Group

1. INTRODUCTION

Corrosion of a metal is broadly defined as reaction with its environment involving conjoint chemical and electrical effects. The former is readily seen while the latter, although generally not noticeable, is important in some corrosion prevention techniques (eg. cathodic protection) and theoretical measurements.

The aims of a corrosion failure investigation are:

(i) to provide a rapid solution to a particular problem and

(ii) to prevent its re-occurrence by improvement to design, operational procedures, etc.

We must decide what factors (environmental, material or operational) are responsible, then if possible to change these to prevent failures from occurring.

2. ANALYSIS

The main sources of information available to us in this scientific detection work are:

2.1 Visual examination of a corroded component (macro examination with binocular assistance). This is the preliminary examination in conjunction with the verbal information from the customer; for example, corrosion product and other marks inside certain corroded stainless steel fire extinguishers indicated they had been filled for an extended period, whereas they were alleged to have been empty over this time. The location of corrosion, its form, and pattern also give useful information.

2.2 Corrosion forms - recognition. Some corrosion forms are recognisable. A practical division is as follows:

a. *Uniform* - very common, but not very informative.

b. *Pitting* - localised corrosion more common in passivating metals, e.g. aluminium alloys, stainless steels, etc.

c. *Galvanic (bimetallic)* - effect of two dissimilar metals coupled together - one may corrode at an accelerated rate. The other is protected. Sometimes recognisable.

d. *Crevice (differential aeration, poultice attack, deposit attack, etc).* Effect of crevice or area shielded by inert deposits on certain metals in agressive environments. Form generally recognisable by its localised nature and geometrical location. Filiform (or "Worm Track") corrosion is another example.

e. *Selective leaching.* Selective corrosion of one or more phases in a multi-phase alloy. Dezincification of brasses is a common example. Easily recognised by colour and by matrix softness.

f. *Intergranular attack.* Corrosion around grain boundaries. Little loss of metal but extreme loss of physical properties. Easily recognised metallographically.

g. *Stress corrosion.* Conjoint action of tensile stress plus corrosion - recognisable cracking. Specific metals and environments.

h. *Erosion corrosion.* Effect of moving liquid on metal.
Impingement ("horseshoe" pits) at medium speeds (generally in saline waters).
Cavitation (rapid metal loss, characteristic deep sharp edged pits) where sudden pressure changes occur in liquid, especially at higher speeds.
At very high speed erosion of the metal may occur. All easily recognised.

2.3 Chemical approach. Analysis of corrosion products gives much evidence as to the actual corrosive environment.

Unusual corrosion product composition can indicate previously unrecognised problems originating in other areas, eg. the presence of nitrate and formate corrosion products inside 20 mm DEFA rounds indicated not only short term propellant deterioration (presence of nitrate) but advanced deterioration (presence of formate indicating earlier presence of formaldehyde).

Nitrates/nitrites may also indicate unwanted electrical discharge.

In the negative sense, the absence of recognised corrodents such as chloride or high acidity may indicate that corrosion is being accelerated by a non-chemical factor such as an unexpected bimetallic effect, etc.

Analysis methods used are:

(i) Chemical spot tests. Used to quickly detect small amounts of suspected corrodent, eg. chloride.

(ii) Instrumental methods:

(a) X-ray diffraction - identification of crystalline compounds.

(b) Scanning electron microscopy with energy dispersive x-ray analysis. Electron probe microanalysis. X-ray fluorescence. Atomic absorption spectroscopy. These methods identify elements.

(c) IR absorption spectroscopy. The identifies radicals, sometimes compounds.

X-ray fluorescence and atomic absorption spectroscopy are commonly used to determine or verify the composition of metallic components.

No one method of examination will necessarily give all the information required and several methods may be needed.

Examination of surfaces to detect and identify foreign embedded particles can be readily carried out in the Scanning electron microscope.

2.4 Metallurgical examination. Metallographic factors (eg. susceptible structure or phase) may be relevant. These are detected by standard metallographic techniques.

3. CAUSE

Having assembled the facts from the previous examinations a proposed cause can generally be derived. This must be compatible with generally accepted corrosion theories.

Having derived the cause, is the failure an isolated instance or does it indicate a wider problem?

The importance of not interfering with corroded samples (eg. removal of a corrosion product etc) is stressed.

Practical application of these approaches was illustrated by detailed examination of several cases, eg. corrosion of transistor leads from communications equipment (deteriorated polychloroprene rubber sleeves), corrosion of APC fuel tanks (crevice corrosion by fungal mats), the use of sea-water resistant materials to prevent crevice corrosion under seals (RAN submarine periscopes), and problems arising within airborne radar equipment due to internal electrical arcing.

4. SUMMARY

In summary, the intention has been to show

(a) how evidence can be gained by visual, surface analysis techniques, chemical and metallurgical laboratory examination of corroded components, and

(b) the breadth of circumstances, materials and components which can be involved in corrosion failures, and which we have tackled in Corrosion Control Group.

If you have corrosion problems, no matter how outlandish, please consult us at an early stage.

STRESS CORROSION CRACKING:

A BRIEF OVERVIEW

D.S. SAUNDERS

Defence Fabrication Technology Group

INTRODUCTION

Stress corrosion cracking (scc) is a common phenomenon in many metallic systems and is often responsible for the failure of components and structures. It is defined as the nucleation and growth of a crack in a material in the presence of *both* a sustained tensile stress *and* a specific corrosive environment. The rate of crack growth under these conditions is faster than either under only corrosive environment or under only the tensile stress. Thus stress corrosion cracking can be regarded as the synergistic effect of a tensile stress with a specific environment.

There are no hard and fast rules for determining the alloy system/ environment combinations which lead to stress corrosion cracking. There are many systems and environments which produce scc and these are well documented [1]. Particular emphasis has been placed on aluminium alloys [2,3]. Examples of stress corrosion cracking are:

- "season cracking" in brass cartridge cases in an ammonia environment.
- aluminium alloy 7039-T6 in an industrial atmosphere.
- austenitic stainless steel in acidic chloride solutions or alkaline solutions.
- martensitic stainless steels in chloride, nitrate and hot caustic solutions or hydrogen sulphide.
- titanium alloys in chloride, iodide or bromide solutions.

The mechanisms of stress corrosion cracking are not discussed in this brief overview, however it is worth noting that in many metals stress corrosion cracks are intergranular.

2. STRESSES IN COMPONENTS AND MATERIALS

In manufactured components there are several sources of sustained tensile or shear stress which can be responsible for stress corrosion cracking. These can be the result of:

- residual stress in the component or parent material.
- installation stresses.
- service or induced stresses.

Several examples of the contribution of these to stress corrosion cracking are appropriate. For example, it is considered that in the US aerospace industry 70% of stress corrosion failures are the result of a sustained, unintentionally induced or residual tensile stress in the short transverse direction in fabricated parent material [2]. As another example, during the manufacture of equipment and structures, component mismatch or distortion which is overcome by bolting or clamping into position can also lead to high tensile stresses. Similarly, interference fits can sometimes produce high tensile stresses.

High residual tensile stresses can also be present in plate materials as a result of rolling operations and in other sections as a result of extrusion. The welding of materials can also induce tensile residual stresses as well as other metallurgical changes which render the component particularly susceptible to scc.

Compressive stresses on the other hand do *not* contribute to stress corrosion cracking; indeed induced compressive stresses can sometimes be used to suppress stress corrosion cracking in some materials which otherwise are particularly sensitive to scc.

3. THE MEASUREMENT OF THE SUSCEPTIBILITY OF A MATERIAL TO STRESS CORROSION CRACKING

In order to assess the suitability of materials for applications in environments which may possibly produce stress corrosion cracking a range of tests have been devised to test susceptibility to stress corrosion cracking [2,4,5]. In some cases an accelerated test is desirable, however the limitations of such a test must be recognised; viz the result from the accelerated test may not reflect behaviour in the service environment. A cycle used for the accelerated testing of aluminium alloys is immersion in a 3.5% NaCl solution for 10 min with 50 min drying; the test running from 30 to 180 days [6].

Test methods for the assessment of susceptibility to stress corrosion cracking are covered by a number of standards [7,8,9]. Three techniques which are commonly used are briefly discussed here, and summarized in Table 1.

(1) The simplest and most commonly used technique is to use a series of uniaxial, tensile specimens (or other simple geometries) with regions subject to tensile fibre stresses (Figure 1) exposed in a corrosive environment. These tests will give a stress level below which failure by scc does not occur; viz a threshold stress. For a series of tests of this type the results could be assessed statistically and a mean critical stress determined. Similarly for a given range of stress levels, it is possible to determine a mean time-to-failure.

(2) The second method of assessing susceptibility to stress corrosion cracking is by the use of the slow strain rate test method for tensile specimens using a machine (and method) developed by Parkins [10]. The theory behind this test method is that if a tensile specimen is deformed at a very slow strain rate in an environment conducive to stress corrosion cracking then the fracture strain may be lower than if the specimen was strained in an "inert" environment. Further, it appears that the ratio of the ductility in the aggressive environment to the ductility in the "inert" environment is a measure of the susceptibility of the material to stress corrosion cracking. This particular method was developed initially for iron-base alloys and, more recently, it has been applied to aluminium alloys. In the case of some aluminium alloys there have been some unusual results. It has been found that the ranking of a series of aluminium alloys using the slow strain rate method is not necessarily the same as that obtained by other scc test methods. A further factor which complicates the interpretation of results from slow strain rate tests is that the parameter measured using this technique (viz ductility ratio) may also be sensitive to the strain rate of the test. For example, the 2000 series aluminium alloys appear less sensitive to strain rate than the 7000 series alloys whereas in fact the reverse situation is true.

While the slow strain rate appears to have inherent characteristics which may produce results which are different to or possibly in conflict with those obtained by other stress corrosion test techniques, the gradual accumulation of data by the use of this test method should provide a valuable alternative data base for structural materials.

(3) The method which appears most suitable to components is through the use of fracture mechanics [4], where the response of pre-cracked specimens to an aggressive environment is measured. The fracture mechanics approach allows the measurement of:

- a fracture stress
- a crack growth velocity
- a threshold stress intensity factor below which cracks do not propagate; this parameter is designated K_{Iscc}.

There is a range of stress corrosion fracture mechanics test specimens available [4,5] for the assessment of materials. These specimens can be either self-loaded or externally loaded. See Figure 2 for details of some commonly-used stress corrosion fracture mechanics test specimens. The most common specimen is the double cantilever beam although other more compact specimens are catered for in the appropriate standards. The fracture mechanics specimens can be used in the following way:

(1) By calibrating the specimen and measuring the edge opening displacement of the specimen this can be related to the stress intensity factor, K. For a constant load, crack velocity V will increase with the crack length because K also increases with crack length.

(2) With the self-loaded specimen it is possible to measure crack growth velocity and a K value at which the crack arrests (or at least the velocity is extremely low, say 10^{-11} m/sec). This threshold is known as K_{Iscc}.

Values of K_{Iscc} for many materials (particularly metals) in a range of conditions of fabrication are well documented, see for example the Damage Tolerant Design Hand Book [11]. However, from a design point of view, it is desirable that the K_{Iscc} value be measured using the material in the fabricated condition and in the service environment as well as using an accelerated test environment.

The general form of the information obtained from the stress corrosion test is a plot of crack growth velocity against the applied stress intensity factor, ie the V-K plot which is illustrated in Figure 3. A typical family of V-K curves for an aluminium alloy is shown in Figure 4, [12].

The most important use for the V-K curves is that they allow alloys in similar environments to be compared on a quantitative basis. Further, it has been suggested that the information from stress corrosion tensile tests and stress corrosion fracture mechanics tests be combined to produce a failure diagram, illustrated in Figure 5. This diagram is potentially useful for engineering applications because it incorporates flaw size. Using a stress corrosion failure diagram for a particular family of alloys an estimate of critical flaw size can be made with a reasonable degree of confidence.

4. REDUCING THE POSSIBILITY OF FAILURE DUE TO STRESS CORROSION CRACKING

Where stress corrosion failures have occurred or where stress corrosion cracking has occurred during an accelerated test then appropriate steps must be taken to reduce the possibility that this mechanism of failure will occur in service. Similarly, when designing new components an attempt must be made to reduce stress corrosion cracking. This can be done by:

* Materials Selection

This can be based on information derived from stress corrosion tests or from documented information on material/environment interactions. It is important to realize that the selection of an alternative material which is known to have an increased resistance to stress corrosion cracking may necessitate a design change in the component or structure because of possible commensurate changes in material properties, eg reduced tensile properties.

- Modification of the Environment

It may be possible to change the corrosive medium to allow the use of a particular material for a specific application. For example, by changing the pH range of a solution (by buffering) it may be possible to reduce the susceptibility of a material to stress corrosion cracking. Also, it is well known that in the case of aluminium alloys stress corrosion cracking is exacerbated by increasing relative humidity. A "dry" atmosphere greatly reduces the crack growth velocity in aluminium alloys [12,13].

As a result of environmental considerations it is important that the conditions of storage of components and equipment be examined, particularly where components are required to have a long storage life (eg weapon systems and ammunition).

The presence of residual stresses in the parent material (e.g. from rolling or extrusion) may be reduced by heat treatment or stress relief. Induced tensile stresses in fabricated components can be reduced by improved design and manufacturing techniques.

- Modification of the Material

The material can be modified by the use of alternative heat treatments. In the cases of age-hardening aluminium alloys the over-aged conditions are more resistant to stress corrosion cracking than the peak-aged conditions (Fig. 6). In the aerospace industry the 7000 series alloys are usually used in the T7 condition (over-aged) which is more resistant to stress corrosion cracking than the T6 condition (aged to peak tensile strength) [2]. That is, the V-K plateau is measurably reduced and K_{Iscc} is often reduced by this treatment [12-14].

Alloying additions may influence the susceptibility of materials to stress corrosion cracking. Extensive work has been conducted on aluminium alloys, particularly in welding technology where alloying additions to the filler wires are used to increase the resistance of welds to stress corrosion cracking [15]. Also, extensive research has been undertaken in the cases of heat treatable aluminium alloys (the 7000 series in particular) in an attempt to improve the resistance of these important alloys to stress corrosion cracking [16 to 18].

- Surface Treatment of Materials

The surface treatment of a material may reduce its susceptibility to stress corrosion cracking. One method is to introduce a compressive residual stress in the surface layers by shot peening since stress corrosion cracks do not propagate under compressive stresses.

Where "end grain" of rolled or extruded products is exposed it is desirable that it be protected from the aggressive environment. (In the case of some aluminium alloys this can be the atmosphere and so the laying of "buttering welds" on the "end grain" is one method of protection [19]). Coatings and paints can be used to protect surfaces and "end grain", however it is considered more important to start with careful materials selection and component design.

5. SUMMARY

This brief overview has attempted to summarize the main points about the phenomenon of stress corrosion cracking. Clearly there is a large amount of written information on the subject available which would enable "informed" materials selection and component design, see for example [11]. Where information does not appear to be available then a range of tests to determine the degree of susceptibility of a material to stress corrosion cracking can be used. Some care must be taken when using results obtained from accelerated tests for stress corrosion cracking, as discussed above, however the accelerated test is most valuable to determine if a material is intrinsically sensitive to an aggressive environment.

6. REFERENCES

1. American Society for Metals, "Stress Corrosion Cracking" in Metals Handbook Vol. 10, 8th ed., Failure Analysis and Prevention, 1975, pp 205-277.

2. Spiedel, M.O. "Stress Corrosion Cracking of Aluminium Alloys", Metallurgical Transactions, 64, 1975, pp 631-651.

3. Sprowls, D.O. "High Strength Aluminium Alloys with Improved Resistance to Corrosion and Stress Corrosion", 1976 Tri-Service Conference on Corrosion, Metals and Ceramics Information Center, Battelle Columbus Labs., MCIC-77-33, 1977, pp 89-120.

4. Smith, H.R. and Piper, D.E. "Stress Corrosion Testing with Precracked Specimens", in Stress Corrosion Cracking in High Strength Steels and in Titanium and Aluminium Alloys, ed Brown, Naval Research Labs., 1972, pp 18-27.

5. Ailor, W.H. "Stress Corrosion Cracking", Handbook on Corrosion Testing and Evaluation, Wiley, NY, 1971, pp 261-269.

6. American Society for Testing and Materials, "Alternate Immersion Stress Corrosion Testing in 3.5% Sodium Chloride Solutions", Annual Book of Standards, 03.02, 1983, Standard G 44-75.

7. Ibid. "Preparation and Use of Direct Tension Stress Corrosion Test

Specimens", Standard G 49-76, 1983.

8. Ibid. "Making and Using C-Ring Stress Corrosion Test Specimens", Standard G 38-73.

9. Ibid. "Making and Using U-Bend Stress Corrosion Specimens", Standard G 30-79.

10. Parkins, R.N. "Constant Strain Rate Stress Corrosion Testing", in NATO Advanced Study Institute Series, Stress Corrosion Research, ed Arup and Parkins, Sijthoff and Noordhoff, Netherlands, 1979, pp 1-27.

11. The Damage Tolerant Design Handbook, A Compilation of Fracture and Crack Growth Data for High Strength Alloys, Metals and Ceramics Information Center, Battelle Columbus Labs., MCIC-HB-01, 1975, section 6.

12. Spiedel, M.O. and Hyatt, M.V. "Stress Corrosion Cracking of High Strength Aluminium Alloys", in Advances in Corrosion Science and Technology, Vol 2, Plenum Press, NY, 1972.

13. Moren, K.E. and Nordberg, H. "The Effect of Quenching Rate and Aging Conditions on the Stress Corrosion Cracking of An Aluminium-Zinc-Magnesium Alloy", Scandanavian Journal of Metallurgy, 7, 1978, 29-32.

14. Thompson, D.S. "High Strength Aluminium Alloy Development", Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio, AFML-TR-73-18, 1973.

15. Cordier, H. and Polmear, I.J. "Effects of Filler Composition and Post-Weld Heat Treatment on Intercrystalline Fracture in a Welded Al-Zn-Mg Alloy", Eurocor 77, Proc. 6th European Congress on Metallic Corrosion, London 1977, pp 607-613.

16. Adler, P. and Delasi, R. "Avoidance of Stress Corrosion Susceptibility in High Strength Aluminium Alloys by Control of Grain Boundary and Matrix Microstructure", Grumman Aerospace Corp. Report RE-468, January 1974.

17. Kent, K.G. "Engineering and Metallurgical Factors Affecting the Stress Corrosion Behaviour of Weldable Al-Zn-Mg Alloys", Monash University School of Engineering, Civil Engineering Dept. Report RS-22, 1969.

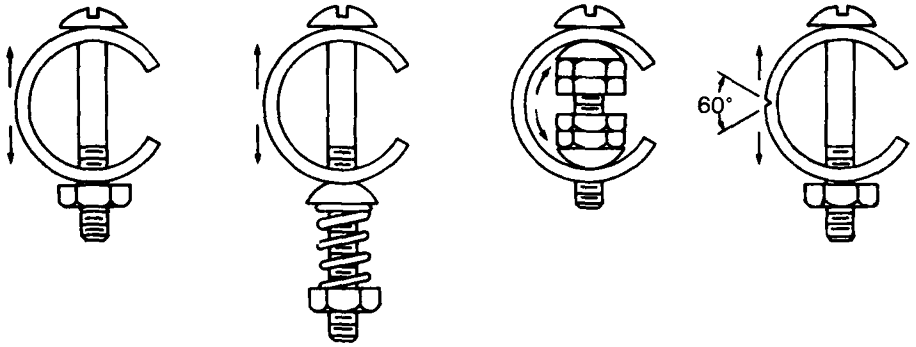
18. Kent, K.G. "Microstructure and Stress Corrosion Resistance of Al-Zn-Mg Alloys", Journal of the Australian Institute of Metals, 15, 1970, pp 171-178.

19. Barnes, R.C. "FSV Scorpion Turret P2", Materials Research Labs. Metallurgy Division Report, MD 80-5, 1980.

TABLE 1

Assessment of the Susceptibility of a Material to Stress Corrosion Cracking

Stress Corrosion Test Method	Stress Corrosion Test Result
Constant Stress or Strain using notched or un-notched tensile specimens. ASTM G-49 ASTM G-38 ASTM G-30	Time to Failure, Threshold Stress, Mean Critical Stress or Strength
Constant Strain Rate using notched or un-notched tensile specimens. Parkins slow strain rate machine.	Ratio of Fracture Strain in an aggressive environment to fracture strain in "inert" environments.
Fracture Mechanics using pre-cracked specimens.	Fracture Stress, Threshold Stress Intensity Factor, K_{Iscc} Stress Corrosion Crack Velocity against Stress Intensity Factor V-K curve

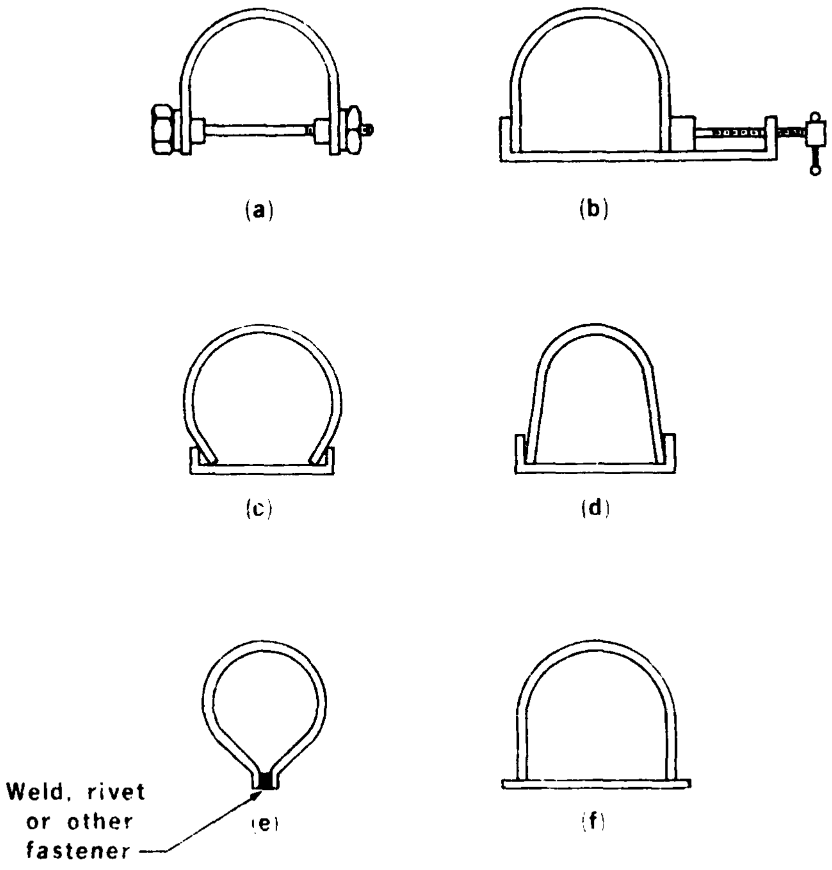


(a) CONSTANT STRAIN

(b) CONSTANT LOAD

(c) CONSTANT STRAIN

(d) NOTCHED C-RING



Typical Stressed U-Bends

Figure 1. Some examples of self-loaded specimens for the assessment of susceptibility to stress corrosion cracking, [8,9].

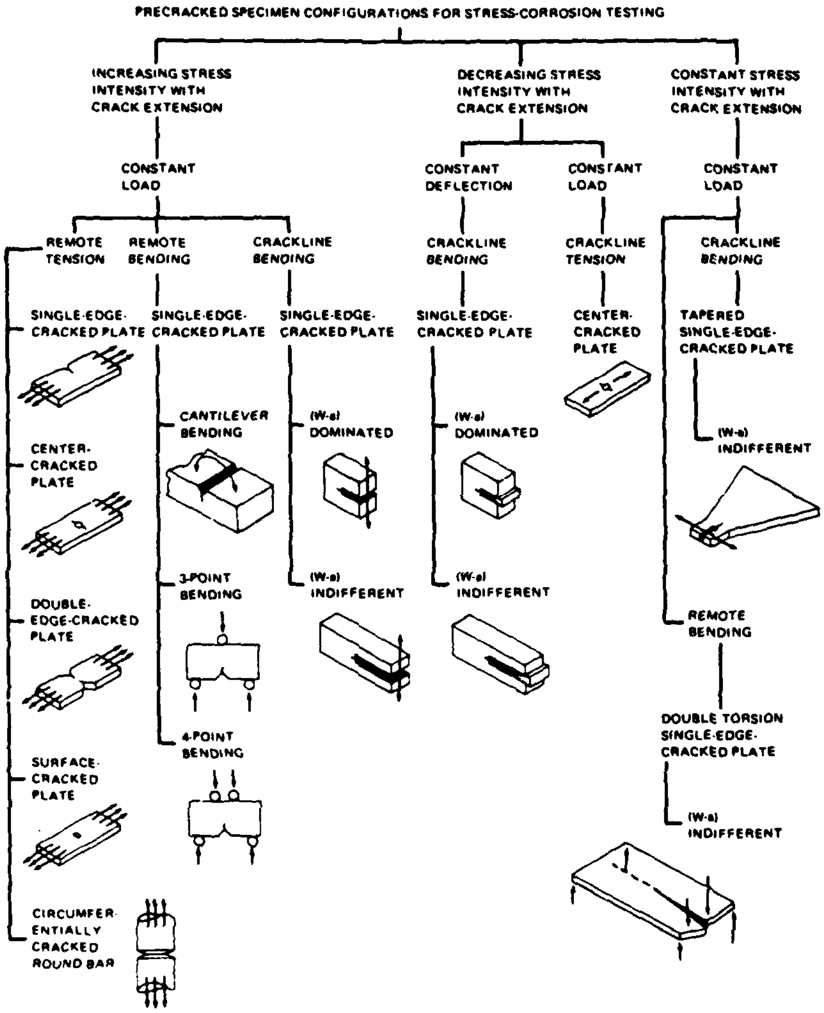


Figure 2. Pre-cracked specimens for stress corrosion fracture tests, [4].

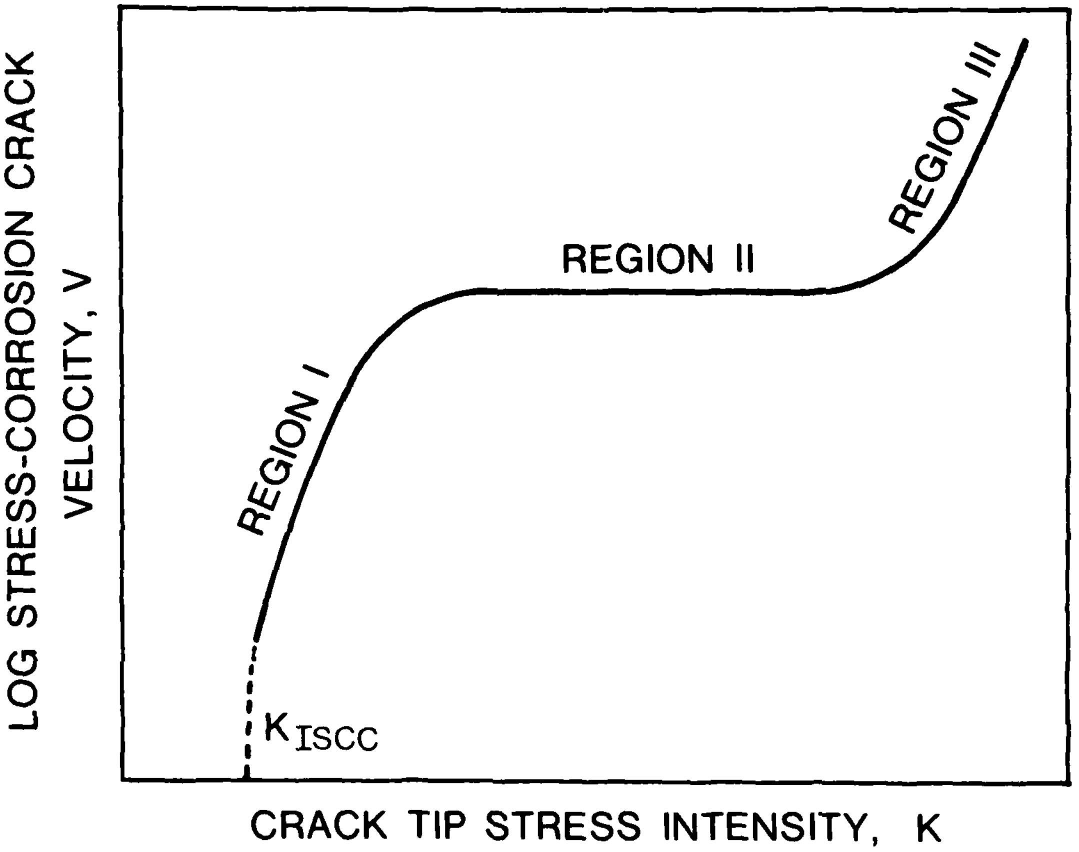


Figure 3. The stress corrosion V-K plot; region II is most significantly affected by environment and metallurgy.

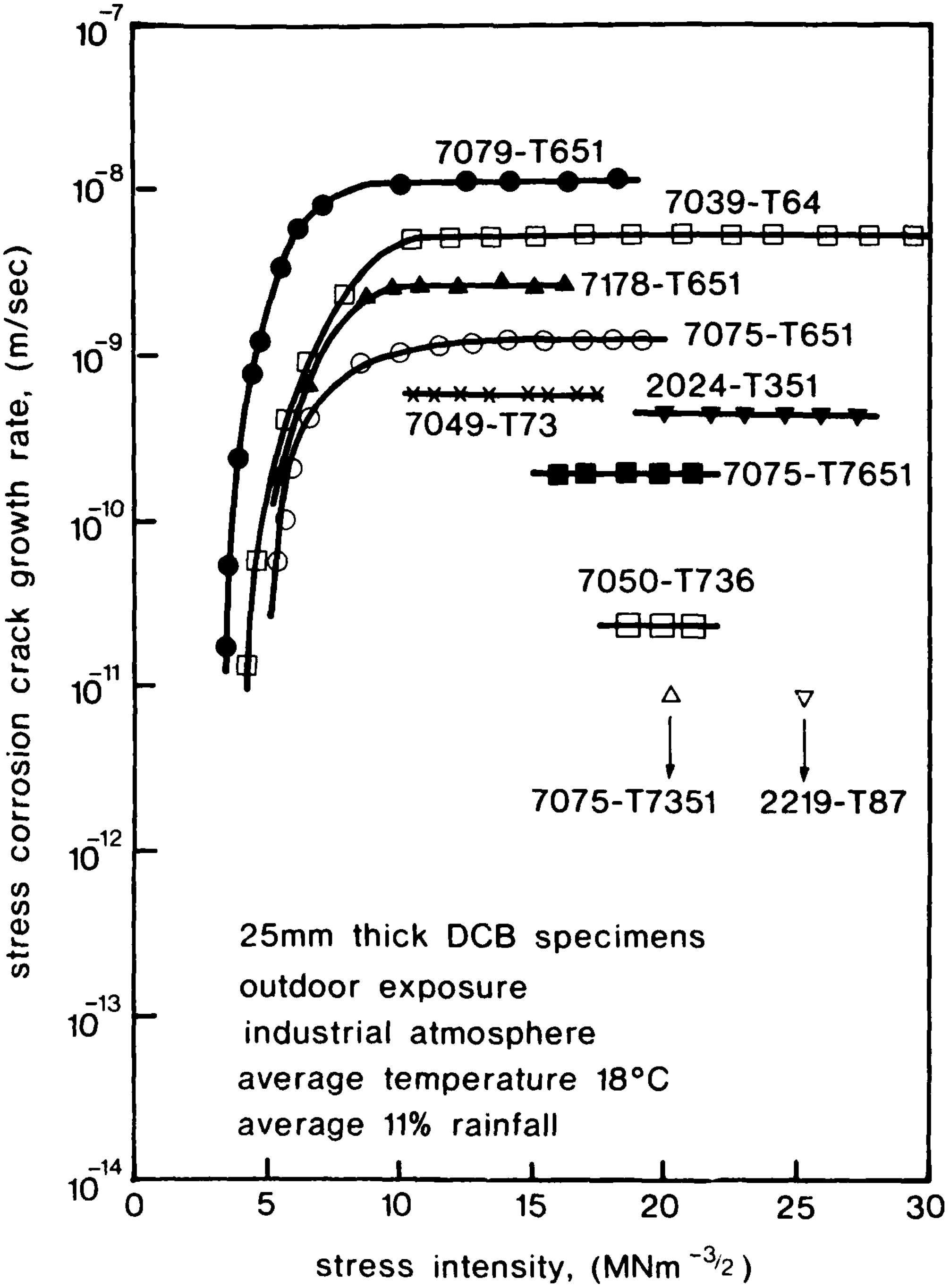


Figure 4. Stress corrosion crack growth rates of high strength wrought aluminium alloys in an industrial atmosphere, [12].

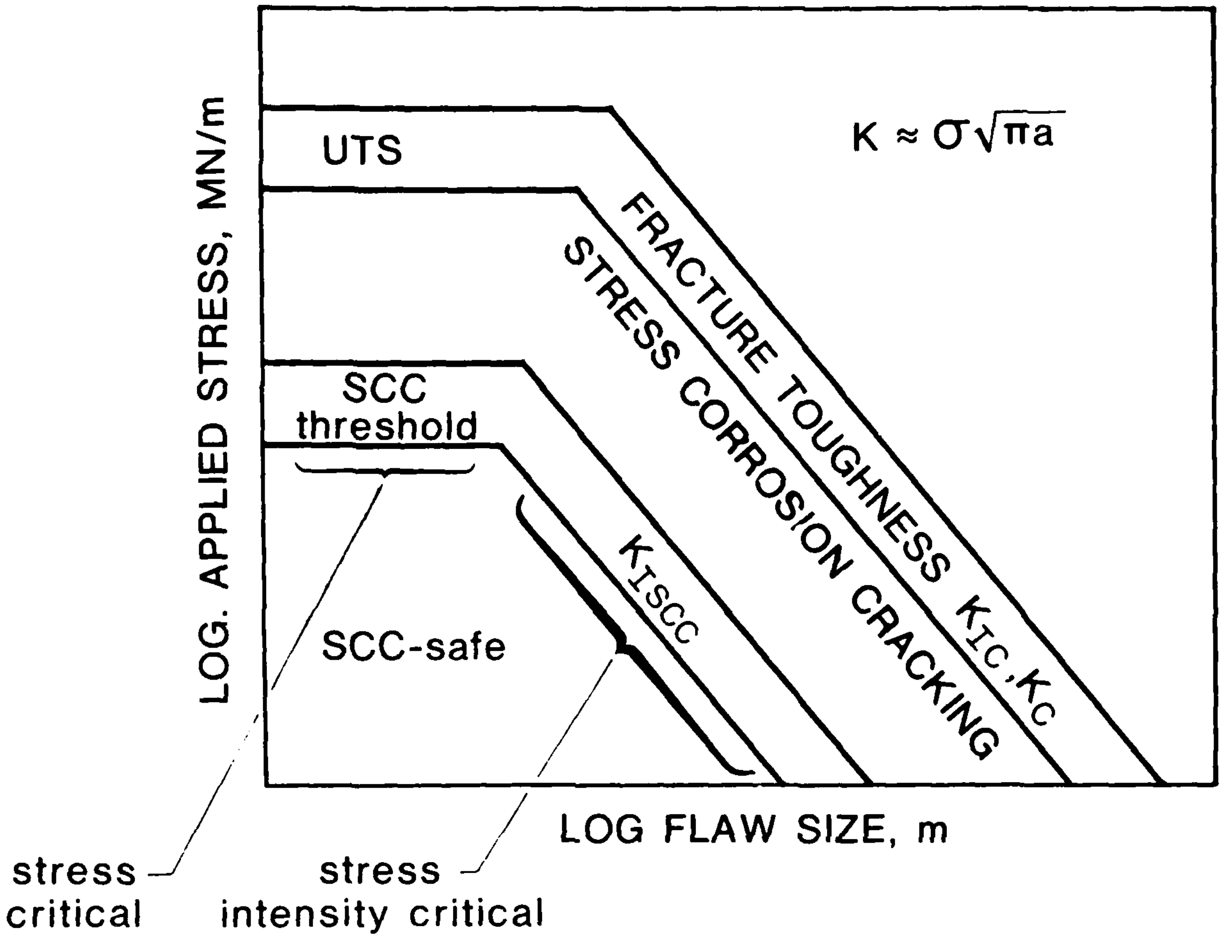


Figure 5. A schematic diagram of materials properties which measure the resistance to fracture under monotonic loading in an aggressive environment. The diagram combines information from smooth specimens and from fracture mechanics tests, [2].

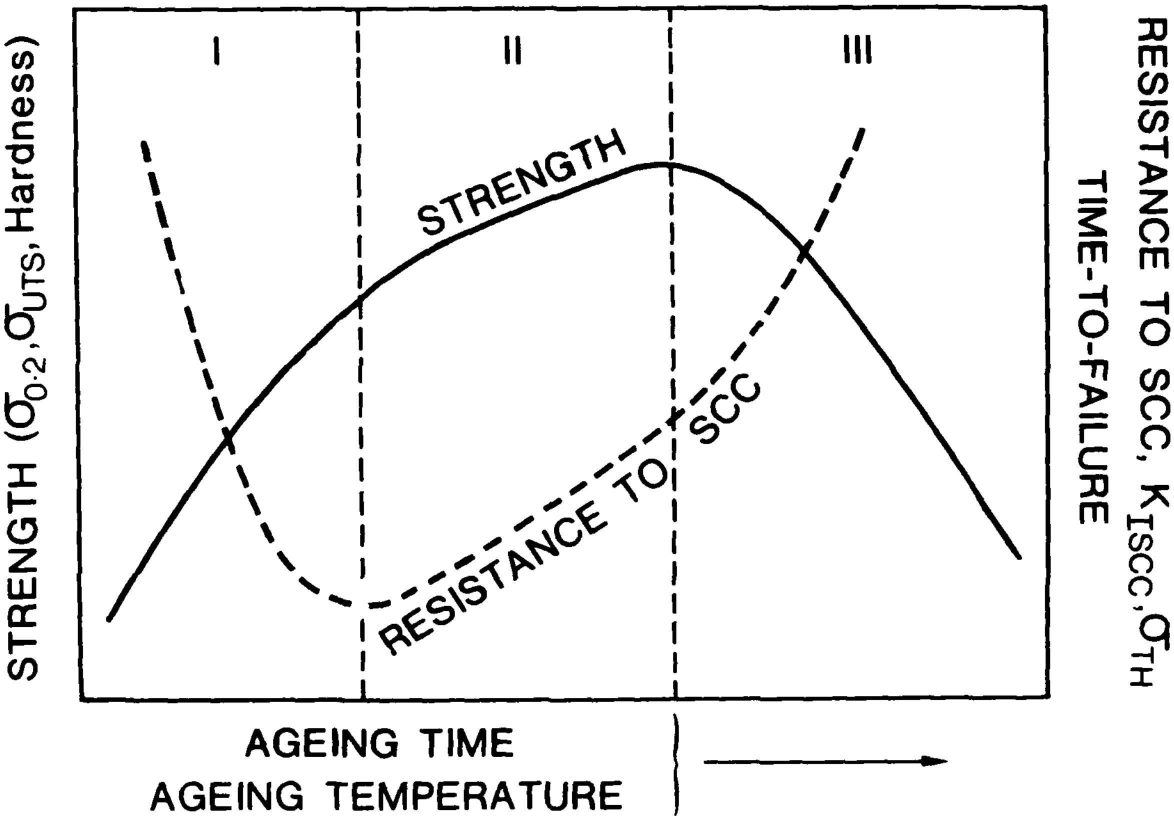


Figure 6. A schematic diagram showing the general relationship between aged condition and resistance to stress corrosion cracking in high strength aluminium alloys, [2].

CORROSION MONITORING:

A BRIEF OVERVIEW

Don Wright

Corrosion Control Group

1. INTRODUCTION

Corrosion monitoring may be defined as the use of electrochemical measurements made at a corroding metal/solution interface to give quantitative data on the rate and mechanism of the loss of metal at that interface. At MRL we utilize a number of techniques for these purposes which we apply under computer control for the collection of the experimental data and its subsequent analysis. Our aim is to give rapid answers as to the nature, extent and seriousness (to the customer) of metal loss caused by corrosion.

Our corrosion monitoring methods may be described as the application of a number of accelerated corrosion tests under varied and easily reproducible laboratory conditions. The methods are both powerful and flexible and, by use of microprocessors and minicomputers, are applied under close scrutiny and control. This is very important for any accelerated test, as all too frequently controversy arises in the interpretation of the test results, or about their reproducibility under field - i.e. long term - conditions.

2. METHODOLOGY

Basically our experimental technique requires that a corroding metal or metal alloy electrode and its equilibrium interface with a solution be perturbed by controlled voltage changes for varying periods of time. By monitoring the electronic changes brought about we are able to deduce parameters that describe metal loss due to corrosion. This can often be achieved in a few minutes and yield results that otherwise would be quite likely to require lengthy field trials. In some cases the metal loss we are measuring can be of the order of a few micrometers a year. Mechanistic information about the chemical reactions of the corrosion process can frequently be deduced and both anodic and cathodic components of these reactions followed quantitatively. This is greatly assisted by the speed and flexibility of the computer control we now tend to take for granted.

3. APPLICATIONS

The techniques are versatile and can be applied to, for instance,

(a) monitor the chemical machining of aircraft alloys which is dimensionally of the order of mm/minute,

(b) or applied to electroless plating which is metal deposition based on chemical, particularly reduction, reactions and is dimensionally 10-15 μm/hour,

We have used it in the laboratory to study,

(c) the corrosion of sintered tungsten alloys with corrosion rates of a few microns/year; and

(d) the corrosion of mild steel (protected by inhibitors) in a chilled water system that is still functioning without leaking after two decades.

Also in the laboratory we have studied,

(1) the corrosion of Ni/Al bronze in neutral solution,

(2) the inhibited corrosion of mild steel in sulphuric acid,

(3) comparison and ranking of a number of samples of non-magnetic stainless steels.

Methods developed or applied in the laboratory allow us

(1) to scan in two dimensions the surface of corroding systems,

(2) study the onset of pitting or crevicing in stainless steel or aluminium alloys,

(3) differentiate between alloys according to their susceptibility to pitting uninfluenced by the onset of crevice corrosion, and

(4) study the efficacy of implantation (surface modified alloys) of metal surfaces when they are exposed to corrosive environments.

4. FIELD APPLICATION OF LABORATORY METHODS

As customers you are probably interested in mechanistic information about corroding systems in the field. Questions such as - how is it controlled or driven by the environment, what effect does oxygen have on the corrosion rate, and are there factors which can passivate the corroding surface and inhibit the corrosion reaction. The quantitative results we obtain in the laboratory can go a long way towards resolving these questions. But we are presently developing a version of our main corrosion monitoring system which will allow deployment of it, and its computer controller, in the field. Considerable effort has gone into making the equipment in design suitable for coping rapidly and accurately with the results of real field systems. As opposed to idealized laboratory systems, field measurements are much more likely to be affected by a number of parameters that are difficult to control.

5. CURRENT PROJECTS IN THE GROUP

5.1 Tungsten Alloys

After the above introduction some examples of the results obtained were shown by overhead projection and slides. Photographic slides showed the loss of metal in sintered tungsten alloys that were to be used for heavy metal penetrators. Several sets of computer data found for various tungsten alloys (from the US, UK and Australia) were presented in graphical form, current plotted against applied voltage. From these figures could be deduced corrosion resistance, corrosion current and hence loss of metal - in most cases of the order of 10-20 micrometers/year.

5.2 Chilled Water System

Similar graphs were also shown of the results obtained for the chilled water system used for temperature control of the electrochemistry laboratory. In this case the corrosion rate was apparently higher than for tungsten - up to 50 micrometers/year - but its value was influenced by the geometry of the sensing probe and some variation in this was discussed. The chilled water system had been protected by the addition of a silicate based inhibitor and its influence on the results was also discussed.

5.3 Onset of Pitting in Steel

Finally, contour maps obtained by a scanning reference electrode on a sample of corroding mild steel in weak NaCl (10^{-3} M) solution were discussed. The initiation of small pits and their spontaneous and induced inhibition (by the addition of proprietory inhibitors) were shown. The reference electrode could follow the onset of corrosion very rapidly and give a time based analysis of this. Quantitative estimates could be made, but for most cases the simple qualitative contour maps with their measured (elapsed) time between maps gave the required monitoring.

CORROSION IN NAVAL VESSELS

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In this paper corrosion in surface ships, namely FFG's, and in Oberon class submarines will be discussed.

1. CORROSION IN FFG'S

The follow-on Australian Frigates (AF) are to be constructed at Williamstown Naval Dockyard to basically the same design as the American-built FFG's. We are fortunate to have the FFG's to evaluate, and from which to learn, prior to actually building the AF. The question is, however, will we learn from mistakes in the FFG's, or will the system force the mistakes to be incorporated into the AF only to require rectification at a later stage in routine maintenance.

There is a principle involved here in the initial purchase and subsequent Australian construction of equipment of overseas design. It is one thing to purchase in the hope that the materials will give satisfactory performance, but another entirely to observe unsatisfactory performance in the purchased units and to do nothing about it. Some designs are basically bad, others are inappropriate to Australian conditions. Regardless, DSTO scientists should be able to assist Defence personnel to be "smart buyers" and "smart constructors".

One of the problem in the FFG's is concerned with the seawater system. For example an inspection of HMAS Adelaide revealed:

(a) Leaking brazed joints, one releasing seawater from a 20 cm sea main into the compartment which contains purified fuel.

(b) Brazed repairs of holes in bends.

(c) Wet insulation.

(d) Pipes with insulation removed.

(e) Rusty mild steel bolts on flanges.

Likely causes of these problems are the use of:

(i) Excessive pump pressures which in turn lead to excessive flow rates which result in turbulence in the systems.

(ii) Pipework which contains small-radius bends only suitable for flow velocities less than 1.5 m/s. It is these fittings which undergo failure due to impingement corrosion caused by excessive water speeds.

(iii) Capillary joints which have been fabricated using brazing alloys which are anodic to the pipe material and hence corrode preferentially to the pipe.

(iv) Mild steel nuts and bolts which would be expected to give satisfactory service in an environment which does not include sea water released from pipework failures.

Obvious remedies to these failures are the use of appropriate pressures, flow rates, bend-radii, brazing alloys and fastener materials (either AISI 304 or DGS 348-nickel aluminium bronze).

2. CORROSION AND FOULING IN OBERON CLASS SUBMARINES

A submarine consists of a pressure hull which has ports for various systems, such as people/equipment, seawater, engine exhaust, propulsion and weapons. For propulsion, two propellor shafts pass through gland and bearings in the stern tube area close to the pressure hull and are supported by A-brackets at the aft end close to the propellors.

2.1 Corrosion problems associated with the propellor shaft

Originally, the shaft was clad with Inconel 625 in the stern tube bearing and gland areas, as shown schematically in Figure 1. It was clad with gunmetal in the A-bracket area, and the remainder of the shaft was coated for corrosion protection, initially with coal tar epoxy, and later with glass reinforced epoxy. In operation problems started.

Corrosion of the steel shaft at the two points marked "A" in Figure 1, under the junction of the Inconel and the fibreglass cladding, led to the decision to extend the Inconel cladding between the two previously clad areas. The corrosion of the steel shaft had been accelerated by its coupling with the more noble nickel alloy by bimetallic or galvanic corrosion. The shaft corrosion was then solved, but replaced by an equally serious problem of corrosion of the steel bearing housing in the stern tube.

The steel bearing housing corrosion is also most likely attributable to galvanic coupling of the steel with the more noble Inconel. In effect, a short circuited battery in which oxygen dissolved in seawater reacts at the Inconel surface dissolving adjacent ferrous materials forms. The larger the area of Inconel the larger the rate at which adjacent reactive metals corrode. In fact, calculations show that the maximum current which can be generated from oxygen reacting at the exposed section of Inconel is 2.4 ampere which is sufficient to remove 1 kg of iron in about 40 days.

The suggested solution to this second problem was to apply a coating to the exposed section of Inconel, thereby reducing its area and hence, in proportion, the rate of galvanic corrosion of coupled ferrous metals. It would not be advisable to use gunmetal for the bearing housing as the housing corrosion, then solved, would be exchanged for a potentially more serious corrosion of the pressure hull in the stern tube area. The irony is that the drawings for shaft cladding show a Detail A (Figure 1) for the junction of Inconel and fibreglass which includes a step in the Inconel under the fibreglass. Had this been incorporated we would have avoided the need for extended cladding and the rectification of the corrosion which has occurred as a consequence.

2.2 Fouling and corrosion in the seawater system

Cooling with seawater is excellent in principle except for the problem of marine organisms which can settle and metamorphose in 24 hours. Once attached they can grow very quickly and block water passageways and heat exchangers. On submarines, as on all Naval vessels, the reliable operation of these seawater systems is vital for survival. There are seawater-cooled heat exchangers for diesel engines, electric motors and generators, refrigeration plants, batteries, bearings and weapons systems.

Fouling and corrosion are linked in that nickel aluminium bronze valves undergo crevice corrosion under marine growth. Thus, if the system can be kept clear of fouling, then that form of corrosion will be controlled.

Australian Oberon class submarines employ a commercial system called CATHELCO in an attempt to control fouling and corrosion. Copper and aluminium ions are produced electrochemically to control respectively fouling and corrosion (of steel). Inspection of the seawater systems reveals that the system does not achieve its purpose to control fouling as extensive fouling by tube worm cases, hydroids and barnacles was observed (Figure 2). Problems have been encountered in the operation of the system, including current not flowing or flowing in the reverse direction. Moreover, it appears that currents in use are unlikely to generate a sufficient concentration of copper ions to prevent settlement of fouling when the submarines are berthed in Sydney Harbour (one of the worst sites for fouling in the world). On the corrosion side, there are no ferrous components in the seawater system so the aluminium anode is redundant.

As an interim measure, it would seem appropriate to raise the levels of copper to three times that used at the present time. This is within the specification of the commercial system. In the longer term, redesigned all-copper anodes could be made in Australia for much less than the presently used combination copper/aluminium anodes which are imported at $450 each. We are currently setting up trials to determine the optimum copper levels necessary to control fouling in the Australian situation. Once determined these can be used in the design of a new controller for the system.

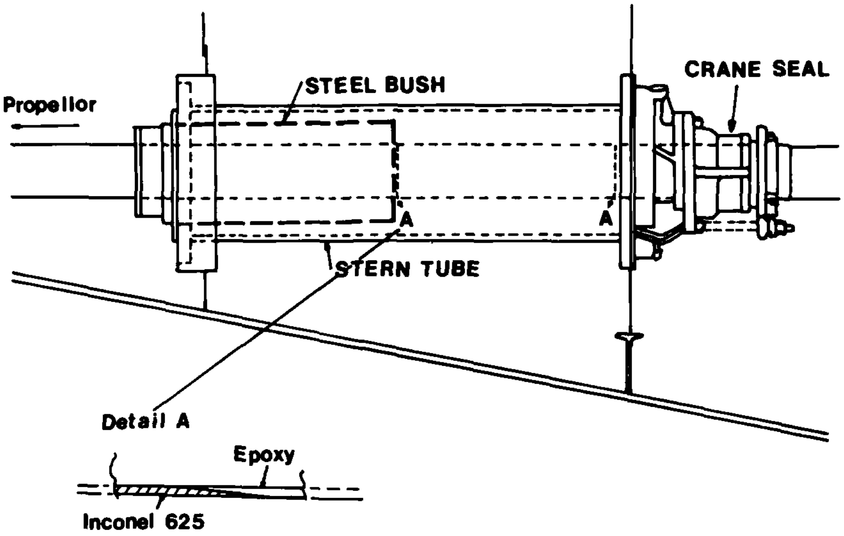

Figure 1. Schematic diagram of stern tube bearing and gland areas, Oberon-class submarine.

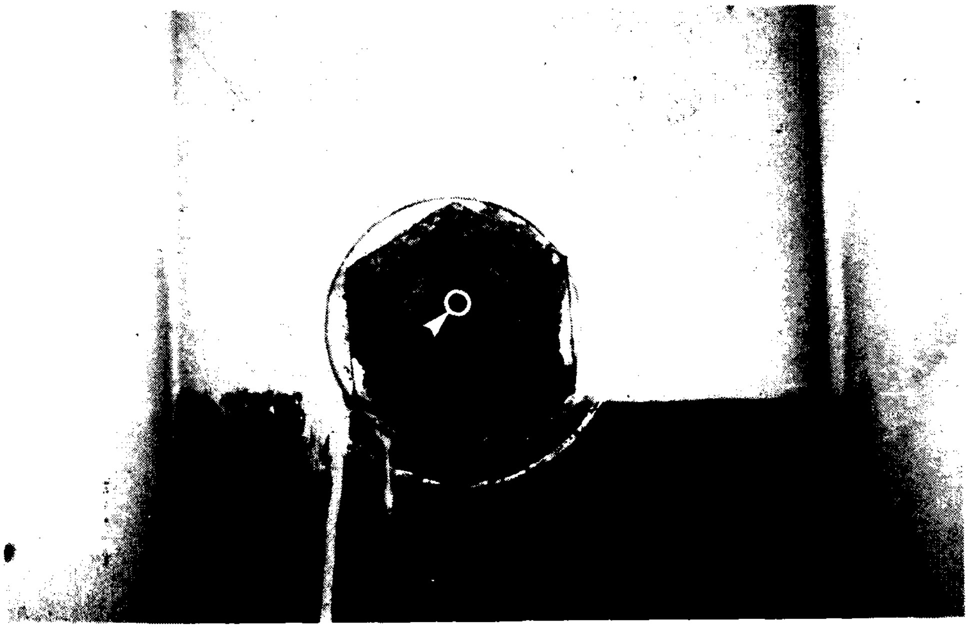

Figure 2. Fouling deposits in seawater system of Oberon-class submarine, HMAS Oxley, which have restricted flow to the internal diameter of the white circle.

DESIGNING TO PREVENT CORROSION

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Corrosion Control Group

1. INTRODUCTION

Despite the knowledge and high level of technology we have today, we still find equipment designed and produced with faults that lead to service failures caused by corrosion. Most of the problems we see are not new. They could be avoided by the correct application of existing knowledge, but designers and manufacturers are obviously not always aware of the pitfalls.

It is the corrosion specialist's task to promote this awareness and to assist designers, manufacturers and users in the application of corrosion control methods. There is no doubt that this is best done at the design stage, when decisions are being made about materials selection, protective coatings, etc. However, although we do have an input into several Australian Defence projects at this design stage, the bulk of our Defence equipment is purchased overseas, and we seldom have any say in the design. Thus we find we need to act as consultants to users, investigating corrosion failures in existing equipment and offering appropriate advice on refurbishment and preventive measures.

The basic design rules that should be followed to avoid corrosion are:

1. *Define the Environments* the equipment will serve in, e.g. temperatures, humidity, salt or other air pollutants, ground waters, liquid velocities.

2. *Select Resistant Materials* appropriate to these environments.

3. *Use Metallic or Non-metallic Coatings* where necessary.

4. *Design for Easy Maintenance.*

5. *Check Compatibility of Associated Materials* - some adhesives, plastics, paints, packaging and insulation materials can cause corrosion if they are poorly formulated or they deteriorate with time.

6. *Consider Modifying the Environment* to make it less corrosive, e.g. corrosion inhibitors in engine cooling systems, vapour phase inhibitors in packaging.

2. INFLUENCE OF DESIGN

I shall now illustrate the effect of breaking some of these rules with some case histories.

2.1 C12 Compass Amplifier Power Supply

Corrosion of circuit boards in these units from Hercules aircraft was caused by condensed moisture dripping from the cabin roof through ventilation holes in the top of the unit housing and onto the top surfaces of all horizontal boards. The conformal coating on the boards was too thin and patchy to give the required protection to the metal surfaces. The possibility of leakage from capacitors being the cause of corrosion was ruled out after analysis of the corrosion products.

Design change was required to either shield or relocate the ventilation holes to prevent condensate access.

2.2 Footbridge Pontoons

Army footbridge pontoons (Fig. 1) purchased from Polar (USA) and made of 6061 aluminium alloy (about 20 years old) are perforating through the bottom skin. Perforation was due to corrosion initiated internally by water leaking into the buoyancy chambers.

The design of these pontoons was such that the aluminium deck sheet was fitted last by cutting it to fit around every rib in the frame and welding it to the ribs and side walls (Fig. 2). However behind each rib was a gap which could not be reached by the welder (Fig. 3). Initially these gaps were sealed by the polyurethane foam which was formed in situ to completely fill the buoyancy chamber, but with time and flexing movement the foam lost adhesion to the walls and bottom. Water was then able to enter at the rib gaps, work its way to the bottom and set up the necessary conditions for crevice corrosion of the aluminium.

By contrast, pontoons of another make (Opelika, USA) in the Army's stock were, except for one, in excellent condition at a similar age. The reason was their superior design in which the rib structure did not penetrate the deck, thus allowing the buoyancy chamber to be fully sealed (Fig. 4).

The one exception was an example of carelessness in manufacture whereby several deposits of iron filings left lying on the bottom of the pontoon had caused bimetallic corrosion which perforated the aluminium sheet.

2.3 Foam Fire Extinguishers

These copper bodied extinguishers were filled with a hydrolysed protein foaming agent mixed with water. After only 2 year's service some extinguishers had failed both by pitting to perforation at the waterline and by stress corrosion cracking of the brass discharge tubes (Fig. 5).

The waterline pitting was caused by a combination of stagnant conditions, high sodium chloride content of the foaming agent and carbon dioxide from decomposition of the hydrolysed protein foaming agent. Decomposition of the foaming agent also produced small amounts of ammonia and amines which led to stress corrosion cracking of the brass discharge tubes.

From the design viewpoint a problem existed which required urgent rectification: both the extinguisher and the foaming agent conformed to their respective specifications, and were specified to be used together, but together they were obviously incompatible. This problem highlights the need to be aware of deleterious interactions when a number of specifications are used in the overall design.

2.4 Non-Magnetic Stainless Steel

The RAN need for a non-magnetic stainless steel for its mine countermeasures vessels has required MRL to assess the corrosion resistance (and other properties) of a candidate material of German origin called Amagnit 3964.

Polarisation tests, accelerated tests, laboratory and field exposures of both parent plate and welded panels have all shown Amagnit to have greatly superior corrosion resistance to comparative alloys such as AISI Type 316L. Amagnit is virtually immune to pitting and crevice corrosion in all these tests. Long term exposures in the ocean at Innisfail, Queensland, are continuing.

The benefit of this work is that, together with assessments of other properties, this information will be available to designers at the design stage.

2.5 F111 Heat Exchanger

Figure 6 shows an aluminium base plate which acts as an air-to-air heat exchanger for electronic equipment on the F111 aircraft. Slots visible at the left of the plate actually continue the full length of the plate but are concealed on the right by cover plates.

Liquid from chemical surface finishing treatments at the manufacturing stage was trapped in the covered slots causing corrosion which became visible only at a later time.

This is typical of a recurring problem when care is not taken to avoid recesses and blind holes in components requiring liquid finishing treatments such as anodizing, passivating or electroplating.

3. CONCLUSION

These case histories illustrate corrosion problems which arose through failure of designers and manufacturers to observe some of the basic design rules, for example:

(1) Lack of appreciation of the actual environment in which the equipment was placed,

(2) the use of incorrect materials for a known environment, and

(3) a lack of care in manufacturing and design practices.

In all cases the technology was available to prevent the problem; but obviously what is needed is more efficient transfer of that technology to those who need it to cope with each stage in the life cycle of the equipment, namely design, manufacture, storage and service. We firmly believe that person-to-person contact is the best means of achieving this. As a final comment, *feed-back* from the user can also be very useful to the adviser.

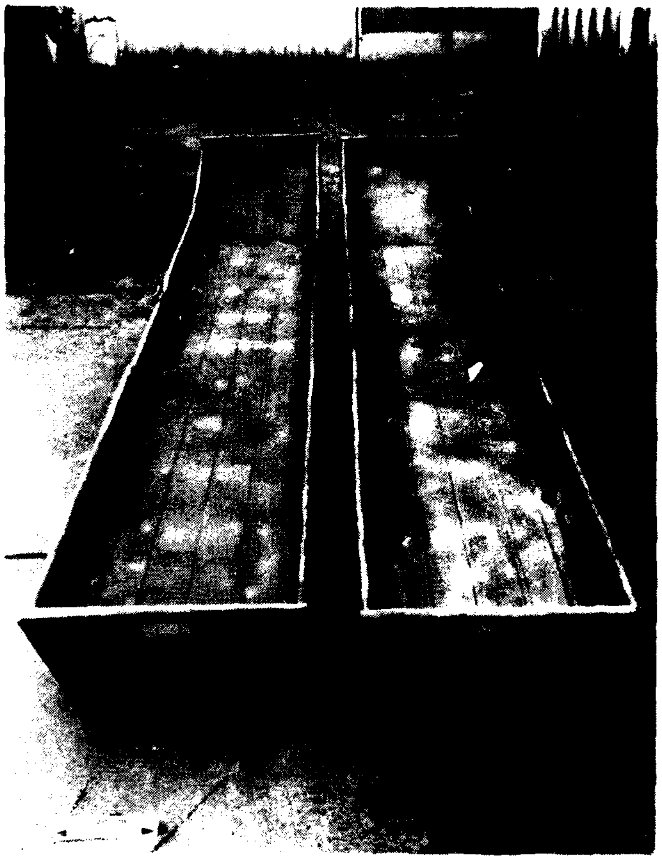

FIGURE 1. General view of both pontoon models (Polar on left, Opelika on right).

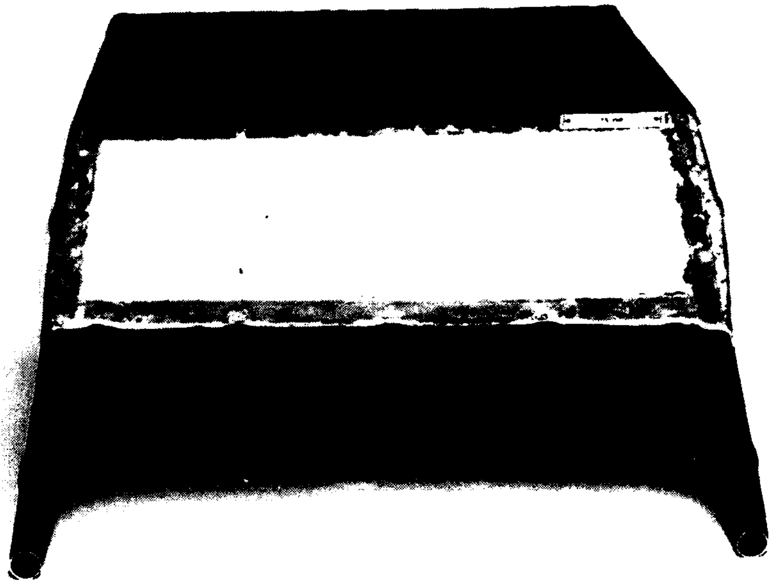

FIGURE 2. Inverted cross-sectional view of Polar pontoon showing continuous rib on each side wall.

FIGURE 3. Typical rib/deck weld on Polar pontoon. The hole to the right of the weld leads directly into the buoyancy compartment.

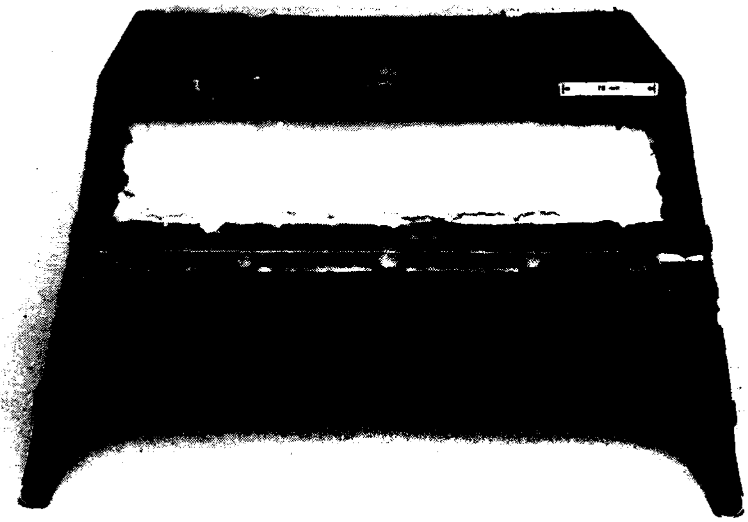

FIGURE 4. Inverted cross-sectional view of Opelika pontoon showing unbroken deck sheet and two separate ribs welded to each side wall and to deck.

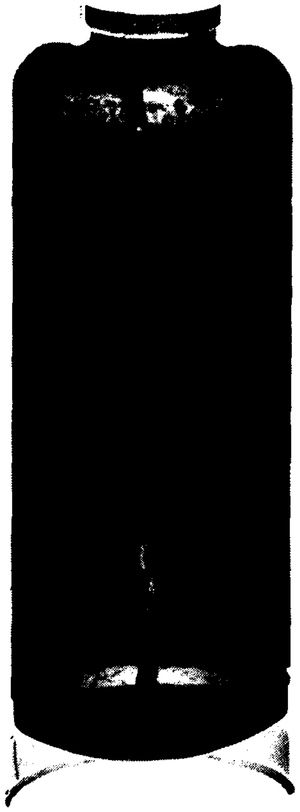

FIGURE 5. Internal view of Extinguisher. Note pitted section (bracketed) and cracked discharge tube.

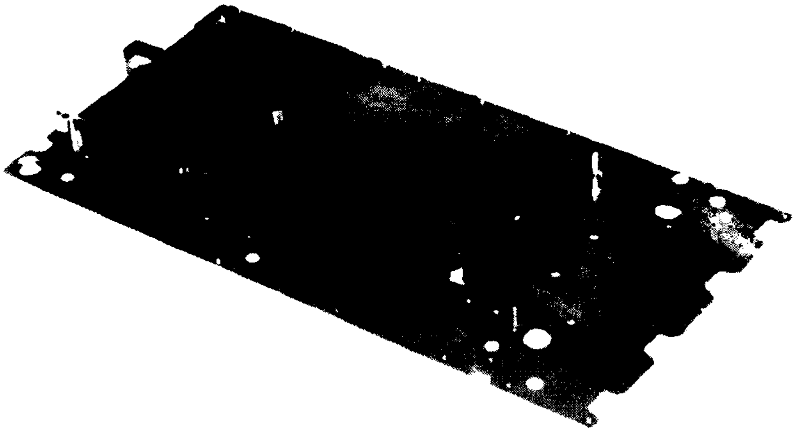

FIGURE 6. General view of the aluminium heat exchanger used in an electronic power supply cooling system on an aircraft.

APPLICATIONS OF ELECTROPLATING

Bruce Wilson
Corrosion Control Group

1. INTRODUCTION

Electroplating of metals and plastics, be it decorative or functional or a combination of both, is done to improve the properties of a substrate, protecting it from an agressive environment. A clear economic justification for electroplating follows as a coated, cheaper or stronger material may be effectively used in situations for which it would otherwise not be a suitable material. For example, cadmium related coatings are used for corrosion protection on high tensile steel undercarriage components, hard chromium plating is used on the interior of gun barrels to protect the barrel from both wear and gas attack, and gold coloured anodised coatings are used on soft aluminium Army buttons, badges and insignia for both wear resistance and decorative appearance.

Electroplating is a specialised coating process which is a combination of engineering and electrochemistry, and is a topic that most people regard as a "Black Art". It is unfortunate that most newer electroplating processes are protected by patents and consequently most technical knowledge on these processes are in the hands of Supply Houses who are very reluctant to release anything but the bare knowledge on how to run the process.

MRL has been investigating electroplating problems as a service to both Defence and Industry for over 50 years. However, continued introduction of new processes and techniques for the preparation and coating of metals, our specialised services are constantly being used. Our job is to transfer our scientific and technical knowledge of electrochemical processes to the defense related electroplating industry so that the coating processes can be more easily understood and controlled. Our background experience gives us opportunity to make assessments on the various commercial coatings systems.

Investigations in the past have covered a multitudinous range of problems including plating of gold on stainless steel and aluminium, silver on stainless steel, silver indium alloy on bearings, phosphating, chromate coversion coatings, internal stress in nickel, stripping of nickel deposits for very high tensile steel components, production of pure chromium, effluent treatment for metal finishing plants etc.

Our work is now divided into a number of major areas namely:

1. Investigation into current electroplating problems for the Services and Factories.

2. Investigation and research into coating processes and techniques.

3. Testing of coating parameters.

4. Examination of new testing methods for coatings.

2. PLATING SYSTEMS AND COATINGS

One of the more complicated plating systems we are presently investigating is the application of electrodeposited chromium coatings to gun barrels. Chromium coatings are known to extend the erosion resistance of barrels by about three times, but at present the physical form of chromium plate requires some modification to improve its erosion resistance and adhesion to the base material still further. The first part of our investigation is to examine the cleaning cycle as a means of improving the adhesion to the steel. This cycle is - solvent clean: alkaline clean: electropolish: alkaline clean: pumice scrub: anodic etch: chromium plate. It must be remembered that mild steel is not being used, but a low alloy steel containing small percentages of a number of alloying elements, each of which may effect the adhesion of the electroplate to the basis metal.

The cleaning steps being investigated are electropolishing and anodic etching as these seem to be very important steps in the process. From past work it is known that electropolishing leaves difficult-to-remove oxidised debris from manganese and silicon on the surface, but it is an essential part of the chromium plating procedure. So examination of various practical cleaning methods to remove this surface debris is necessary. The present practice is to laborously hand clean the surface with pumice powder.

The next aspect is to optimise conditions for the anodic etching prior to the chromium plating. Anodic etching is an unusual cleaning step in plating, as in normal plating the surface is required to be as clean and active as possible prior to plating. Here, the steel surface is deliberately anodically oxidised in the chromium plating bath producing a visible oxide film on the surface, rather like the anodising of aluminium. It is believed that this surface oxidation is very necessary for good adhesion of the chromium to the steel. Defects in the oxide film could provide small cathodic sites and when plating occurs these defects in the oxide film have a resultant very high current density due to the insulating effect of the film, thereby aiding the reduction of chromium ions.

The last aspect of this investigation is to improve the form of the chromium plate itself. Chromium as presently plated is a highly stressed coating. The stresses cause the coating to crack and generally the chromium plated coatings have low cohesive strength. Application of different plating bath conditions and compositions can alter this and it may be possible to reduce the stress level and still retain maximum adhesion. Alternatively, it may be possible to use different current application methods to achieve a much better coating.

With most plating processes used at the present time, DC power is supplied by rectified AC with an AC ripple of no more than 10%. However, with the introduction of higher power SCR's and micro circuits it is now possible to control the actual plating cycle. The ability to control not only the amplitude, but the frequency of each part of the cycle has meant that great control can be applied to the plating process. Overseas work has indicated that, using pulse plating, chromium coatings can be produced crack-free by allowing hydrogen to diffuse out of the previously plated metal during the anodic or off period of the cycle. The type of cycle used was 15 sec plating and between 30 to 50 millisec non-plating. Pulse plating of chromium coatings will be investigated as a part of the current study.

One aspect of electroplating often forgotten is the removal of the coatings without attacking the basis metal. MRL has been called on many times to investigate methods of removal of coatings. Any method must be tailored to suit the component. If the component is a very high tensile steel component the normal acid pickling must not be used under any circumstances for this could lead to hydrogen embrittlement of the steel. Other methods, preferably in alkaline solutions, need to be investigated and even some of these have drawbacks as often the organic chemicals used break down partially when heated and can cause attack on the basis metal. Each system must be examined individually and assessed.

Coating systems based on zinc and cadmium are also being investigated. The main purpose of this is two fold, *firstly* to possibly improve the corrosion resistance of zinc by alloying with other metals, and *secondly* to use zinc alloy systems as a replacement for cadmium for high tensile steel components. Preliminary work on cadmium plating has shown that some of the commercially available low hydrogen embrittlement cadmium alloy plating systems are highly suspect in their effectiveness and it is extremely difficult to control their alloy composition.

3. TESTING OF COATINGS

The other major aspect of our work is testing of coating parameters. Coatings used on Defence equipment are mainly functional and the Department of Defence as a major user of electroplated coatings requires these coatings to meet certain test criteria, be it thickness, corrosion resistance, hardness, adhesion, internal stress, etc., to ensure that the coatings are of the best practical quality for their end use. Unfortunately, once specified, these tests are often blindly accepted without recognising that some test criteria are often arbitrary and dependent on operational assessment.

To redress this last aspect, over the last few years Corrosion Control Group have been looking at methods of assessing coating parameters from a more fundamental viewpoint. One major parameter which causes much heartburn is corrosion resistance. This parameter has been, and still is, assessed by the salt spray test and a more arbitrary test is yet to be devised. The major coating system used in the Defence Department and most often tested in the salt spray is the zinc plating and chromate passivation on steel.

The plated components being tested should last some 72 hours in salt spray. Failure is assessed visually by the appearance of white "rust" or red rust; i.e. breakdown of either the chromate passivation film or breakdown of the zinc film. However, past investigations have shown that the corrosion resistance of similarly plated and passivated components can vary up to 300% using different salt spray cabinets. Also, if passivated chromate films are heated above 65°C before salt spray testing, they will invariably fail; whereas heated and unheated zinc plated and chromate passivated films exposed at various corrosion sites in Australia, show no difference in their corrosion resistance. This indicates one of the problems of accelerated testing. This problem has been investigated very thoroughly in the past and no reproducible basis could be found for another assessment method to replace the salt spray test. However, with the introduction of the computer assisted mapping described in an earlier talk, it may be possible to have a new basis for assessing the corrosion resistance of zinc plated or passivated coatings. Preliminary results indicated that badly cracked films could be assessed by the potential mapping method over a 6 hour period, when recovery of protective values are achieved. It is still in the development stage, so considerably more work is needed to prove the method.

Adhesion of the plated coating to its substrate is a very important parameter, especially in heavy duty coatings. Adhesion of plated coatings is normally measured qualitatively by fairly rudimentary methods. Quantitative adhesion measurements require separate and special test pieces and, consequently are generally used only in research projects. We are currently looking at three quantitative adhesion methods.

The simplest of quantitative adhesion tests is the Ring Disc Test, where a plated annulus of known area is forced through a die to measure the adhesion, in shear.

It would seem that to make any improvement in the adhesion of a coating system, measurement of tensile adhesion is essential. However only one fundamental measurement system has been developed. This involves spinning a magnetically suspended coated spindle in a vacuum with sufficient speed to force the coating off the spindle by centrifugal force.

The electrochemical method of adhesion testing takes a very different approach. It is based on the assumption that at the start of the plating process, deposition occurs on separate small portions of the cathode surface and the extent of this deposit determines the adhesion between the deposit and the substrate. If the cathodic polarisation curves at this initial stage are examined and compared between clean and soiled surfaces, a comparison measurement of adhesion can be established, or more accurately, a measure of surface cleanliness is obtained. Trials have shown that this method is feasible and can easily detect differences in surface cleanliness. We hope to use this method in the chromium plating project.

Another parameter we have looked at is the thickness of multilayer coatings by coulometric and potentiometric methods. These, besides giving the thickness of various coating layers, can in the case of nickel coatings give an indication of the corrosion resistance of the layer as well as the internal stress.

4. FUTURE DIRECTIONS IN ELECTROPLATED COATINGS

Further advances in electroplating appear likely in the area of alloy plating using pulse plating techniques. Difficult-to-plate metals can now be attempted, and rethinking protective coating systems in 5 years time will be necessary.

Two papers at a recent International Congress on Surface Finishing stood out as real contributers to metal finishing. The first paper was on the plating of nickel chromium alloys at a thickness of 50 microns with corrosion resistance as good as the 300 series stainless steel. Alloy coatings of up to 20% Cr with Ni were produced and tested. The alloy coating was produced by the pulse plating technique from a trivalent chromium and divalent nickel bath. On first sight it does not seem to be too particularly innovative *except* that the paper was produced by the National Bureau of Standards, who have in the past been responsible for very many of the advances in the electroplating field, including the first commercial electroless nickel plating bath. Plating of stainless steel will certainly become more prominent in the near future.

The other topic of significance is not about metal finishing, but about metal preparation and paint removal. The high cost of removal of high duty paints from aircraft components, tank hulls and ship hulls is well known. A major cost is often the removal of either the blast medium or else the environmentally hazardous paint strippers containing chemicals like methylene dichloride, cresolytic acids, etc. The method of paint removal is innovative and ingenious. Instead of using a solid blast medium this method uses one that sublimes, ie dry ice: liquid CO_2 at -20°C and at 300 psi, expanded through a nozzle to produce CO_2 snow which is compacted to produce pellets of CO_2 of 97% density. The blasting pressure needs to be higher than normal due to the lower density of dry ice, namely, 1.5SG compared with steel of 8SG. Costs would appear to be cheaper than most conventional blast cleaning.

5. CONCLUDING REMARKS

Finally, there is a tremendous amount about electroplating that is still unknown. It is obvious that with the application of new techniques and plating solutions, electroplated coatings are still going to compete very competitively with other coating methods for many years. Queries on electroplating and metal finishing problems should be directed to the author.

SURFACE MODIFICATION OF NICKEL-ALUMINIUM BRONZE

George M. Weston
Wear Technology Group

1. INTRODUCTION

A wear technology group has been formed within the Metallurgy Division at MRL with the purpose of applying new surface technologies to improve wear and corrosion performance of defence components. Development tasks in plasma vapour deposition (PVD) and laser surface melting (LSM) of defence material is currently underway. Further, with Corrosion Control Group, these techniques are also being used to improve the corrosion performance of defence components.

In this paper, one aspect of this work, involving LSM followed by rapid self quenching of the near surface layers of nickel-aluminium bronze (NAB) alloy DGS-348, will be discussed. This work was undertaken with the view of improving the above alloys in-service crevice corrosion performance.

2. BACKGROUND

The above NAB alloy is widely used in marine applications and in general has excellent corrosion resistance and mechanical properties. However, under certain service conditions where closely-fitting surfaces or marine growth build-up form surface crevices, this alloy is susceptible to crevice corrosion. Research indicates that crevice corrosion in this alloy is assisted by the semi-continuous nature of the coarse as-cast lamellar Kappa III eutectoid phase surrounding the alpha-grains. Replacement of this multiphased surface microstructure with a homogeneous single phase structure by means of LSM accompanied by rapid self quenching was considered a possible avenue to improve crevice corrosion performance.

3. METHOD OF LASER SURFACE MELTING (LSM)

A nominal 1.2 Kw continuous CO_2 laser was used to achieve surface melting with the above NAB alloy. Small discs of this material were attached close to the outer edge of a horizontally mounted aluminium wheel coupled to a variable speed motor.

This specimen rotation assembly was fixed to a numerically controlled table, a schematic diagram of this assembly is shown in Fig. 1. Incident laser irradiation was focussed onto the rotating specimen surface to achieve maximum power density and near surface melting. Each rotation of the specimen resulted in a melt strip across the surface. Overlapping of individual melt strips was sought to ensure disolution and homogenization of all second phase particles present and continuous area coverage.

4. SURFACE MICROSTRUCTURE

Microstructural examination of longitudinal sections after LSM showed that within the surface region, the normal as-cast multi-phase microstructure had been replaced with a single phase structure (Fig. 2). Examination at higher magnifications using the scanning electron microscope revealed that with the maximum power density available, cooling rates were such that precipitation of a very fine second phase could not be prevented (Fig. 3). The very fine discontinuous nature of this precipitation was considered unlikely to influence crevice corrosion performance.

Element line scans normal to the specimen surface supported the metallographic observation of a primarily homogeneous single phase microstructure within the LSM region (Fig. 4). The higher non-equilibrium solute concentration within the LSM region resulted in hardness levels approximately 30% above those recorded for the bulk material.

We would like to acknowledge the assistance given to this project by the Ordnance Factories at Bendigo and Maribyrnong.

5. CORROSION EVALUATION

Initial laboratory tests on areas where artificial crevices have been formed indicates that corrosion activity occurring on the LSM samples was less intense than that observed on the surfaces of the as-cast samples. However, because of technical difficulties immersion times were only a matter of days. As crevice corrosion is a slow process occurring over many months, longer term marine trials will be undertaken to fully evaluate the potential of this approach.

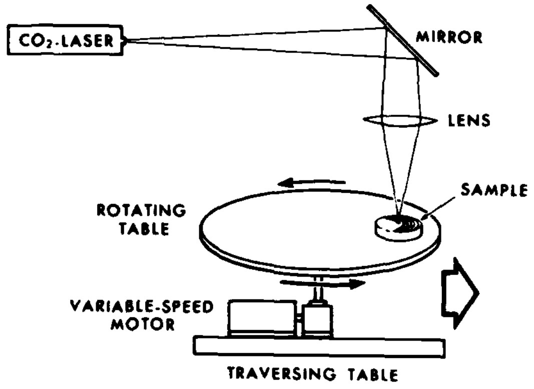

FIGURE 1. Schematic diagram of laser surface melting equipment.

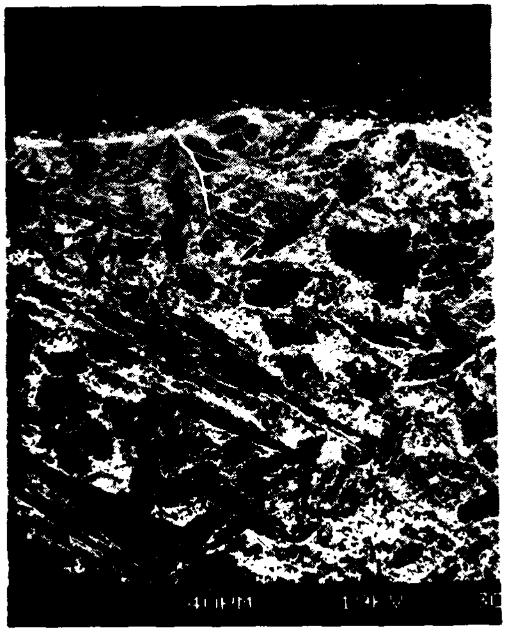

FIGURE 2. NAB alloy showing a single phase LSM region above the as-cast microstructure.

FIGURE 3. LSM region showing very fine second phase precipitation.

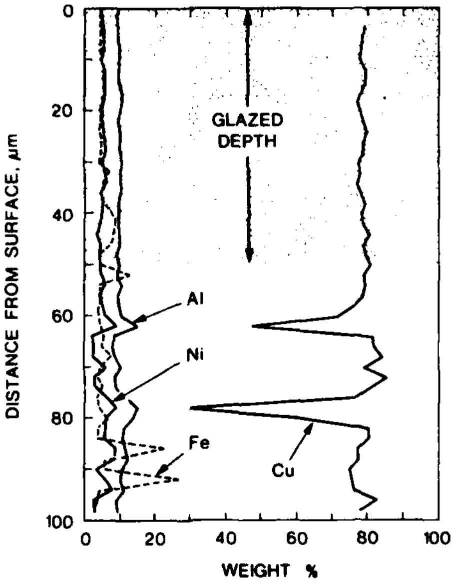

FIGURE 4. Element line scans normal to the surface showing the uniformity of element distribution within the LSM region compared with the bulk material.

PAINTING TO PREVENT CORROSION

Frank Marson

Head, Paints Group

1. INTRODUCTION

The paint chemist's job is to devise coating systems which not only protect the substrate from deterioration, but also provide those other elements required such as decorative appeal or camouflage. However paints do not work alone, they are part of a four stage process. Each stage is critical for success. The first is the design of the structure to be painted; the second the preparation of the surface; the third is the choice of the coating system, and the fourth is the correct application of that system. The first and second are covered to some extent by other papers and the fourth should follow, fairly straightforwardly, from the choice of the system.

Put simply, paints contain a pigment or pigments which may help to protect the surface and provide decorative properties; the pigment is bound together and made adherent to the surface by a paint vehicle, usually organic in nature, with the addition of a solvent to allow application. Traditionally paints consisted of naturally occurring minerals as pigments bound together with naturally occurring vehicles such as egg white, blood, lacquers from shellacs and natural oils like linseed oil. The two common surviving members of these traditional paints are probably french polish (with no pigment other than a little talc) and the red lead in oil anti-corrosive paint. Modern paints are comparatively recent innovations; Fig. 1 shows the major primary chemical developments which have led to them and that most of the development has occurred in the last forty years.

2. THE DEVELOPMENT OF MODERN PAINTS

Nitro-cellulose finishes were the first of the new synthetic vehicles to be extensively used and they are still used occasionally in the refinishing of motor cars. Alkyd resins gained acceptance in the mid-forties and are the basis of nearly all our solvent based house paints. The same period saw the acceptance of chlorinated rubber industrial maintenance paints. Polyvinyl acetate (PVA) emulsions appeared in the late forties and are still used for interior paints.

The early polyester and urethane coatings followed and gave good gloss retention; both were and are used in the furniture industry. The mid 50's gave us epoxy paints, which see their major use in industrial and marine applications. The acrylic emulsion paints in 1960 are the basis for exterior water based architectural paints, while the thermoplastic and thermosetting acrylics introduced in the sixties are now the major resins used in the car industry.

Two recent developments which are still gaining acceptance are zinc phosphate pigments used in non-toxic anti-corrosive primers; and the bead pigments developed by Dulux in Australia which provide such excellent scrub resistance at low cost to interior paints.

The above paragraphs mention most of the potential paint systems that will be used in industry and in defence, apart from very specialised areas.

3. PAINTING STEEL

Below a relative humidity of 50 per cent, in clean air, the corrosion rate of steel is negligible, but it increases rapidly as the humidity increases and in the presence of soluble salts in marine and industrial environments. The corrosion rate can be reduced by applying a paint or coating as a barrier, to increase the electrical resistance between the anodic and cathodic areas, thus reducing the corrosion current and consequently the corrosion. To be effective such coatings should have a high water resistance and also limit the amount of water and oxygen which can reach the metal surface. This is why coatings which rely largely on the barrier function should be thick. A second method of reducing corrosion is by inhibition; this method uses chemically inhibitive pigments such as zinc chromate. A third method is by cathodic protection, using coatings in which a metallic pigment sacrifices itself anodically thus preventing the corrosion of the steel. The best known of these are zinc rich paints.

What are the requirements for an effective anti-corrosive primer? If it relies predominantly on the barrier effect it must be thick enough to protect the peaks and the hackles of say, an abrasive-blasted surface, otherwise spot rusting will occur. If it relies largely on inhibitive pigments, there must be sufficient paint present to provide a reservoir of these, and they must be available from the paint film. Thus the more water resistant the paint film, the more soluble the pigment providing the reservoir of ions must be. If the film is relying on cathodic protection, then it must be realized that the film's performance is directly related to the amount of zinc dust (or scarificial pigment) present in the film and hence the performance is related directly to film thickness and pigment volume content.

The service life of a zinc rich paint system related to film thickness is illustrated in Fig. 2. For something like two mils film thickness in a rural environment you get 16 years life; whereas in seawater immersion the same thickness gives about two years. Similar sets of curves could be made for the other two paint types. Film thickness almost invariably increases effective life. At sharp edges paint film thickness is decreased and this is one of the weak spots in painting any structure, particularly a complicated one. If the sharp edges are 'smoothed out' improved performance can be obtained; if they cannot, then it is probably better to put an extra coat on those areas where the conditions of use are severe. This so called 'stripe' painting frequently gives improved performance out of all proportion to its cost.

4. COMMON PRIMING PAINTS

Fig. 3 shows the properties of some common primers. The first, red lead in oil, is a very good anti-corrosive paint, and its particular advantage is that it is very tolerant of surface preparation. However, it is slow drying and toxic, which prohibits its use in many cases. It also has poor water, chemical and solvent resistance and naturally it is not weldable. The most common primers used under mild conditions are zinc-chromate/alkyd primers and they can be good anti-corrosive paints provided the zinc chromate content is adequate. They are cheap, although less cheap with increasing amounts of zinc chromate. They suffer from the same sort of disadvantages as the red lead paints in that they are fairly permeable and have poor water, chemical and solvent resistance. They have somewhat lower film build and once again they are not weldable. Even so, under mild conditions they are probably a primer of choice.

The inorganic zinc rich primers are not used as much in Australia as overseas despite being largely developed here, one type at MRL. They are also available in chemically cured types. They are non-toxic and have a range of drying times, are weldable under certain conditions, have good abrasion resistance and are electrically conductive. If you want to combine temperature and corrosion resistance they are practically the only commonly available primer. They are also solvent resistant, make excellent shop primers and there are higher build types available for structural steelwork. Their disadvantages are that the one pack types are dependent on ambient conditions for curing, and recoating must be carried out according to a strict regime. They have poor alkaline and acid resistance and require excellent surface preparation for effective use. Because their protection of the surface is of the cathodic type their film thicknesses need not be as high to prevent corrosion, but in the course of protection the zinc is gradually used up.

Epoxy zinc rich paints are very similar in performance, the major differences are that they are generally somewhat less abrasion resistant and they probably tolerate slightly poorer surface preparation. Epoxy red oxide paints rely on providing a barrier to the environment, to provide protection of the surface. Their disadvantages are that they are not rust inhibitive and are not weldable but they are suitable for immersion and have a good chemical and water resistance. The epoxy red lead primer is somewhat similar, its disadvantages again are that it is toxic, not acid resistant and not weldable, it is however reputed to be rust inhibitive.

Having looked at the advantages and disadvantages of these common paints and primers, how do you choose the correct one for the job? We must define the environment in which the primer is to be used and chose the most appropriate one for that environment. For example, if you want a primer for equipment which comes in contact with lubricating oils, fuels, hydraulic fluids or solvents, it is fairly obvious that you would not choose either the oil or alkyd based primers, but one of the other four. If the primer was to be used on a steel walkway or deck you would probably choose either the inorganic zinc rich or the epoxy xinc rich because one would expect the system to be damaged. This would expose the underlying steel structure and the cathodic system protects a bigger gap in the paint film than the chromate inhibition type of a primer does.

5. FINISHING COATS

Figure 4 shows some common top coat systems with their advantages and disadvantages. The advantages of alkyd paint (which is the most common solvent based architectural paint) are that they are available in a wide range of colours including white, have excellent outdoor durability, are relatively non-toxic and cheap. Their disadvantages are that they are slow drying, and of high permeability and hence low water resistance. They also have low chemical and solvent resistance, yield a relatively soft film and are not recommended for continuous immersion. Chlorinated rubber top coats which dry by solvent loss are available in high and low build types, show good outdoor durability and have high water and chemical resistance. They are suitable for continuous immersion. They are relatively fast drying and have excellent recoating properties. Their disadvantages are that they have low solvent resistance, low resistance to vegetable and animal fats, limited heat resistance and a relatively soft film.

The chemically cured epoxies are available in low, high build, and solvent free types and white and coloured paints are available. They have a low moisture permeability, high water and chemical resistance, are relatively non-toxic, have good solvent resistance with high abrasion resistance. The film is tough and flexible and suitable for continuous immersion. The disadvantages are that they are two pack systems and they are not always suitable for exterior use, require strict recoating conditions, and tend to yellow with age. The epoxy coal tar or coal digested pitch epoxy coatings are somewhat similar and both high build and solvent free types are available. They have a low water permeability and are water and chemical resistant. They are relatively cheap, suitable for immersion and more tolerant of surface preparation than straight epoxies. They are only available in dark colours and overcoating is therefore required for decorative use, are not recommended for contact with potable water and food stuffs and have a lower solvent resistance than straight epoxies.

Polyurethane based coatings are available in low and high build types, both white and colours show excellent outdoor durability and colour retention, while they have high water and chemical resistance. The film is non-toxic, flexible and has good abrasion resistance, as does the epoxy system. Their disadvantages are strict recoating conditions and expense, because they are probably the most expensive system. On the other hand correctly formulated urethanes probably have the highest outdoor durability, and are the only systems suitable for N.B.C. usage. Aircraft paint systems on test panels show little degradation after 5 years semi-tropical or tropical exposure. Last in this list are vinyl systems which are somewhat similar to the chlorinated rubbers but with the advantage that they usually have somewhat better resistance to vegetable and animal fats and oils.

6. SELECTION OF PAINT SYSTEMS

How do you choose the finishing coat? Once again you have to look at the environment. It it an aggressive environment? Is it acid or alkaline? Does it contain solvents? Is there contact with foodstuffs? Is the decorative look important? And is it subject to ultra violet light and radiation? Let us examine one or two possible cases and see which system we would choose, bearing in mind that the top coat must be compatible with the primer which was selected.

Let us suppose we have a solvent reclamation plant, the majority of which is out of doors exposed to the environment. The structural steel work of the plant, because it was to be left during the period of construction has been coated with an inorganic zinc silicate. The exterior durability requirements would make us wish possibly to use an alkyd but this is rejected on two counts; one is a tendency to saponification at damage points because of the alkalinity which is generated by the cathodic protection mechanism of the primer; the second is at its poor solvent resistance. Because decorative properties are required, the epoxy coal tar is unsuitable as the topcoat. We cannot use either the vinyl or chlorinated rubber systems because of solvent spillage and this leaves us with epoxy or epoxy tar plus urethane topcoat. In all probability the best choice could well be epoxy paint overcoated with a urethane to provide the decorative properties.

As another example one could look at the armature of a vehicle alternator with requirements for corrosion, abrasion and heat resistance, close dimensional tolerances, and freedom from pin holes etc. Here solvent borne coatings and traditional methods of application are insufficient and the choice could well be polyester or epoxy powder coatings which appear to perform well.

A very different object might be an Army tank, subject to very rough usage, which must retain its colour and its IR reflectance and be decontaminatable from chemical agents. The only suitable system at present would be an epoxy primer followed by urethane topcoats.

Approx date of acceptance by industry	**Material**	**Main present use**
1920	Nitrocellulose finishes	Refinishing of motor cars
1935	Oil-modified alkyds	Solvent based house paints
	Chlorinated rubber	Industrial maintenance paints
1936	Polyvinyl chloride resins	Industrial maintenance paints
	Phthalocyanine pigments	Tinting pigments
1940	Urea resins	Stoving enamels
1945	Melamine resins	Stoving enamels
1948	P.V.A. emulsion paints	Interior architectural paints
1950	Unsaturated polyesters	Polyurethane and polyester paints
1956	Epoxy resins	Industrial maintenance paints
1958	Quinacridone pigments	Motor car finishes
1959	Urethane oils	Cheaper floor finishes
1960	Siliconised resins	Specialised architectural paints
	Acrylic emulsion resins	Water based architectural paints
	Thermoplastic acrylic resins	Automobile finishes
1961	Air dried silicone vehicles for paints steel work	Pre-construction primers and anti-corrosive paints for structural
1965	Thermosetting acrylic resins	Car and appliance finishes
1967	Zinc phosphate pigment	Non-toxic anticorrosive primers
1976	Vesiculated bead pigments	Scrub resistant interior paints

FIGURE 1. Development of Modern Surface Coatings

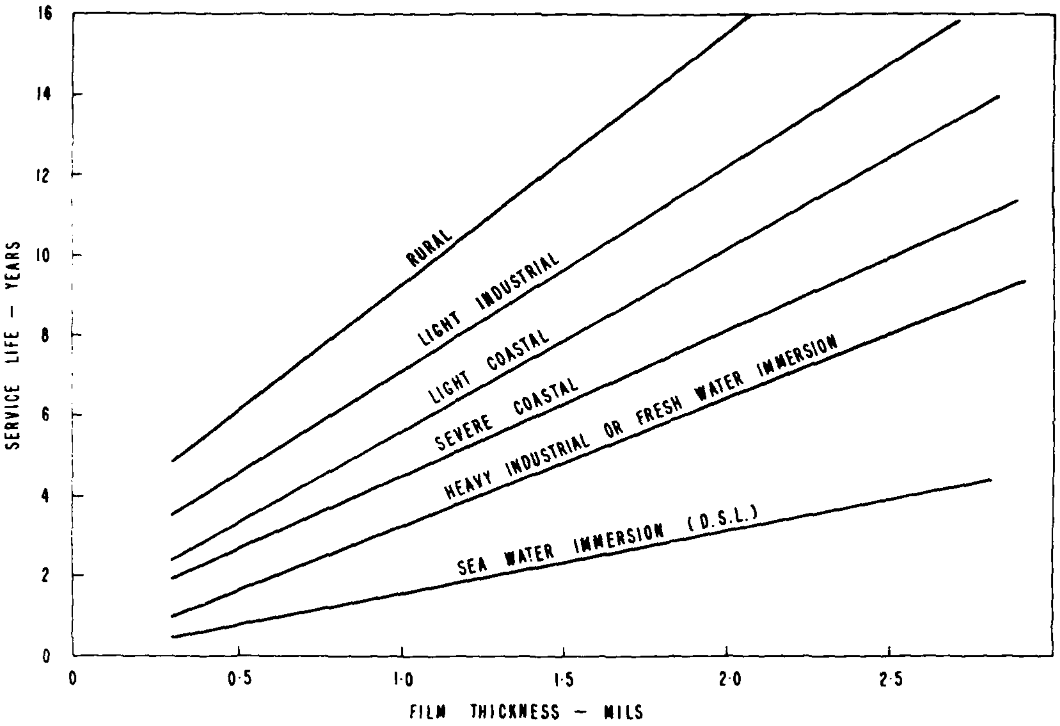

FIGURE 2. Relationship between service life of zinc rich paints and coating thickness for a range of environments.

Type	**Method of Dry**	**Advantages**	**Disadvantages**
Red/lead oil/alkyd	Air	Single container Good anticorrosive Good wetting properties	Slow drying Toxic High permeability Poor water, chemical and solvent resistance Not weldable
Zinc chromate/alkyd	Air	Single container Good anticorrosive	High permeability Poor water, chemical and solvent resistance Low film build Not weldable
Inorganic zinc-rich	Air or chemical cure	Cathodic and rust inhibitive Non toxic Range drying times available Weldable Abrasion resistant Temperature resistant (to 650°C) Solvent resistant Excellent shop primer High build type available	Curing one pack types dependent on ambient conditions Strict recoating conditions Poor alkali and acid resistance Requires excellent surface preparation
Epoxy zinc-rich	Chemical cure	Cathodic and rust inhibitive Non toxic Fast drying Weldable Excellent shop primer High build type available	Two container type Strict recoating conditions Poor alkali and acid resistance Good surface preparation required
Epoxy red oxide	Chemical cure	Low moisture permeability Good water and chemical resistance Non toxic Suitable for immersion Hard film High build type available	Two container type Strict recoating conditions Not rust inhibitive Not weldable
Epoxy red lead	Chemical cure	Low moisture permeability Good water and chemical resistance Rust inhibitive Hard film High build type available	Two container type Strict recoating conditions Not acid resistant Toxic Not weldable

FIGURE 3. Properties of Some Common Primers

Paint Type	Method of Dry	Advantages	Disadvantages
Alkyd	Air-dry (single container)	White and colours show excellent outdoor durability Non-toxic; Relatively cheap	Slow drying; Relatively soft film High permeability, unsuitable continuous immersion Low water, chemical and solvent resistance
Chlorinated rubber	Solvent loss (single container)	Low and high build types White and colours show good outdoor door durability Non-toxic; high water and chemical resistance Fast drying; excellent recoating properties	Low resistance to solvents, vegetable and animal oils and fats Limited heat resistance; Relatively soft film
Epoxy	Chemical cure (Two container)	Low and high build and solvent free types Whites and colours available Low moisture permeability, suitable immersion High water, chemical and solvent resistance Hard flexible film; High abrasion resistance	Unsuitable exterior use if gloss retention required Strict recoating conditions Coatings yellow with age
Epoxy-tar	Chemical cure (Two container)	High build and solvent free types Low moisture permeability, suitable immersion Water and chemical resistant; Relatively cheap	Only dark colours, overcoat required for decorative use Unsuitable contact with potable water and foodstuffs Low solvent resistance; Strict recoating conditions
Polyurethane	Chemical cure (Two container)	Low and high build types White and colours show excellent outdoor durability Low moisture permeability, suitable immersion Non-toxic; high water and chemical resistance Hard flexible film; Good abrasion resistance	Expensive Strict recoating conditions
Vinyl	Solvent loss (single container)	Low and high build type White and colours show good outdoor durability Low moisture permeability, suitable immersion High water and chemical resistance; Non-toxic Fast drying; excellent recoating properties	Low solvent resistance Limited heat resistance

FIGURE 4. Properties of Some Common Paints

ENROLMENT LIST : REGISTRATIONS (OFFICERS AND THEIR AFFILIATIONS)

MEA (MELBOURNE)
- Maj J. Hunter
- Capt Flowers
- Capt W. Healy
- Capt L. Koster
- Capt D. Lowry
- WO1 P. Kubernat
- WO1 J. Nicholson
- Mr P. Allen
- Mr Wright

HQSC (RAAF) MELBOURNE
- Flt Lt P. Jackson
- F Sgt G. Johnson
- Sgt W. Scholtes
- Sgt M. Powell
- Grp Capt Bartram
- Wg Cdr Ellis
- Flt Lt B. Jacobsen
- Flt Lt R. Wilson
- Sgt T. Palframan
- Flt Lt G. McDougall

QAD (ARMY) VICTORIA
- Mr L. Bye

DEFENCE STANDARDIZATION COMMITTEE (VICTORIA)
- Mr T. Wintels

RAAF (RICHMOND) NSW
- Flt Lt P. Lanagan

RAAF (NSW)
- Flt Lt D. Tramoundanis

COMMONWEALTH AIRCRAFT CORPORATION
- Mr R. Pettis
- Mr P. Cook

TELECOM ENGINEERING (RAAF) CANBERRA
- Wg Cdr D. Smedley

EDE (VICTORIA)
- Mr L. Churchward
- Mr Payne
- Mr K. McRae

EDE (VICTORIA)
- Mr N. Garland
- Mr R. Christensen
- Mr H. Wong
- Mr B. Jones
- Mr R. Watkins
- Mr R. Willman
- Mr J. Juffs
- Mr Paterson

AUSTRALIAN AIRCRAFT CONSORTIUM
- Sq Ldr R. Preston
- Mr J. Catersen
- Mr G. Lawrence
- Mr O. Broughton

MATERIEL BRANCH (ARMY) CANBERRA
- Major S. Boon

INO (NAVY) VICTORIA
- LCDR M. Leach
- Mr P. Sullivan
- Mr R. Fryer
- Mr G. Tibbett
- Mr W. Hester
- Mr S. Nadudvary

AFFSE (TASMANIA)
- Mr P. Cavanough

EME (ARMY) MELBOURNE
- Lt Col W. Rotow

QUALITY ASSURANCE LABS (AIR FORCE) VICTORIA
- Mr G. Terrell
- Mr G. Kelly
- Mr R. Chong
- Mr C. Butt
- Mr J. Rodda
- Mr Coleman

NOI (NAVY) CANBERRA
- Mr R. Prescott

MTL ALEXANDRIA NSW
- Mr G. Cooke

GOSI (NAVY) VICTORIA
Mr G. Abela
Mr C. Wood
Mr D. Gray
Mr I. McClellan
Mr R. Breckon

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Lt C. Appleby

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Mr I. Cutler
Mr Rich
Mr J. Martin
Mr M. Bennets
Mr J. Hatty
Mr F. Egan

JTTRE INNISFAIL QLD
Mr J. Wright

SAMAR (NAVY) CANBERRA
Mr C. Brandon

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Mr P. Ramsden
Mr M. Rose
Mr K. McCarthy
Mr A. Fischer

DESIGN GAF VICTORIA
Mr M. Horn

HQSC (RAAF) WEAPENG MELBOURNE
Flt Lt N. Biggar
Flt Lt R. Equid
Flg Off P. Lovell
Flg Off Smedley

DMED DOD CANBERRA
Mr J. Lane

ARL DSTO DOD MELBOURNE
Dr N. Ryan
Dr B. Hinton
Dr W. Pollock

ORD FACTORY DOD BENDIGO
Mr P. Keown
Ms A. Horrocks

RAAF BASE LAVERTON
Flt Lt D. Hobday
Flt Off A. Johnson

EXPLOSIVES FACTORY MULWALA
Mr M. Booth
Mr P. Henderson

AMMUNITION FACTORY FOOTSCRAY
Mr N. Walters
Mr R. Wilborg
Mr J. Zapra

MRL MARIBYRNONG
Dr M.E. de Morton
Dr G.R. Johnston
Dr J.J. Batten
Dr D.A. Wright
Dr R.J. Taylor
Mr P.J. Knuckey
Mr B.A. Wilson
Mr B.S. Smith
Mr F. Marson
Dr D.S. Saunders
Mr G.M. Weston
Mr D. Comery
Mr J. Roseblade
Dr D. Oldfield
Mr R. Barnes

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