PROTECTION OF METALS FROM CORROSION IN STORAGE AND TRANSIT

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Preface

The scope of this book reflects my own experience in carrying out research into corrosion mechanisms, assessing the susceptibility to corrosion of alloys, evaluating the protection offered by metal finishes and exploring the properties of new materials, and in applying the results to the design of new equipments to ensure that they did not suffer corrosion in manufacture, transit, storage or use, and in investigating instances of corrosion when they have occurred.

During the course of my career many changes in materials, transport, storage conditions and manufacturing methods have taken place. The intensive capitalisation of processing and the application of management techniques to the analysis of designs for cost effectiveness (or Value Engineering), reliability, availability, maintainability, durability and safety, now more than ever reveal the key role of corrosion and its prevention. Nevertheless corrosion still strikes unexpectedly, as quixotic as the Scarlet Pimpernel, mocking those who predict reliabilities through elaborate fault analyses to fine levels of precision. The cause is typically an oversight of some apparently minor change of materials, processing or storage conditions, or ignorance of the potential problems of incompatibility between some of the materials used.

In this book I have tried to present the problems of corrosion and the principles of protection in a way that is not essentially linked to a particular type of design or engineering discipline but as a general philosophy which may be applied to all designs. I have attempted to make the text generally intelligible to those with some technical training without compromising the chemical explanation. I have followed the approach which has proved successful within the Ministry of Defence in guiding designers in guarding against corrosion, and in training specialists in Quality Assurance in the techniques of metal finishing. Once a basic understanding of a comparatively few principles has been attained their general application to what appears to be a widely varied range of phenomena provides an intellectually satisfying application of theory to practice. It was this later connection which inspired U. R. Evans to speak of the sheer joy of seeing the beauty of the scientific pattern emerge from a study of the otherwise apparently ugly and morbid subject of corrosion. I have also tried to make the text useful to corrosion specialists by providing a comprehensive account of the corrosion hazards encountered in storage and a summary of the methods of protection available.

My own work on corrosion has been as a member of a team, and part of the wider community of those involved in corrosion research throughout the country which has provided me with both technical support and lasting friendship. I would like to thank those who have been colleagues during my studies of corrosion, especially Dr E. Longhurst, Jack Andrew, John Stringer, Tom Heron and Henry Cole, and the many members of committees on which I have served, for their work and continued help and inspiration on which much of this book depends. In preparing the text I have been fortunate in the forebearance of my family and the help of my wife Angela and daughter Lucy in typing and preparing illustrations. I am very grateful to Henry Cole, Derek Holmes and John Stringer for their dedication in reading the manuscript and for their many suggestions for improving the text. Any remaining deficiencies or mistakes are mine.

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The Need

Metals have shaped the development of the modern world and are now fundamental to our material well-being. Goods made in whole or in part of metals are a major portion of the world's increasing wealth and the distribution of these ever more sophisticated artefacts within and across national boundaries is a characteristic of our civilisation.

As the wealth, aspirations and technological capabilities of nations have risen, the resulting pattern of exchanges of manufactured products has grown in both extent and complexity. An informal system has evolved for moving large quantities of goods rapidly and efficiently around the globe in response to market demands. This system, based on bulk transport, mechanical handling, large interstage storage areas and fast communications, has an inherent flexibility which allows commodities to be rerouted to meet changes in established markets or to develop new markets.

This capability in transport, communications and marketing has to be matched by an ability of the supporting technologies to ensure that goods remain fit for their intended purpose and, just as importantly, are of 'marketable' quality when they are delivered into the hands of the customer. To the customer this means that they should not only be in a serviceable condition but that they should also look attractive and be 'as new'. If merchandise is to arrive in this pristine state it must be protected not only from physical damage but also from the more insidious depredations of staining, rotting, attack by animals, chemical interactions and corrosion.

From the earliest days of trading, protective methods evolved which were often effective, although some spoilage was usually considered inevitable. A pragmatic and evolutionary approach often proved adequate for the comparatively few types of items of simple and robust design which then moved predictably over the same routes, with any changes to the pattern of trade, or the types of commodity transported, occurring only slowly. Methods of protection could evolve on a basis of trial and error, to meet new hazards which resulted from modifications in designs or conditions of transport. However, a more fundamental understanding was needed to combat the sudden onset of serious deterioration when rapid changes in the designs of merchandise, or in the destinations to which they were being sent, became common practice.

The need for greater understanding was very forcibly presented to the United Kingdom during the second world war when the products of the new technologies such as radio sets, aircraft, vehicles, high performance guns, ammunition and spare components were frequently found to be severely corroded and unusable when they arrived in the tropical theatres of war. To quote just one example from that period:

> Two aircraft were received at Cape Town after a two month voyage in slightly ventilated wooden packages . . . steel parts were heavily rusted, aluminium was corroded with some pitting. The wood was heavily discoloured . . . oozing growths were present on the wood.

There was initially a tendency to accept such incidents with resignation as 'tropical corrosion' but earlier successes of research, such as those of U. R. Evans of Cambridge University, into the mechanism and causes of corrosion fortunately offered a more constructive approach to these problems. Government scientists, with Evans and his colleagues, began a series of investigations which provided explanations of many of these war-time failures, and this new understanding allowed better practices to be developed which provided potential solutions to the problems of corrosion and deterioration. Improved codes of practice and specifications covering the selection of materials, protective finishes, methods of packaging, and design procedures were followed, and this led to a marked reduction in corrosion failures in Government equipment in the tropics and elsewhere.

Lest readers infer from these remarks that tropical conditions are intrinsically corrosive it should be noted that very low rates of corrosion are often recorded in tropical areas — the Delhi Pillar for instance is made of iron and has remained uncorroded for centuries despite being unprotected and fully exposed in a tropical area. Even in tropical jungles corrosion rates are often lower than in temperate industrial areas, but *when a metal is contaminated with certain active compounds and is then exposed to the hot humid conditions typical of wet tropical areas, then very rapid corrosion often ensues*.

It was known to those involved in transporting and storing UK equipment in World War 2 that corrosion increased with humidity and with temperature, so that some increase of corrosion rates was to be expected under warm damp conditions. It was however the haphazard occurrence of corrosion and especially the often devastating attack on sophisticated equipments, packaged to what was considered a high standard, which was the cause for most concern.

Rusting of steel components of the packaged aircraft quoted earlier was a typical example of this problem. These components had been protected with electrodeposited cadmium, a coating which had been selected after extensive trials because it had been shown to protect steel against corrosion for many years when fully exposed on a tropical surf beach — the worst conditions which could have been envisaged, and yet, when shielded from the weather in a protective package the cadmium coating had corroded through and the steel had been seriously rusted, all in a matter of two months. In this instance the effect was later shown to be due to acetic acid given off by the wood of the packing case. Timber at that time was in short supply and the relatively new process of kiln-drying wood was being introduced in place of the natural seasoning which had been the previous practice. Under the hot moist conditions of the kiln the acetyl groups which are bound within the cellulose of the wood had hydrolysed and released acetic acid which had little time to escape before the timber was incorporated into a package.

More will be said of the problems caused by wood and other sources of contaminants in the later chapters of this book, but before leaving the particular instance of the packaged aircraft, the 'oozing growths from the timbers' illustrates another aspect of the problems of corrosion. Corrosion of metals is often associated with deterioration of organic materials which may be part of the structure being protected, or of the packaging, because the warm damp conditions under which corrosion most readily occurs are well suited to both microbiological growth and to the hydrolysis of some of the less stable polymers. There is indeed often an interaction and sometimes an interdependence between the various processes of deterioration. The materials of the protective barriers or of the coatings may suffer biological degradation and cease to afford protection against corrosion; frequently the breakdown products from adjacent materials are corrosive and occasionally the products of corrosion accelerate reactions in surrounding materials. Because of this relationship between different forms of degradation, a summary account of the deterioration of materials other than metals has been included in this book, with emphasis on their roles in causing or accelerating corrosion of metals.

The discoveries of early investigations into the causes and cures of the corrosion of metals and the degradation of organic materials in storage and transit, allied with advances in the physical protection of items in transit and the development of new materials, laid the foundations of packaging and preservation as a technology in its own right. The industry sustained by this technology has matured over the last forty years to become one of the largest of modern industries in terms of capital investment, manpower employed, tonnage of goods handled and geographical extent.

The scientific studies of corrosion and the protection of metals have extended to match the breadth of problems which has arisen, although the extent of these activities is not at first evident since they are fragmented among the diverse component industries.

Understanding of corrosion and its prevention has progressed to the point where it is rare to find an incidence of corrosion that could not have been predicted and prevented if available advice had been followed; yet many corrosion failures still occur. One explanation often advanced is that it makes economic sense to reduce the money spent on corrosion prevention to the point where a small percentage of components will fail prematurely through corrosion. Although the force of this economic reasoning is difficult to resist, the increasing costs of raw materials and of fabrication, the greater emphasis on conservation, improvements in protective treatments, the frequently high consequential costs of failures in delays and breakdowns, and the greater discernment and sophistication of customers, all reduce the occasions when any corrosion can be tolerated before goods reach their final user. The vagaries of statistical predictions should not be forgotten; although probabilities of failure may be low, say 0.1%, these failures may be very embarrassing if clumping of these low probability events occurs in time or space and the items in one shipment or one week's production all corrode before they are in service.

More frequent reasons for corrosion failures are lack of knowledge and neglect. These twin reasons were identified as the major causes of unnecessary financial losses to corrosion by an official survey carried out by a committee of experts under the chairmanship of T. P. Hoar (1971) which reported on the costs of corrosion to the United Kingdom. This survey found that the direct annual cost of corrosion in the United Kingdom was at least £1300M, that a quarter of this sum could readily be saved, and that most industries continued to experience examples of serious corrosion. Although some instances were identified where new knowledge was needed, the cause of the continuing ravages of corrosion at such a high level was 'the general problem of poor communications and lack of awareness'.

A more recent Australian study using an econometric model estimated that A$2000M could be saved (at 1982 costs) within the Australian economy if known methods of corrosion protection were efficiently applied. This sum was equivalent to 1.5% of the Australian GNP and it did not include consequential damage.

The methods and materials available for protecting components have improved dramatically over the past thirty years with the developments of plastics and with the mechanisation of many processes which were previously either impracticable or were laborious and often unreliable since they had to be carried out by hand. Synthetic polymers now provide a range of versatile and robust materials for containers, barrier wraps, cushioning, supports and protective coatings. Grit blasting, metal spraying, paint spraying, electrophoretic coating, dip coating, solvent degreasing, vacuum evaporation and ion beam deposition are among the many processes now widely available in automatic or semi-automatic operation to aid the application of protectives. Over the same time, however, the tasks confronting those involved in protecting metals have multiplied with the advent of new technologies, the need for fast processing, the appearance of many new alloys and the tendency of designers to exploit to the full the load-bearing properties of metals so that some of the more intractable corrosion problems which involve the conjoint action of stress and corrosion, such as stress corrosion, corrosion fatigue and hydrogen embrittlement, are becoming more commonplace. The decreasing size of components in many applications, but especially in electronics, has made them ever more sensitive to corrosion. The critical nature of these reactions on the active elements of integrated circuits in particular is now an area of intensive study since it is a limiting factor in their long-term reliability.

The greater use of mechanical handling equipment, unit load containers and air-conditioned storage areas now allows the environments in which goods are stored to be maintained under favourable conditions for much of the time that they are in transit, and this has helped to reduce the hazards from corrosion. These facilities however are not always available at many smaller ports, and inspection and repackaging of the contents of containers in humid, wet and salty atmospheres is still commonplace; inspection at national boundaries by unskilled personnel may also leave containers unsealed and their contents at risk. Often the cost of providing good storage conditions is too high and protection must be attained by coatings and wraps. Knowledge and expertise is needed in selecting the appropriate method of corrosion prevention.

This book is intended to help bridge the gap between the corrosion expert and the concerned designer by providing a guide to the principles of the corrosion and protection of engineering metals which gives an account of the theory and then relates this to practice. A parallel intention is to provide practical guidance to those involved with the day to day protection of metals. References have been used sparingly in the text since the aim is to present a consensus rather than debate the issues from original papers; apologies are offered to any authors accidentally omitted.

Two principles have been followed in ordering the presentation. The first is to give a logical development from basic principles; the second is to keep the reader informed of the relevance of the principles to the practical problems of packaging. The next chapter contains a short description of the hazards, in which some of the major conclusions of subsequent chapters are anticipated, to give perspective to the theme of the subject. The chapters that then follow introduce the theoretical and experimental basis of corrosion, metal cleaning and protective treatments, with an emphasis on the environments encountered in storage and protection. The final section is devoted to the materials used in packaging. It has been assumed that the reader has some basic knowledge of chemistry and metallurgy, but an endeavour has been made to ensure that the book is intelligible and useful to those without this knowledge.

The books of Shreir (1976), Evans (1963, 1968 and 1976) and Parkins (1982) are recommended to readers seeking a full account of corrosion theory and practice. New information is published in a range of journals including *Corrosion Science, British Corrosion Journal* and *Transactions of the Institute of Metal Finishing*.

Standards are a major source of information referred to throughout the book. The British Standards are the major national standard. The Ministry of Defence, as a major customer, has its own series of guides and standards, which are widely available and often have a national status. The leading defence specifications are the Defence Standards (DEF STAN), but Defence Specifications (DEF), Defence Guides (DG), and DTD, CS and TS standards are also issued. International (ISO) Standards are also now more widely used, and in many instances are accepted by the British Standards Institution and some are published as British Standards.

Many other sources of information are available. The leading one in the field of corrosion, set up as a response to a proposal of The Hoar Report (1971), is the National Corrosion Service, National Physical Laboratory, Teddington, Middlesex, TW11 OLW. They offer a comprehensive advisory service and publish a valuable series of technical guides on aspects of corrosion.

Specifications and Standards are referred to frequently in the text and a comprehensive list of specifications, standards and guides related to the protection of metals in packaging is contained in the Annex at the end of the book.

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Hazards

The ultimate result of good protective practice is nothing: no problems, no tarnishing, no corrosion rejects and no customer complaints, but equally: no added value and no appeals for more or better; possibly financial overseers may even be heard murmuring for less and cheaper. As these financiers will point out, money spent on corrosion protection above the essential minimum is money wasted. But insufficient attention paid to protection can result in complaints, problems, expensive reclamations, rejects, a valueless product and angry customers.

The aim of corrosion protection, as with other aspects of protection from deterioration in storage and transport, is to ensure sufficient protection but little more, and to provide it at minimum cost. Getting the balance right requires an overall knowledge of the hazards, and of the methods of combatting them through selection of materials, processing, protectives, storage conditions, and packaging methods and materials. Ignorance in these areas may not only lead to unnecessary expenditure but may give both high costs and high failure rates.

Ensuring that a product is capable of resisting corrosion throughout its service life is inevitably, and rightly, the responsibility of the Product Designer. Protection of raw materials and of components during manufacture is often left to the Production Engineer, and protection during delivery to the Package Designer. Although a degree of delegation is desirable, these three activities are all ultimately the responsibility of the Product Designer, and should be considered by him in conjunction with the Production Engineer and Package Designer from the earliest stage. It is advisable to start this task from basic principles and specifications, although due consideration should be given to previous experience with similar designs, and with the intended methods of storage and delivery. Successful corrosion protection is determined on the drawing board.

Although failures are costly and best avoided they can be turned into an asset if the correct lessons are learned and applied. Much of the theme of this book is an analysis of other people's failures, which, fortunately or unfortunately according to one's point of view, are likely to be long with us to be exploited in this way. A perceptive explanation of the continuing occurrence of examples of bad design or bad practice leading to corrosion failures is contained in the closing remarks of a valuable survey of *Classic Blunders in Corrosion Protection* by Oliver Siebert (1984) — 'We get so soon old, but so late smart'.

Experiments, experience and scientific deduction applied in a formal analysis of the requirements and environments likely to be encountered throughout the life of components is essential in identifying hazards and possible failure modes.

A first step in the selection of a protective scheme is to define the hazards to be encountered and their possible effects on the materials being used. This requires an analysis which determines the duration of exposure, the ambient environments, and the possible problems of compatibility likely to arise between the materials being used.

The hazards liable to be encountered may be broadly grouped as environmental and physical, and are summarised in Table 2.1.

Table 2.1 — Hazards in storage and transit.

Environmental (climatic)		Physical
Temperature extremes		Dropping
Temperature variation	Diurnal cycle	Bumping
Humidity		Vibration
Rain and other precipitation		Impact
Solar radiation		Puncture
Water immersion		Bending
Salt spray		Crushing
Dust, soot and solid debris		Lifting
Corrosive vapours		Dragging
Incompatible materials		
Wind		
Pressure variations		
Biodegradation		
Inspection, pilferage, and attack by rodents and insects		

CORROSION SUSCEPTIBILITY

Table 2.2 contains a summary of the conclusions of later chapters. It shows the range of metals encountered in general engineering (those most widely used are underlined) arranged in the first column on the basis of energy available for oxidation, and in the second column in an order which approximates to their resistance to general atmospheric corrosion. There is