

AN ENGINEER'S VIEW OF CORROSION

BY

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Foreword

It is not to be imagined that the corrosion of metals is a simple study. Many books have been written on, and lives devoted to, this one subject. This brief survey is intended to present corrosion from the point of view of an engineer, who must be a jack of many sciences and master of none. To a physicist, a chemist or a metallurgist some statements may appear a little imprecise or over simplified. To them, the author can only say that much of the over simplification, and none of the imprecision, is intentional.

Before proceeding, the reader is invited to consider on the one hand, the number of defects and breakdowns in his experience in which corrosion played a part, and on the other, the maintenance effort necessary to prevent an even greater number. He will then appreciate that the enormous influence corrosion has on the reliability and availability of ships, demands that the subject should be studied by all concerned with the design and maintenance of machinery which must operate in, or near, that highly corrosive medium, the sea.

THE MECHANISM OF CORROSION

To dismiss the cause of a defect as 'normal corrosion' is a defeatist attitude all too frequently adopted. It is true that corrosion is a normal process in that metals tend to revert to their natural state of metallic ores, but corrosion is seldom inevitable. Certain conditions are essential for its occurrence, and if these conditions are known and can be altered, the corrosion can be halted.

There are two distinct methods by which corrosion can occur.

Direct Oxidation

The first, and simpler, is the direct oxidation of metals by atmospheric oxygen. This is normally only serious at elevated temperatures although some metals, in finely powdered form, will burn in air without the application of heat.

The oxide scale, formed on plain carbon steels when heated, is porous and mechanically weak, with the result that it becomes detached and exposes fresh metal to oxidation. Various alloying elements can be introduced to cause the formation of tough tenacious oxide films which, though thin, effectively prevent further oxidation. Scaling of steel can also be reduced by chromizing and aluminizing, in which processes a skin of these metals is formed, diffusing into the base metal under the action of high temperature, and again forming protective oxide films on the surface.

Electrolytic Corrosion

The second mechanism, which accounts for the vast majority of cases of corrosion met in service, is electrolytic, in which the presence of an electrolyte and the flow of electricity are essential features.

The mechanism of electrolytic corrosion is essentially the same as that of a primary electric battery, and since the latter is generally better known it forms a useful starting point.

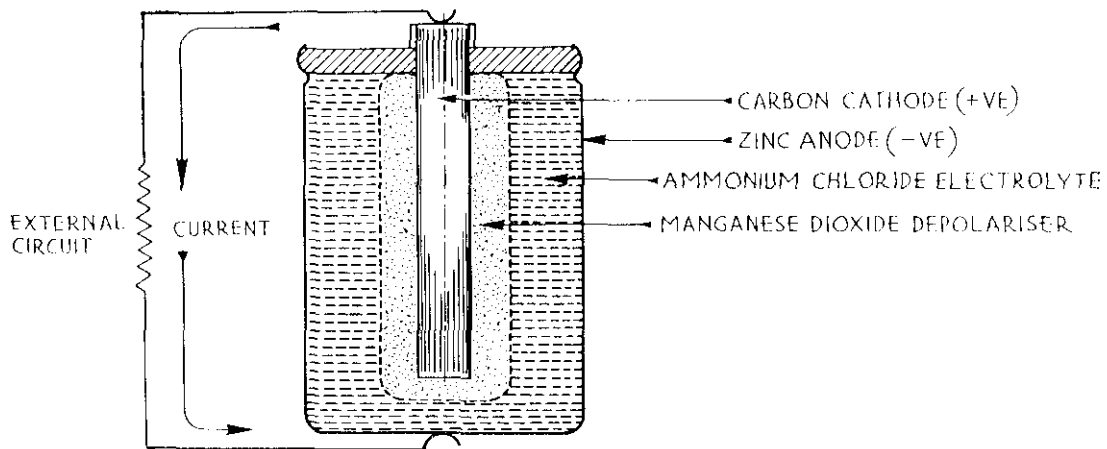


FIG. 1—DRY BATTERY CELL.

The ordinary 'dry' battery cell (FIG. 1) has two electrodes ; a carbon cathode and a zinc anode. Separating the electrodes is an electrolyte, in this case a solution of ammonium chloride in water, to which gelatin is added to prevent spilling.

A cathode is a positive electrode from which the current flows round the external circuit to the anode or negative electrode. Inside the cell the current flows from the anode through the electrolyte to the cathode to complete the circuit. An electrolyte, almost always an aqueous solution, contains 'ions', which are molecules with an excess or deficiency of electrons, giving them negative or positive charges. These charges cause them to be attracted to the cathode or anode. This two-way movement of ions is the means whereby the current flows in the electrolyte. In a metal, current flows by the migration of electrons in one direction only.

Surrounding the cathode, and permeated by the electrolyte, is a mass of manganese dioxide known as the depolarizer.

On open circuit, the carbon cathode has a potential of some one-and-a-half volts above that of the zinc anode. When an external circuit is made, a current flows, the energy of which is derived from the electro-chemical reactions within the cell ; one of these reactions is the disappearance of zinc from the anode.

In more detail, zinc molecules leave the anode and pass into the electrolyte as zinc ions, leaving behind their associated electrons. These electrons travel round the external circuit from anode to cathode (note that by convention an electric current flows in the opposite direction to electrons). On arrival at the surface of the cathode, these electrons meet and discharge ammonium ions into the electrolyte. The resulting ammonium group (NH_4) then breaks down into ammonia (NH_3) and hydrogen. The former escapes as gas, and the hydrogen combines with some of the oxygen from the manganese dioxide to form water. Meanwhile the zinc ions released at the anode have combined with the other electrolyte ions of chlorine to form zinc chloride.

The result is the disappearance of metal from the anode (corrosion), the formation of products of corrosion, zinc chloride near the anode and ammonia near the cathode, and the oxidation of hydrogen at the surface of the cathode.

Polarization

In the absence of the source of oxygen at the cathode (the manganese dioxide depolarizer), the hydrogen would build up on the cathode and set up an opposing voltage which would reduce, and finally virtually stop, the flow of current.

This effect is known as polarization and is naturally to be avoided in cells designed to produce electricity. In acid electrolytes, hydrogen may be evolved as gas and is removed by flotation of the bubbles. In this case depolarization by oxygen is unnecessary.

The Corrosion Cell

FIG. 2 shows diagrammatically a corrosion cell. Its similarity to FIG. 1 can be seen. The anode, where the current enters the electrolyte, is corroded, but the cathode is normally unattacked. Products of corrosion are formed in the electrolyte near the electrodes, and hydrogen is evolved at the cathode. In this case depolarization takes place fortuitously, and usually incompletely, by means of oxygen dissolved in the electrolyte. Other products of corrosion, deposited in an insoluble state on either electrode may assist in polarizing the cell, which is of course desirable in this case.

The Electro-Potential Series

In the primary cell, described above, it will be remembered that the initial difference in potential between carbon and zinc was about one and a half volts.

It is found that all metals may be placed in an order of potential measured from some arbitrary datum. This order, known as the electro-potential series, is shown in the following table. The order may vary slightly in different electrolytes, with different current densities flowing, and at different temperatures.

The series will therefore give some indication of the initial potential difference between two metals when connected together in an electrolyte. The lower of the two will be the anode and will therefore tend to corrode.

It must be emphasized that this list does not give the relative corrodibility of individual metals by themselves, for instance aluminium, low down in the table is inherently more corrosion-resistant in sea water than is steel. If the two are placed in contact however the aluminium is liable to corrode. Nor does the series indicate that the corrosion of one metal is inevitable when connected to one higher in the list, it only indicates a tendency. Such a cell might rapidly be polarized by the products of the initial corrosion.

Electro-potential series

Cathodic End	Platinum
	Gold
	Graphite or Carbon
	Stainless Steel (Passive)
	Monel
	Gunmetal
	Cupro-nickel
	Copper
	Nickel
	Brasses
	Chromium
	Tin
	Lead
	Stainless Steel (Active)
	Iron & Steel
	Cadmium
	Aluminium
	Zinc
Anodic End	Magnesium

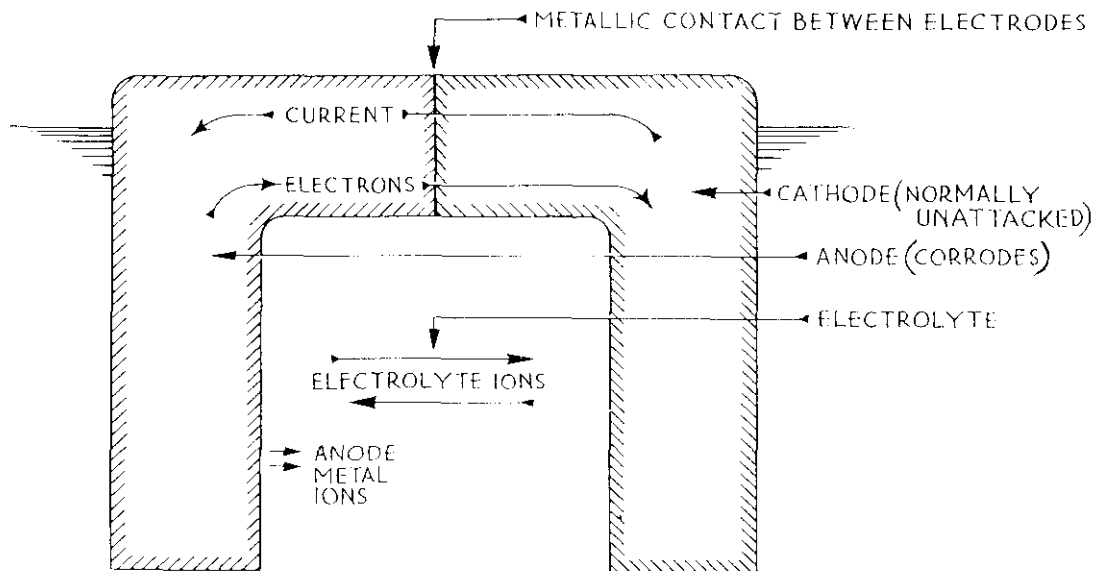


FIG. 2—CORROSION CELL

It will be noted that stainless steel appears twice in the list, widely separated and suffixed 'active' and 'passive'. To understand this it is necessary to digress. It was mentioned earlier that direct oxidation of metals was not serious except at elevated temperatures. Nevertheless most 'engineering' metals are superficially oxidized at normal temperatures by oxygen in air or water, but this oxide film is thin and invisible to the naked eye. In the so-called stainless materials, this film is tenacious and impervious, preventing further attack and maintaining the original lustre of the metal. If the film is mechanically abraded it will heal itself rapidly, providing oxygen is available.

This film has a considerably higher potential than its parent metal. If the metal has a film, for which the presence of sufficient oxygen is necessary, it will be passive. If it has no film due to lack of oxygen, or is abraded mechanically as quickly as the film forms, or cannot form a film in its impervious form because of the chemical constitution of the electrolyte, it will be active.

Corrosion Cells in Practice

FIG. 2 shows a corrosion cell diagrammatically. In practice the essentials of a corrosion cell, which have already been seen to be two portions of metal at different potentials in contact in an electrolyte, may take various forms not immediately recognizable as such.

The two electrodes may be two different metals or they may be, and frequently are, different areas of the same piece of metal which have different potentials due to local differences of metallurgical structure, stress, or temperature. They may be areas of different electrolyte concentration or oxygen concentration therein. They may be areas of metal, one of which is covered with a cathodic oxide film and the other not. These differing areas may be so many, so close, or so small as to be indistinguishable.

The external circuit may be direct contact between two metals, or a third may be interposed. It may even include another electrolytic bridge.

The electrolyte, besides being sea water as in submerged corrosion, may consist of condensed moisture trapped in a crevice or absorbed in some porous

material such as lagging, packing or cardboard. It may be merely a thin film of moisture on a surface, or even a single drop. Salt water, even when diluted, is a powerful electrolyte, and drops of condensed moisture with traces of salt or atmospheric pollution form good ones.

It is fortunate that most corrosion cells in practice are polarized to some degree, and many almost entirely. Otherwise the problem of maintenance would be even greater than it is.

TYPICAL FORMS OF ELECTROLYTIC CORROSION

Rusting

The superficial oxide skin formed in air on steel is slightly cathodic to the base metal and is never perfectly continuous. Fresh or salt water, or condensed atmospheric moisture containing traces of salt or absorbed gases, form effective electrolytes and a multitude of minute electrolytic cells are formed. The ions of iron migrate from the bare anodic areas into the electrolyte where they meet hydroxyl (OH) ions from the electrolyte and form ferrous hydroxide, the main constituent of rust. This is incapable of stifling the anode, at which a small pit is produced. The cathode is effectively depolarized by the presence of atmospheric oxygen diffusing into the electrolyte.

Bi-Metallic Contacts

Enough has already been said to explain the effect of connecting two different metals in an electrolyte, and many examples will spring to mind: the corrosion of a steel hull near gunmetal fittings, of steel propeller shafts near the gunmetal liners, of steel 'corrosion pieces' in copper pipe-lines. Even the old sailing navy knew the disease of 'nail-sickness' where iron nails corroded when the ships were copper-sheathed.

There is, however, a more subtle form which often occurs. If sea water, or even fresh water, passes through a copper or copper alloy pipe or fitting, some of the copper is dissolved into the water. Should this water subsequently come into contact with another metal lower in the electro-potential series, for example steel, the copper in solution will 'plate-out' on the steel, just as a penknife dipped into copper sulphate becomes covered with a thin coat of copper. These particles of copper, which will not be visible in low concentrations, form minute bi-metallic contact cells with the steel and the steel corrodes rapidly. This effect may be seen on inner bottom plating on which falls the effluent from copper drain pipes, or the condensation from copper or gunmetal pipes or fittings.

Similar, but even more severe, corrosion will occur to aluminium alloys when in contact with copper-contaminated water. It should be noted that metallic contact between the copper pipe and the steel or aluminium is not necessary for this process to continue.

One final point on bi-metallic contact corrosion should be noted. The quantity of metal removed from an anode is directly proportional to the quantity of current that has flowed. One amp flowing for one year will remove 20 lb of steel or 22 lb of copper. If this current is concentrated on a small anode, the average depth of attack will be greater than if a larger anode were present. Thus the ratio of the size of anode to the size of cathode affects the severity of attack, a small anode connected to a large cathode being particularly dangerous.

The average depth of attack, however, is not necessarily a good indication of severity. A single deep pit may be more likely to fail than widespread shallow attack.

Dezincification

This occurs in brasses in sea-water and the mechanism is obscure. It is essentially electrolytic corrosion caused by metallurgically differing areas of the metal acting as minute anodes and cathodes. This results in corrosion of the alloy and the redeposition of the copper as a porous matrix, with scarcely any mechanical strength.

The tendency to dezinc increases with zinc content, being negligible below 15 per cent zinc. The addition of arsenic or tin almost eliminates it in the single phase alloys (up to about 30 per cent zinc), but the dual phase brasses (between 30 per cent and 40 per cent zinc) are liable to this trouble, particularly the wrought high tensile brasses often misleadingly called manganese bronze.

Brazing metal (60 per cent copper, 40 per cent zinc) will dezinc rapidly when exposed to sea-water. Silver solder should be used for piping when large areas are exposed to sea-water.

Impingement Attack, or Corrosion-Erosion

This occurs in parts exposed to turbulent flowing sea-water. Such parts are usually copper or copper-base alloys, and it is in these that it is usually found. Typical subjects are condenser tubes, particularly at inlet ends, sea-water circulating pipes, firemans, and fire and bilge pump casings.

The cause is the mechanical removal of the protective surface film on the metal by the turbulence of the water, aided by the minute but intense shocks caused by entrained air-bubbles breaking up when they impinge on the surface. The areas of metal so exposed are anodic to the remainder of the film-covered metal, a small electrolytic cell is formed and a pit appears. This pit aggravates the turbulence locally and the attack continues. Plenty of depolarizing oxygen is available in the flowing water and all products of corrosion are washed away.

In tubes and pipes the attack often takes the shape of a horseshoe pit (the open end downstream) with bright metal showing at the base.

Cavitation-Erosion

This is distinct from corrosion-erosion in that it occurs only when vacuum or water-vapour bubbles are formed in flowing water, where the pressure is reduced locally below the vapour pressure. These bubbles subsequently collapse (often audibly), and the resultant forces are sufficient both to destroy the protective film, as in corrosion-erosion, and also actually to tear out particles of metal.

Although this form of attack can be produced by liquids such as oil, which are not electrolytes, it is probable that all cases in sea-water are considerably aggravated by simultaneous corrosion.

Such attack may be found on the suction face of propellers, in impellers and suction eyes of pumps running under conditions of vacuum. The attacked metal has a honeycombed porous appearance, very different from the water-worn appearance of corrosion-erosion.

Deposit Attack

Alloys which rely for their corrosion-resistance on the oxide films they grow, are prone to this form of attack. An area covered by a deposit of mud, a splash of paint or a barnacle is denied the quantity of oxygen necessary to grow a fully protective film. It is thus left anodic to the remainder of the metal and corrosion occurs beneath the deposit.

Crevice Attack

This is due to the same mechanism as deposit attack. The oxygen supply to the metal is restricted in any crevice (under a bolt head, or in a propeller shaft lying in a rubber bearing, for example) and corrosion pits are formed in the crevice.

Differential Aeration Cells

In general, any area, the oxygen supply of which is less than that of the surrounding metal, is liable to become anodic and corrode. Such areas are known as oxygen concentration or differential aeration cells.

Corrosion Fatigue

Metals subject to alternating stress in a corrosive medium, fatigue much more rapidly than in air. Corrosion pits provide starting points for cracks, which develop rapidly as deep corrosion fissures, continuously extending in depth by the combined effect of the stress concentration and corrosion at the root, due to the restricted supply of oxygen that can penetrate—a form of crevice attack.

It is noteworthy that metals do not have a corrosion-fatigue limit, because there is no stress below which corrosion fatigue will not eventually occur if the number of cycles is large enough. This is distinct from ordinary fatigue in which some metals do show a limit.

It should also be noted that, whereas the ordinary fatigue strength of steels is roughly proportional to the tensile strength, the corrosion fatigue life of high tensile steel is little, if any, better than mild steel.

Corrosion fatigue cracks have been found in propeller tailshafts, submarine main engine frames, and in many other parts including internal combustion engine valve springs exposed to a marine atmosphere. Similar engines run on shore showed no sign of this trouble.

Stress Corrosion

Areas of metal subject to steady tensile stresses in a corrosive medium are liable to crack. Although stressed metal is slightly anodic to unstressed metal, the majority of the attack is probably due to the opening of corrosion fissures under the action of the stress, exposing fresh metal at the root of the crack to further attack.

Season cracking of brass tubes, in which cold-drawing leaves residual stresses, is due to stress corrosion, the electrolyte being condensed moisture containing traces of ammonia or some other contaminant. The name originates from the cracking of brass cartridge cases in India when the advent of the monsoon raised the humidity sufficiently for an electrolyte film to form on the metal.

THE PREVENTION OF CORROSION

Since corrosion arises from the flow of electricity from the anodic metal of the corrosion cell, any method which prevents this flow of current is an effective antidote. There are various lines of approach. The most obvious is to remove the electrolyte from contact with the metal. Another is the interruption of the electric circuit by insulation; others are the chemical inhibition of the reactions at the electrodes which will effectively polarize the cell, and the reversal of the natural direction of the current by the application of an artificially contrived voltage.

Paints

Contrary to popular belief, few paints are entirely impervious to water. Their effectiveness in the prevention of corrosion arises, not from their ability to keep the electrolyte from contact with the metal, but in their high electrolytic resistance and, in the case of oil-based paints pigmented with metallic oxides or salts (e.g. red lead in linseed oil), in the formation of chemical compounds at the metal face which inhibit the electrode reactions.

Certain cellulose and synthetic resin or rubber paints are impervious, and some high duty paints, such as Detel DMU and Tretol HH, contain a high proportion of metallic zinc powder which has a further protective action (see later under cathodic protection).

Other Non-Metallic Coatings

Rubber sheet and various plastic and synthetic resins may be applied to metallic surfaces in substantial thicknesses, to provide completely impervious coatings which effectively exclude the electrolyte from contact with the metal, and these are finding increasing applications. Propeller shafts of new ships are now sheathed in rubber, and experimentally with synthetic resin reinforced with glass fibre cloth. Copper bellows-pieces and steel condenser doors have also been successfully rubber covered. Main circulator inlets are now being treated with neoprene rubber paint, thus avoiding the bugbear of loose zinc protectors damaging main circulators.

Surface Preparation

Paints and inert coatings cannot adhere to metal unless scrupulous care is taken in cleaning the surface. Paint applied to a rusty or greasy surface, or over old flaking paint, is almost a complete waste of time. Time and trouble taken in scaling, chipping, sand-blasting and other preparative treatments is amply repaid by the subsequent life of the coating.

It is appreciated that this is a counsel of perfection in the case of machinery space bilges and other places where cleaning and drying are almost impossible. This problem is receiving vigorous attention.

Metallic Coatings

Another widely used method of prevention of corrosion is the application of inherently non-corrodible metal coatings, such as chromium, nickel, copper, tin, aluminium, zinc or cadmium, by electroplating, spraying or hot-dipping.

It should be noted that of these metals, chromium, nickel, copper, and tin are cathodic to steel. This means that if the coating is porous (and thin electroplating and sprayed metal is) or if it is scratched or damaged in some way, a small area of the underlying anodic metal will be exposed, surrounded by a large area of cathodic metal, and intense corrosion at the break will occur. The use of these metals is therefore dangerous unless particular care is taken to see that the coatings are sufficiently robust and impervious.

Aluminium, zinc and cadmium are, however, anodic to steel and a small area of steel exposed will be cathodically protected by the surrounding coating. The use of these metals is therefore much more satisfactory except where hard surfaces or good looks are primarily required.

In hot water, zinc may reverse its potential relative to steel, thus aggravating corrosion instead of preventing it. This partially accounts for cases of severe corrosion of galvanised steel hot fresh-water pipes.

Electrical Insulation

In a few cases complete electrical insulation between dissimilar metals is possible, but care must be taken that such insulation is complete. The poor mechanical properties of many insulating materials frequently make this difficult.

Inhibitors

Certain chemicals, when added to an electrolyte, have the property of forming surface layers on the anode or cathode, which inhibit the chemical reactions that would otherwise occur. They are used in closed circuit cooling water systems of I.C.E.'s and gun-barrels, and in the acids used for chemical descaling, to prevent attack on the underlying metal.

Vapour Phase Inhibitors (V.P.I.) are used in packaging. They are solids which volatilize and exert their inhibitive influence against atmospheric corrosion when in the vapour phase.

Cathodic Protection

This is a comparatively new name for an old and well tried method.

In order to prevent current leaving a vital part and entering the electrolyte, a current is forced to enter the parts from the electrolyte. This can be done in two ways.

First, the sacrificial anode, corrosion piece or protector block. A piece of metal, anodic to the part to be protected, is placed in metallic contact with it. The latter then becomes the cathode of this purposely contrived cell and is protected at the sacrifice of the anode.

This method is exemplified by the zincs fitted to steel hulls to prevent their corrosion by adjacent non-ferrous fittings, and by steel corrosion pieces in copper pipes, gunmetal condensers and heat-exchanger doors.

Unfortunately zinc frequently becomes polarized after a short time by the products of corrosion, and protection ceases. The fact that zincs are 'in good condition' merely indicates that they have ceased to fulfil any useful function!

Steel is, however, highly anodic to copper and copper alloys, and little polarization occurs. There is rapid corrosion of the steel, and this results in the well-known maintenance burden of renewing corrosion pieces.

Experiments are being made with various zinc alloys, and magnesium anodes are used for cathodic protection of buried pipe lines, jetties, ballast tanks and the hulls of idle ships. Hydrogen gas is evolved from magnesium, which introduces a risk when used in confined spaces.

The second is the impressed current method. The part to be protected is connected in an electric circuit supplied with power from an external source, and arranged so that it is the cathode. An inert anode, for example carbon, is usually employed. Current is therefore forced to enter the part to be protected, and corrosion cannot occur.

This method is also used for the protection of buried or floating structures, and is in use in the Reserve Fleet. It has been applied experimentally to active ships in the R.C.N.

Dehumidification

Atmospheric corrosion of metals will not occur, provided that the relative humidity is low enough to prevent a film of moisture condensing, and acting as an electrolyte. In enclosed spaces, air may be artificially dried by means of hygroscopic chemicals, such as silica gel and quicklime. Dehumidification is effectively applied to sealed instruments, in packaging, and to large portions of reserve fleet ships between decks.

CONCLUSION

While the author agrees with the poet that a little learning is a dangerous thing, he believes that no learning may be even more dangerous. It is hoped that this brief survey may assist some engineers in their everlasting battle against corrosion ; a battle in which it pays, handsomely, to know your enemy.

The cost of corrosion and preventive work has been estimated to amount in Great Britain to £200,000,000 annually, and in the United States to £2,000,000,000. No figure is known for its cost to the Navy, but it is undoubtedly enormous.

There exists the Admiralty Corrosion Committee whose advice and assistance are always available to the Navy in combating corrosion. A.F.O. 959/53 details its purpose, and the method of obtaining its assistance. In order to carry out its function, it must be informed of cases of corrosion, even those which at first sight may be dismissed as 'normal corrosion'.
