

Chemistry Background Book



Corrosion



Part 1 what is corrosion?

Corrosion in a familiar aspect.
This burnt-out van will
eventually rust away completely.



A car, unless it is carefully looked after, soon develops patches of rust on the bodywork. Silver spoons and forks must be polished frequently to prevent tarnish on them. Copper steeples and bronze statues become coated with a greeny-blue film. Stone traceries on city buildings are slowly eaten away. Reactions of this kind—reactions of substances with the atmosphere or whatever the surrounding environment may be—are called corrosion. You have certainly seen corrosion. It is going on around you all the time. In this book, we are concerned with the commonest kind of corrosion, the corrosion

of metals. It has been estimated that metallic corrosion and its prevention costs this country over 500 million pounds a year, or about £10 for each member of the population.

There are several things that can be done to prevent corrosion. The surface of the metals can be covered with a protective barrier (for example paint); the properties of the metals can be modified (by, for example, alloying them with another less reactive substance); or their environment can be changed with suitable chemicals. Before looking at methods of prevention, first we must see how corrosion happens.



An electron micrograph showing the formation of an oxide film on the surface of aluminium metal. (Magnification $\times 15,000$).
Aluminium Federation

Stability of metals – How corrosion takes place can be studied in the Earth's crust. If you were to dig in the right place and if you dug carefully enough, you might find a nugget of gold or a lump of silver. But however hard you looked you wouldn't find any aluminium or chromium or titanium or sodium. These metals, and almost all others, exist in nature only as compounds. They are combined with such elements as oxygen and sulphur, and the compounds so formed are more stable than the metals themselves.

Before any use can be made of the metals, they must be extracted from their compounds; the compounds must be reduced by heating them with carbon (usually coke) or by passing an electric current through them. However, once a metal has been extracted and has been shaped into a car body or the hull of a ship or a drain pipe or whatever it may be, there is always a tendency for the metal to revert back to one of its more stable compounds – or, in other words, to corrode.

Oxide films – The most obvious, if least damaging, kind of corrosion is direct oxidation of a metal by the oxygen in the air. The result of this reaction is to form a film of oxide on the metal surface. At room temperature almost all metals (gold and platinum are exceptions) are covered with a film of oxide. With such metals as aluminium, nickel, and zinc, the film seldom grows to more than 100 ångströms thick and is therefore invisible, but this is enough to prevent further oxidation. With such metals as magnesium, sodium, and calcium, the oxide film tends to crack, thus exposing the metal underneath and so allowing progressive corrosion deep below the surface. Of these metals, only magnesium is of importance to engineering. On some common metals such as iron and copper the oxide films are protective at room temperature but

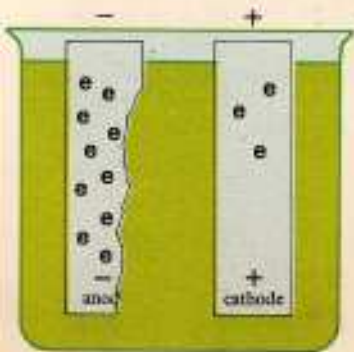


disrupt as the temperature increases. Alloying the iron with chromium or the copper with aluminium can protect these metals against direct oxidation because the chromium and aluminium form a more stable coating of oxide.

But corrosion is far too widespread to be explained by direct oxidation alone, because corrosion is much more severe where metals are impure, where two different metals are in contact, and where moisture is present. A car, for example, rusts much more quickly if it is left in the rain than if it is kept in a garage.

Electrochemical corrosion – The most damaging kind of corrosion results from electrochemical attack on the metal. A typical electrical cell consists of two electrodes (often two different metals) immersed in a liquid electrolyte such as water. If the electrodes are joined by a substance that will conduct electricity (usually a metal wire), electric current flows along it from one electrode to the other. At the anode, the electrode substance loses electrons (oxidation) and passes into the electrolyte as ions. At the cathode, ions present in the electrolyte pick up electrons (reduction) to become free atoms. Thus the anode of the cell is slowly eaten away.

This is what happens in electrochemical corrosion. Although well-constructed electrical cells such as we use in the laboratory do not exist on the surface of a piece of metal, we can envisage a number of crude cells being formed there. Water, either from the atmosphere or from the sea or river if the metal is submerged, forms the electrolyte. Where two different metals are in contact, these two metals form the electrodes. Which metal is the anode, and is therefore eaten away, and which the cathode, depends very largely on the positions of the two metals in the electrochemical series. This,

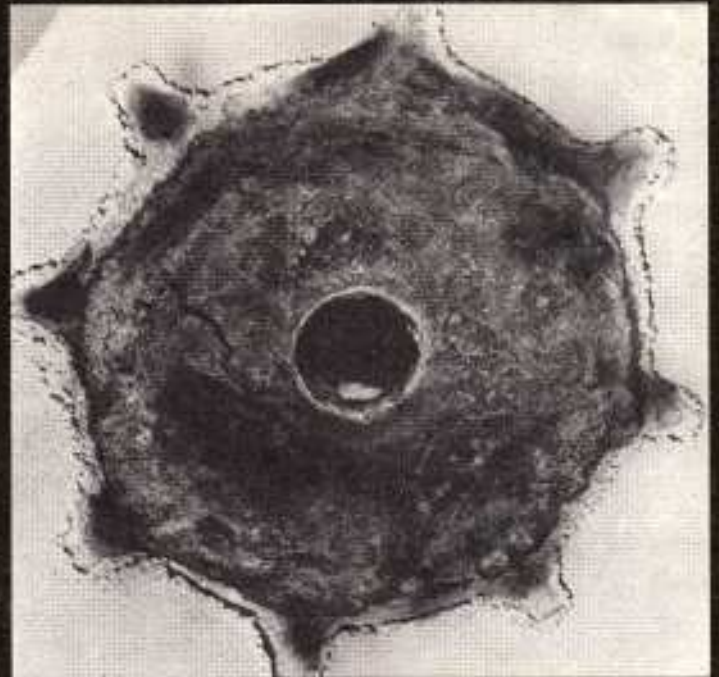


In an electrical cell it is the anode which is eaten away.
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With two different metals dipping into an electrolyte, there is a difference in electrical potential between them. The magnitude of the difference depends on the two metals and the electrolyte. As this voltmeter shows, the potential difference between zinc and copper in sodium chloride solution is 700 millivolts.
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A familiar form of corrosion –
the rusting of corrugated steel
sheet.
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This stone head of an elephant
on Bristol Cathedral has been
corroded by the industrial
atmosphere – especially by
acidic fumes of sulphur dioxide.
The corrosion of stone is the
result of direct chemical attack,
not of an electrochemical
process.

With two different metals in contact, electrochemical corrosion can be very severe. Here magnesium (forming the anode) is cast around a hollow steel core (forming the cathode). At the interface between the magnesium and the steel, the magnesium has begun to corrode.
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in turn, depends on the relative ease with which the metals lose electrons (are oxidized) or gain electrons (are reduced). For example, lead water piping is joined to an iron storage tank. Lead is lower in the electrochemical series than iron, and therefore the lead piping forms the cathode and the iron tank the anode. It is the iron tank which corrodes. Iron is lower in the electrochemical series than zinc, and if there is a crack in the zinc coating of a galvanized iron roof, it is the zinc which corrodes, not the iron. The further apart the two metals are in the electrochemical series, the greater is the potential difference of the cell and the more damaging is the corrosive attack.

The order of some metals in the electrochemical series:

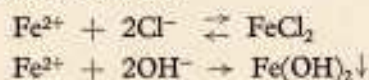
- Sodium
- Magnesium
- Aluminium
- Titanium
- Zinc
- Iron
- Nickel
- Tin
- Lead
- Copper
- Silver
- Platinum
- Gold

The severity of corrosion is also influenced by the electrolyte. Distilled water is only a very weak electrolyte and metals hardly corrode in it. But the moisture in the air usually contains substances such as carbonic acid and, in places near the

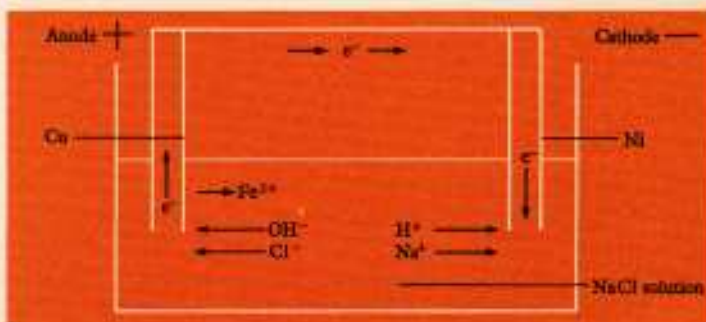
sea, sodium chloride. Acidic substances, in particular, accelerate corrosion. Because of the presence in the atmosphere of the acidic gas sulphur dioxide, iron may corrode four times as quickly, and zinc six times as quickly, in industrial areas as in country districts. Metals that are submerged beneath the sea – for example, ships' hulls or jetties – are also exposed to corrosive attack from dissolved salts.

The action of a typical corrosion cell set up between two metals is shown in the following example. Iron plates on a ship's hull are fastened with copper rivets. Iron is higher in the electrochemical series than copper and therefore forms the anode (see diagram below). Sodium chloride solution (or the sea) forms the electrolyte.

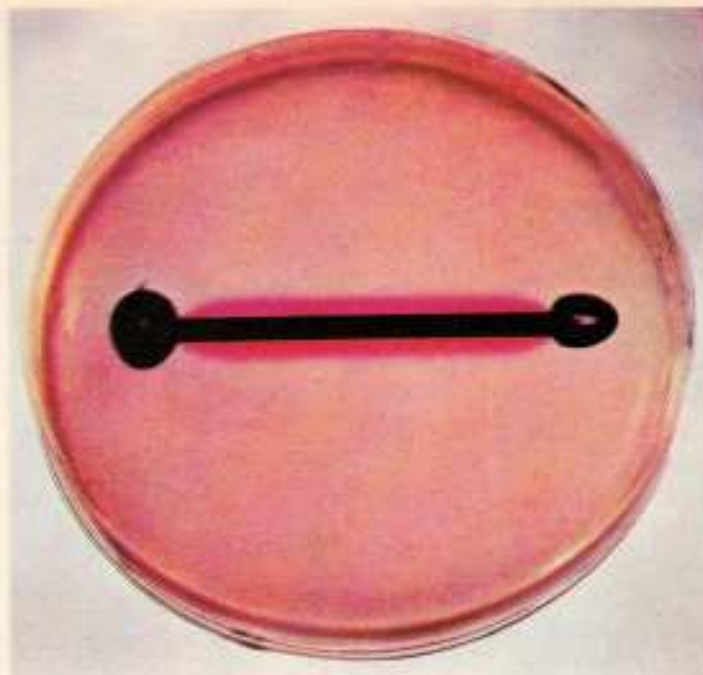
1. Electrons (e^-) travel from the anode to the cathode by the external circuit which is the metal or oxide film between the two separate electrode areas.
2. Iron goes into solution as cations (Fe^{2+}), leaving electrons behind.
3. Cations already in solution (H^+ and Na^+) migrate towards the cathode where hydrogen ions combine with electrons and are discharged as hydrogen gas.
4. Anions already present in solution (OH^- and Cl^-) migrate towards the anode and are discharged on encountering Fe^{2+} ions to give iron (II) chloride and iron (II) hydroxide, as follows:



Iron (II) chloride is soluble in water and dissociates to form iron (II) and chloride ions. Iron (II) hydroxide forms a solid



As this photograph shows, an anode and a cathode can be present on a single metal. The solution round the shank of the nail is red – from reaction of phenolphthalein indicator with hydroxyl ions at the cathode. The solution round the head and point of the nail, where the metal has been heavily stressed, is dark from reaction of potassium ferricyanide with iron (ii) ions passing into solution from the anode. Thus the shank of the nail forms a cathode and the head and point of the nail form anodes.
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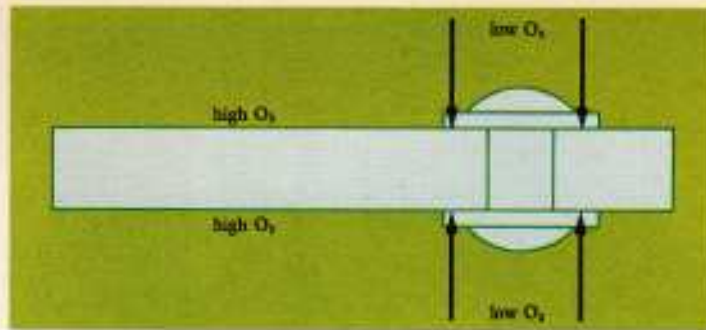
Phenolphthalein and potassium ferricyanide indicators show that when a drop of sodium chloride solution is put on a clean steel plate an anode forms at the centre of the drop (blue coloration) and a cathode at the surface (red coloration). The potential difference between the centre and the surface is due to difference in oxygen concentration.
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precipitate which reacts with oxygen to form a mixture of iron compounds, mainly such hydrated oxides as $\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$. These iron oxides are collectively known as rust. It will be noticed that the concentration of sodium chloride in solution remains the same and thus a small quantity of salt can keep on attacking the metal anode without losing strength.

If corrosion of this kind were allowed to proceed unchecked, the ship's plates would be slowly eaten away – although, as explained in the caption on page 8, the corrosion is less damaging this way than if the plates were made of copper and the rivets of iron. Careful choice must be made of rivetting metals, and periodically ships must go into dry dock to have their hulls protected with a coat of paint.

Electrochemical corrosion of a single metal – The formation of an electrical cell where two different metals are in contact is not difficult to understand. Yet metals can corrode without such contact and far more severely than can be explained by direct oxidation. This is because it is possible for both cathodes and anodes to be present on the same piece of metal. There are several explanations: there may be impurities or



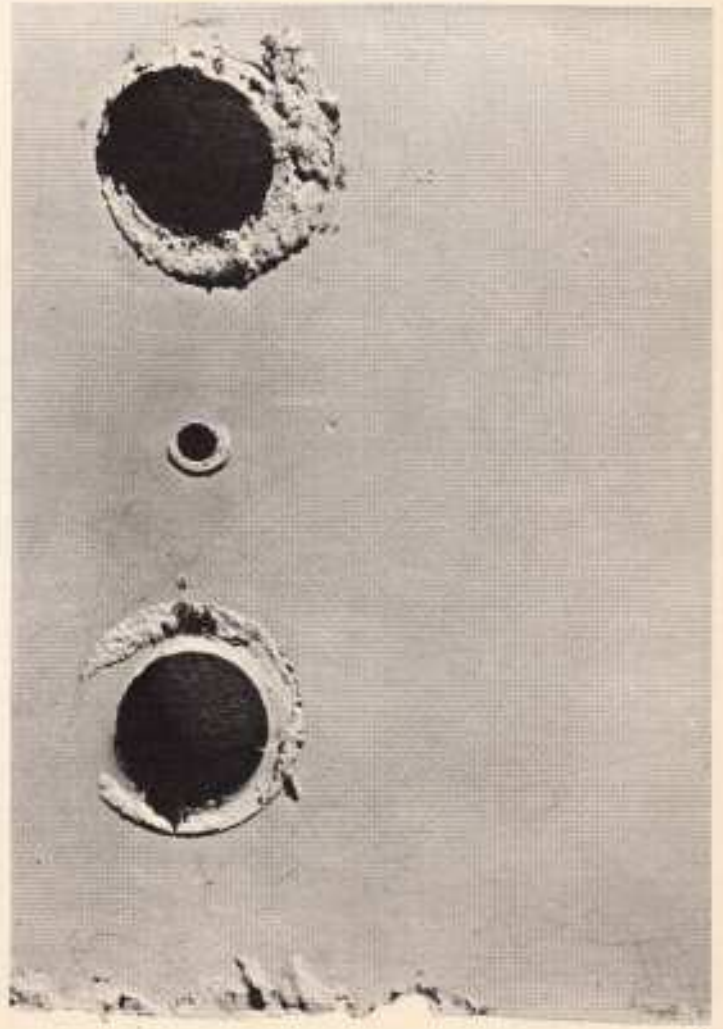


Crevice corrosion where a metal plate has been covered by screws and washers. Corrosion has resulted from oxygen shortage below the washers. The diagram shows how the corrosion cell is formed. *International Nickel Ltd.*

alloying elements in the metal; a potential difference between the pure metal and its oxide film; roughness or strains in the metal; or, as is shown here, differences in the concentration of oxygen at separate areas of the metal.

The following experiment shows that electrochemical corrosion of a single metal can occur. To a few millilitres of N/10 sodium chloride solution are added one drop of phenolphthalein indicator and one drop of potassium ferricyanide. A single drop of this solution is pipetted onto a piece of clean steel plate. At the surface of the drop, oxygen from the air can dissolve easily in the solution, but at the centre of the drop oxygen cannot penetrate directly. Therefore there is a difference of oxygen concentration in the drop and a 'concentration cell' is set up in which the area where there is most oxygen (the surface) forms the cathode and the area where there is least oxygen (the centre) forms the anode. Evidence for this is the appearance of a patch of blue at the centre of the drop, where the potassium ferricyanide reacts to give a characteristic blue colour with iron (II) ions passing into solution from the anode, and the appearance of the red coloration at the surface of the drop, where the phenolphthalein reacts with the hydroxyl ions at the cathode. After about half an hour, an area of yellow rust begins to show between the centre and the surface. Concentration cells of this kind, stemming from differences in oxygen concentration, are particularly damaging in crevices in metals where water collects, for the oxygen concentration tends to be much higher at the top of the crevice than at the bottom.

Extent of corrosion – As with oxide films, the products of electrochemical corrosion can form a protective coating over the metal which prevents further attack. But usually they are



prevented from doing this because they dissolve in the electrolyte or are washed away, or because they are precipitated in the space between the anode and the cathode and so cannot affect the reaction.

Indeed, if the corrosion products reduce the area of the anode without covering it completely, the result can be far more damaging. For the reaction is in no way diminished but becomes concentrated on a much smaller area. This leads to pitting of the metal which weakens it far more than if the corrosion is spread thinly over a large area.

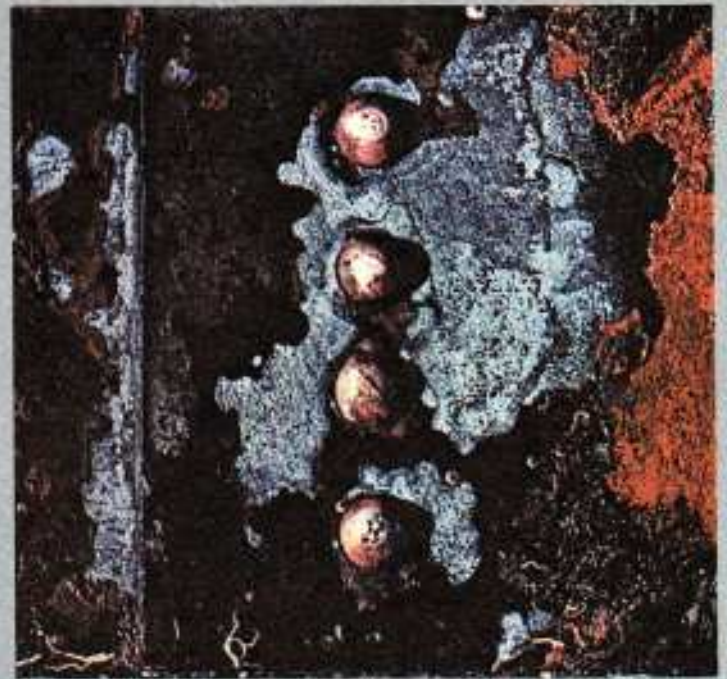


Pitting in a metal surface resulting from local corrosion under marine organisms that have become attached to the plate during immersion in sea-water.

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The smaller the area of the anode the more concentrated and damaging is the corrosive attack. Top right: copper rivets (cathodic) in steel plates (anodic) have resulted in mild corrosion over a large area of steel. Bottom right: steel rivets in copper plates have resulted in severe corrosion on the small area of the steel rivets.

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Part 3

how corrosion is prevented

A number of fanciful methods of preventing corrosion have been proposed at one time or another. You may remember that of Lewis Carroll's White Knight!

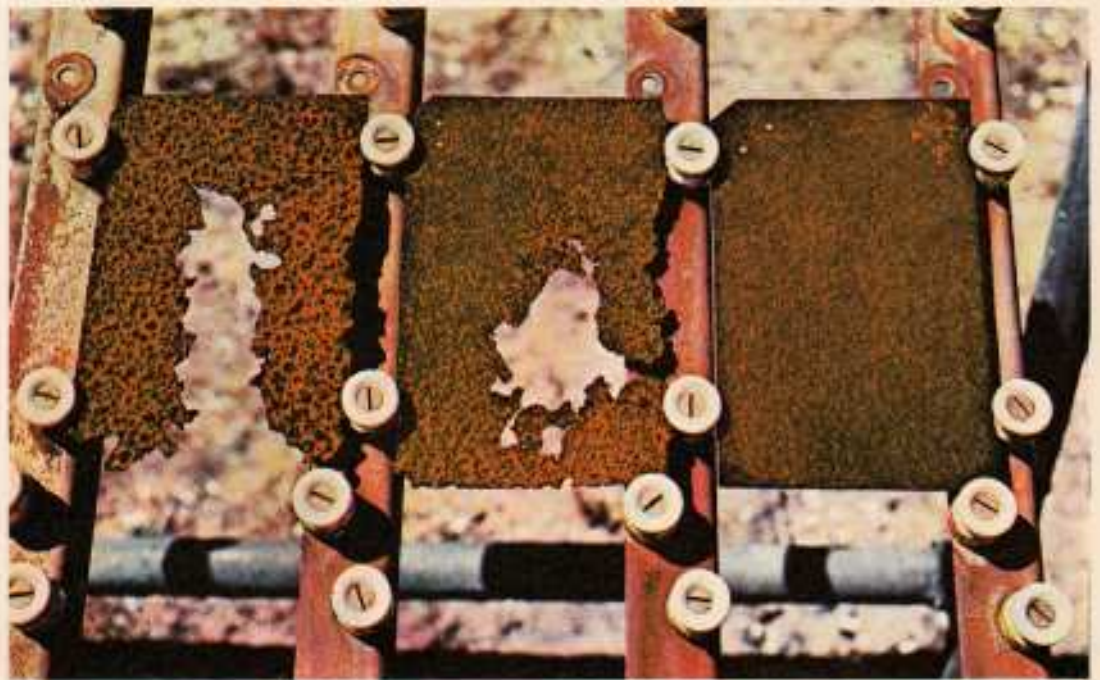
'I heard him then for I had just
Completed my design
To stop the Menai Bridge from rust
By boiling it in wine.'

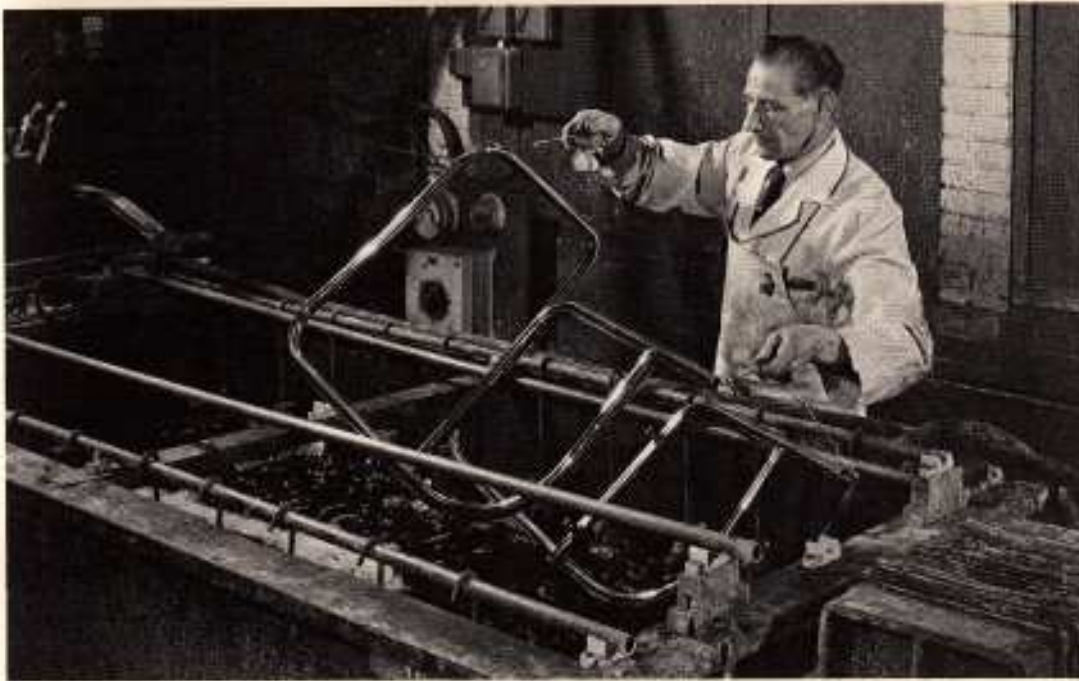
The methods in use vary according to circumstance. The kind of metal to be protected, the object into which it is made (a

gear wheel or a building support), the environment in which it will operate, and the object's economic worth – all these have to be taken into account. At the beginning we listed three common methods of prevention. Let us look at these in more detail.

Modifying a metal's properties – The first completely reliable stainless steel was made by Michael Faraday over a hundred years ago. He made alloys containing large amounts of platinum. Platinum is a metal that does not corrode but which is usually far too expensive to use in alloys. Nowadays

The prevention of corrosion depends very largely on the correct choice of metal or alloy for the job to be done. Here three different steels have been exposed to corrosive attack from a marine atmosphere. The low-copper steel on the left has been practically eaten away; the ordinary steel in the centre has been severely corroded; and the nickel-copper-chromium steel on the right is still intact.
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Electroplating tubular furniture with nickel and chromium.
International Nickel Ltd.

steel is protected against corrosion by alloying it with very small quantities of certain metals or with much larger quantities of a metal such as chromium that forms a film which is resistant to oxides.

The choice of alloying metal depends very largely on the environment. In acid conditions, silicon and molybdenum help to resist corrosion. In alkaline conditions, magnesium and nickel should be used. But the choice of alloying metals must be made carefully because, as we have seen, two different metals in contact with each other can bring on corrosion. The strength of aluminium can be greatly increased by alloying it with magnesium or with copper. But magnesium is generally preferred because alloys of aluminium and copper corrode far more easily. Aluminium magnesium alloys are often used to build light high-speed naval craft. (For further details of metal alloys see the Background Book, *Metals*.)

Modifying the environment of metals - In aqueous solutions (though not in a huge body of water like the sea) the addition of suitable chemicals can sometimes stop the functioning of either the anode or the cathode in corrosive cells. These

chemicals include sodium hydroxide, sodium carbonate, certain phosphates, and sodium chromate. Where corrosion is due to differences in oxygen concentration in a solution, this can be cured by heating the solution or by flushing out the oxygen with a gas such as nitrogen.

In the atmosphere, electrochemical corrosion can be reduced by keeping the surrounding air as dry as possible, either by refrigerating the air or by passing it through a substance such as quicklime that will absorb water. Volatile organic chemicals, called vapour phase inhibitors, are sometimes used to envelop loosely sealed metal articles in a protective atmosphere.

Protective barriers - Corrosion starts as an attack on the surface of a metal. By covering the surface with a suitable protective, corrosion can be prevented. As we have seen such metals as aluminium and chromium provide their own protection by forming a resistant oxide film. These metals are used to provide protective coatings on other metals. Iron is frequently coated with zinc. If the coating is scratched, the zinc corrodes in preference to the iron beneath and thereby



Painting is one of the commonest methods of protecting metals against corrosion. Here is a man painting the metal girders of the Forth Railway Bridge.
British Railways

protects it (see 'Cathodic protection' below and page 12). Such metals as gold, silver, and platinum can also be used as protective coatings but tin is the coating we know best on cans and kettles. These metals strongly resist corrosion, although, as the blackening on silver-plated egg spoons suggests, silver tarnishes easily in the presence of sulphur compounds. With these metals, since they are low in the electrochemical series, it is important that there should be no scratch in the coating, otherwise corrosion of the underlying metal is likely to be very severe. The metal coatings are applied by dipping, by spraying, or more commonly by electroplating.

The most usual way of protecting a metal surface is to cover it with paint. (For information about paints, see the Background Book, *Colour*.) The first coat of paint is usually a primer which is not resistant to moisture but inhibits corrosion once moisture has penetrated. The more coats you put on, the more resistant to corrosion the metal will be. But the trouble with paint is that it does not last for ever and, once it starts to wear away, the metal must be repainted, otherwise corrosion will start. The painting of the metal girders of the Forth Railway Bridge never stops: it takes several years to complete and as soon as the painters have finished they must start again at the beginning. Plastics are more durable but more expensive protectives. Warships are 'cocooned' in plastics when they are put into storage.

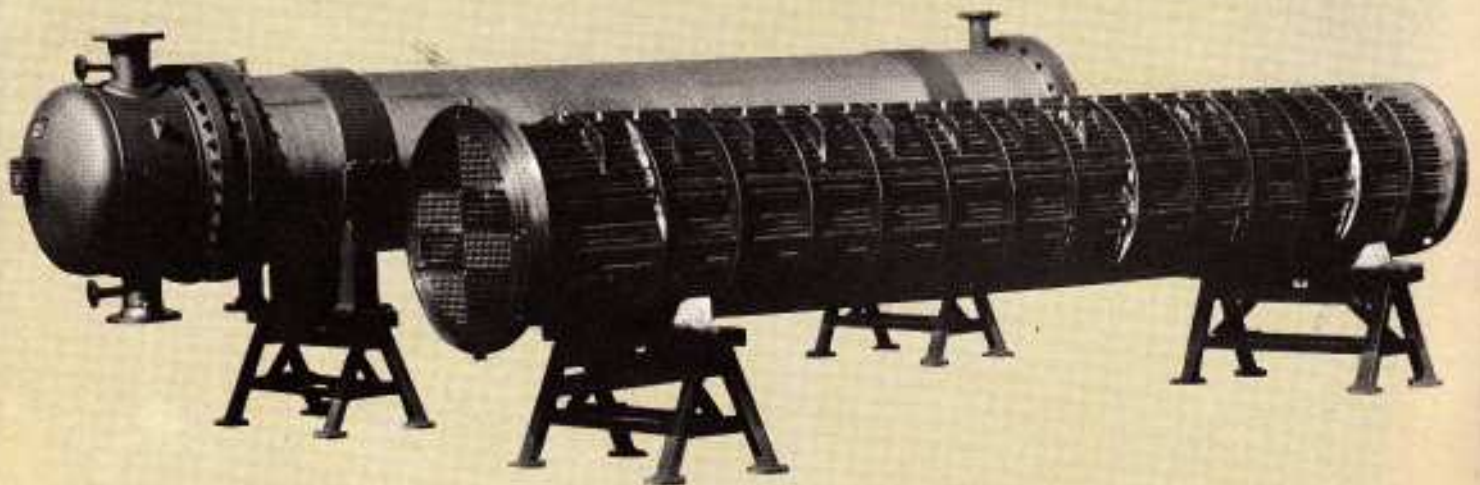
For temporary protection, metals are often covered with a water-resistant film of oil or grease. These films can be removed with suitable solvents or by wiping with a cloth.

Cathodic protection – This is an important method of preventing corrosion, which is mentioned briefly above. In 1824 Sir Humphry Davy suggested to the Admiralty that the corrosion

The battle against corrosion – We have seen that, although corrosion is usually electrochemical in its nature, it can result from a number of causes – from two different metals in contact, differences in oxygen concentration, impurities in the metal, etc. There are other factors we have not considered: temperature for example. At temperatures above 70°C, the polarity between zinc and iron is reversed: zinc forms the cathode and iron the anode, and therefore galvanized iron is restricted in its uses to the temperatures below 70°C. Demands made on metals by modern engineering create their own corrosion problems. A corrosion problem that proved to be a particular headache was that of the condensers in ships' boilers. These condensers consist of a nest of tubes about twelve to twenty feet long and three-quarters of an inch in diameter. Cold sea-water is circulated through the tubes and exhaust steam from the ship's boiler is passed over them: the steam condenses to pure water and the water is returned to the boiler to generate more steam. Corrosion of the tubes which, in a steamy atmosphere with sea-water running through them, is likely to be very rapid, leads to sea-water leaking into the boiler and corroding the whole works.

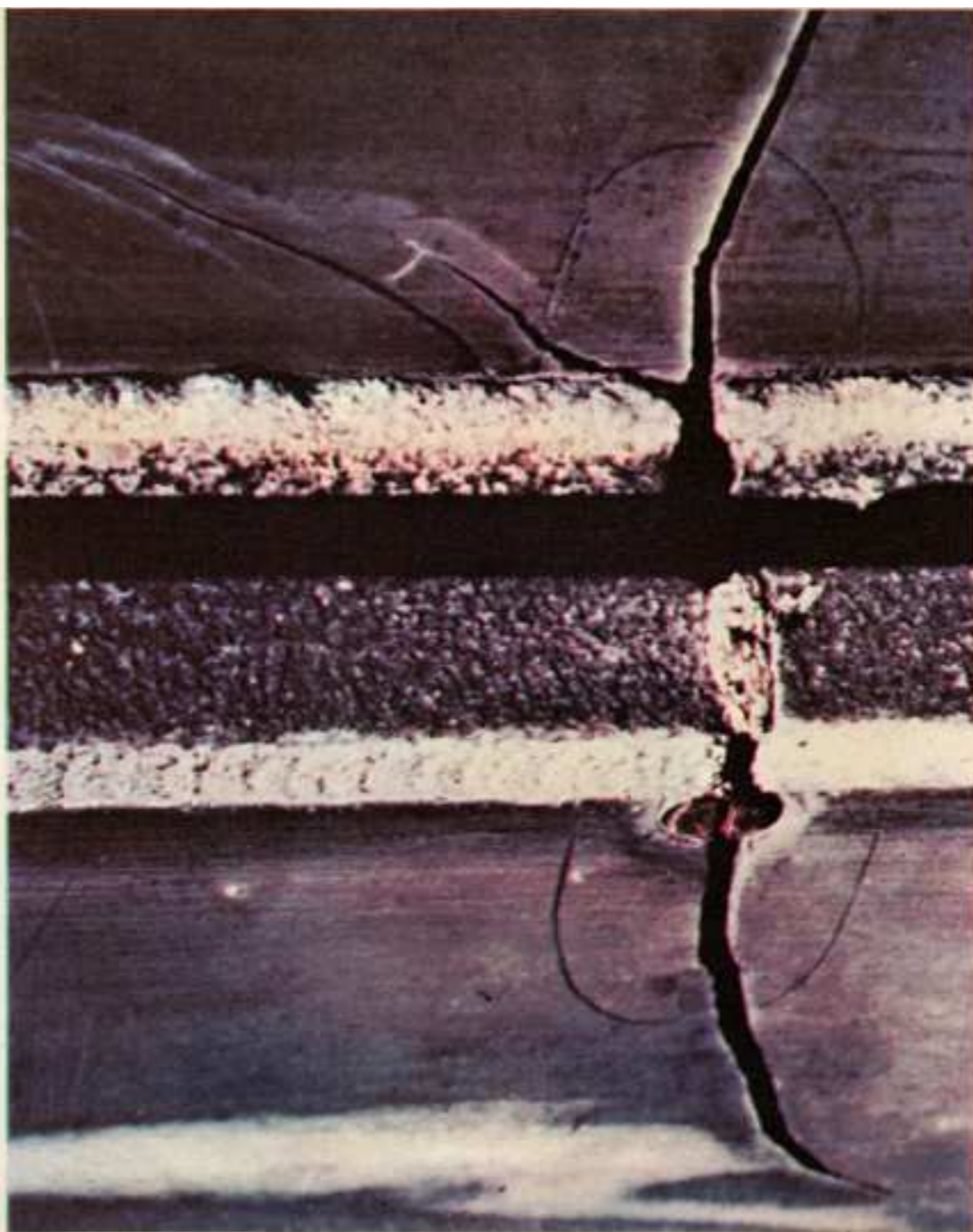
During the First World War, the condenser tubes in naval vessels were made of brass, and their average life was no more than about three to six months. The vessels then had to limp back to port, suffering from what was commonly called 'condensitis'. By the time the Second World War came round, the use of improved alloys had prolonged the life of these tubes for up to seven years and nowadays, with the use of an alloy containing 70 per cent copper, 28 per cent nickel, and about 1 per cent each of iron and manganese, they will last up to twenty years. Their resistance to corrosion has been further improved by filling the sea-water entries with Polythene insets to protect the metal against the turbulent flow of the water. The turbulent, as opposed to the streamlined, flow of liquid along a pipe causes what is known as cavitation corrosion: blisters are formed which, on collapsing, peel away protective films and expose small areas of bare metal. Another kind of corrosion comes about from strains in a metal: areas of strain are anodic towards unstrained metal, and in aircraft corrosion of this kind may cause crashes.

Nowadays corrosion is the subject of a great deal of research. Accelerated corrosion tests are carried out in con-



Cracking in a metal induced by corrosion and strains in the metal. Strains in a metal are anodic towards unstrained metal.
International Nickel Ltd.

In the foreground is a condenser opened up to show the condenser tubes. In the background is a condenser ready for installation. These are condensers for use in industrial plant. For a long time the corrosion of these condensers proved to be a great problem, — especially in ships' boilers — but now, thanks to the use of corrosion-resistant alloys, the problem has been largely solved.

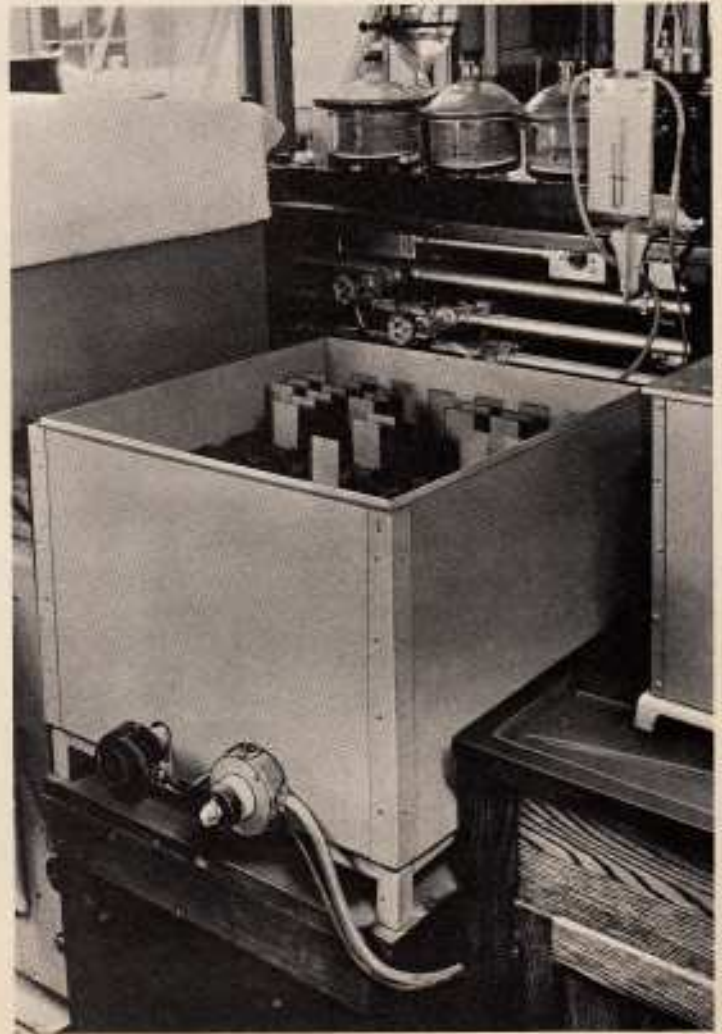


The cover lifted from a humidity cabinet to show the metal test pieces inside. The temperature in the cabinet is usually about 50°C, and water is evaporated in the cabinet to give a high humidity. Using cabinets of this kind, experiments on corrosion can be greatly speeded up.
Shell

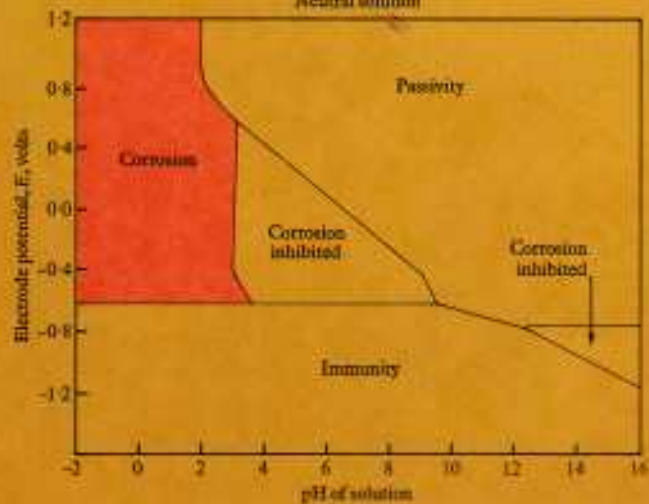
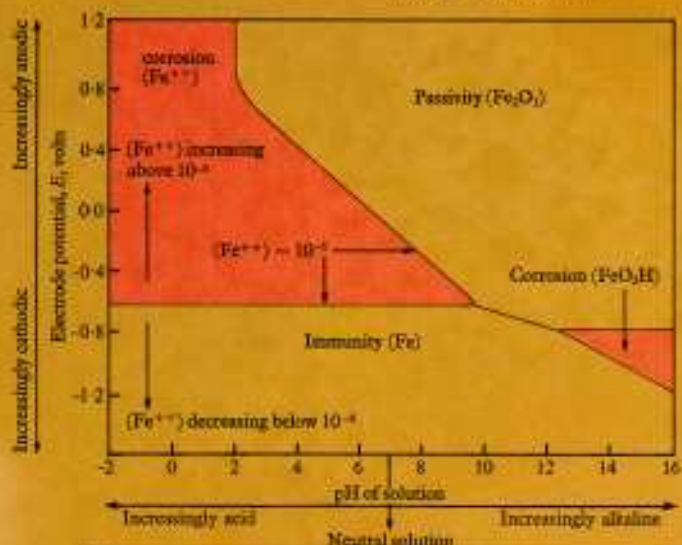
trolled experimental conditions to give information which otherwise might take years to acquire. Test samples of metals and their alloys are stacked in humidity cabinets, are sprayed with corrosive liquids such as salt solution or dilute acid, are subjected to tolerance tests and are examined for the effect of strain. All these tests lead to a new understanding of how corrosion comes about, how it is affected by the conditions, and how it can best be prevented. Although it is unlikely that corrosion will ever be completely overcome, it is likely in the future to be greatly diminished by the use of better corrosion-resistant alloys and tougher protectives.

Questions

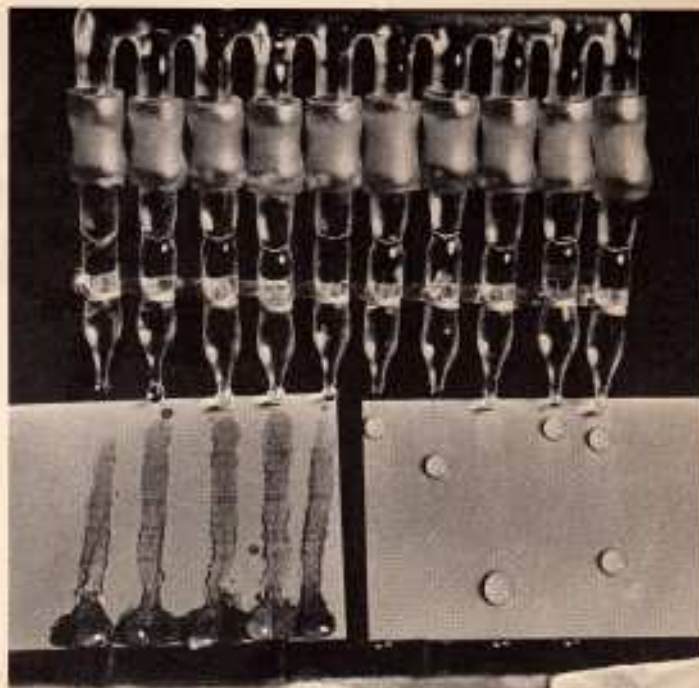
1. Polarization reduces the potential of an electrical cell. Find out for yourself what polarization is. Will it increase or decrease corrosion?
2. Why do you think wedding rings are made of gold or platinum?
3. Which would you expect to corrode more severely – nickel in contact with iron, or silver in contact with titanium? Which metal would be eaten away in each case?
4. How would you protect the following against corrosion?
 - a. The bodywork of an aircraft.
 - b. A shipment of machinery to the tropics.
 - c. A solid gold watch.
 - d. Iron railings.
 - e. An underground pipe.
 - f. The stonework of city buildings.
 - g. An iron kettle.



Recently the study of corrosion has been helped by the use of Pourbaix diagrams, representing graphically the effect of electrode potential and pH on the corrosion of a metal. The simplified Pourbaix diagram below shows iron in water at 25°C. The diagram on the bottom shows how regions of corrosive attack are reduced by adding iron chromate.



Water-drip apparatus to test the protective efficiency of different oil layers on identical metal plates. Spreading of the water is desirable in a protective agent and the oil layer on the lefthand plate does this much better than the one on the right. Shell



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... fun ... of
perfect corrosion-resistance and tough protection.

Questions

1. Polarization reduces the potential of an electrical cell. Find out for yourself what polarization is. Will it increase or decrease corrosion?
2. Why do you think wedding rings are made of gold or platinum?
3. Which would you expect to corrode more, nickel in contact with ... or ... ?
Why?