PRINCIPLES OF CORROSION

BY

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PREVENTION OF CORROSION (Art. 2)

Early in the first article in this series (Vol. 9, No. 1), the point was made that ' corrosion is a process as natural as that of water running down hill '. Lest the inference be drawn that corrosion is inevitable and therefore one can do nothing about it, it should be remembered that water can be prevented from running down hill ; by the same token, corrosion can be prevented—if not universally, then certainly in far more cases than is commonly supposed.

The methods used to achieve this end are many and diverse ; and it is evident that, within the compass of this brief survey, not more than the merest outline can be attempted. Nevertheless, it is hoped that the arrangement of available methods of prevention in groups of related topics (TABLE II) may assist in

TABLE II

METHODS OF PREVENTING CORROSION OUTLINE SCHEME	
I. *Methods based on Modifications of Procedure*	
(a) By attention to design of structure.	(A, W & G)*
(b) By attention to surface condition.	
(c) By application of cathodic protection.	(W & G)
II. *Methods based on Modifications of Enviroment*	
(a) By deaeration of water or neutral solution.	(W)
(b) By purification or de-humidification of air.	(W)
(c) By addition of corrosion inhibitors, etc.	(W) (A & G in special cases)
III. *Methods based on Modification of Metal*	
(a) By increased purity of metal (also control of structure by heat treatment).	}(A, W & G)
(b) By addition of alloying elements.	
IV. *Methods based on Protective Coatings*	
(a) Coatings of reaction product (Chemical or electro-chemical treatment of metal surface).	(A & W)
(b) Organic coatings: paints, resins, etc.	}(A, W & G)
(c) Inorganic coatings: enamels, cements	
(d) Metal coatings	
(e) Temporary protectives.	(A)

* *Environmental conditions in which applications occur:*

    (*A*) *atmospheric*   (*W*) *underwater*   (*G*) *underground.*

conveying some impression of the field as a whole and in giving at least some idea of the ways in which the principles already discussed may be applied to the prevention of corrosion in service.

I. METHODS BASED ON MODIFICATIONS OF DESIGN OR PROCEDURE

Clearly, all methods of prevention, except those which aim solely at the insulation of the metal from its environment (i.e. some, but by no means all, of the methods of Group IV) must depend ultimately upon the control of the corrosion mechanism. Sometimes this can be achieved by modification of the environment (Group II) or of the metal (Group III). Under the present heading we approach the subject from the point of view of what can be done by modification of procedure.

(a) Design of Structures

Outstanding in this category is the influence of design—partly because its importance is common to immersed, atmospheric and underground corrosion, but also because it is obviously one of the first things to be considered by the engineer—although only rarely, it is to be feared, from the point of view that ' prevention of corrosion should begin on the drawing board '. The importance of taking corrosion factors into account in the design of structures may well be urged upon engineers, since quite commonly failures in service are directly attributable to errors in design. Of these, contacts between dissimilar metals (galvanic coupling) have been the cause of disastrous failures in the past and still remain a prolific source of trouble ; their transgression of some of the more basic principles that we have discussed will be sufficiently evident.

The correct procedure, clearly, is to avoid dissimilar-metal contacts as far as possible where the electrolyte is favourable to local action, or to choose materials whose electrode potentials in the given electrolyte are not too dissimilar. Attention is especially called to a recent document, Corrosion and its Prevention at Bimetallic Contacts (London: H.M.S.O., 1956, 1/6 net). Of general industrial importance, this was prepared (U. R. Evans and V. E. Rance under the auspices of the Corrosion and Electrodeposition Committee of the Inter-Service Metallurgical Research Council) primarily for the guidance of Service designers in Admiralty and Ministry of Supply. Alternatively, an insulating coating may be applied to prevent access of electrolyte to the junction ; or electrical contact may be broken by insulating fittings available for that purpose. If none of these courses is practicable, the design should be modified so that increased attack locally on the anodic member is provided for by increased thickness or, possibly, by arranging for its ready replacement.

In a closed (circulatory) system, trouble may arise even if the dissimilar members are not in direct electrical contact. Thus, in certain water supplies, galvanized iron tanks undergo rapid failure if copper pipes are present in the same system. Copper ions, carried forward by the water, are displaced by zinc and produce local galvanic attack on the zinc coating, leading to perforation of the coating and ultimately of the steel. A change of practice, directed to the metal either of the tank or the pipes, is clearly the solution to this problem. For similar reasons, aluminium alloys and copper alloys in proximity are almost always a potential source of danger.

Under freely aerated conditions, where dissimilar metals are in contact, considerable importance attaches to the relative areas of anodes and cathodes. If such exposed areas are unavoidable, it must be remembered that the association of a large cathode (providing a large catchment area for oxygen) and a small anode (yielding a high current density) is particularly dangerous.

DUST AND WATER
COLLECT ON THIS
LEDGE

WATER

WATER

RIVET
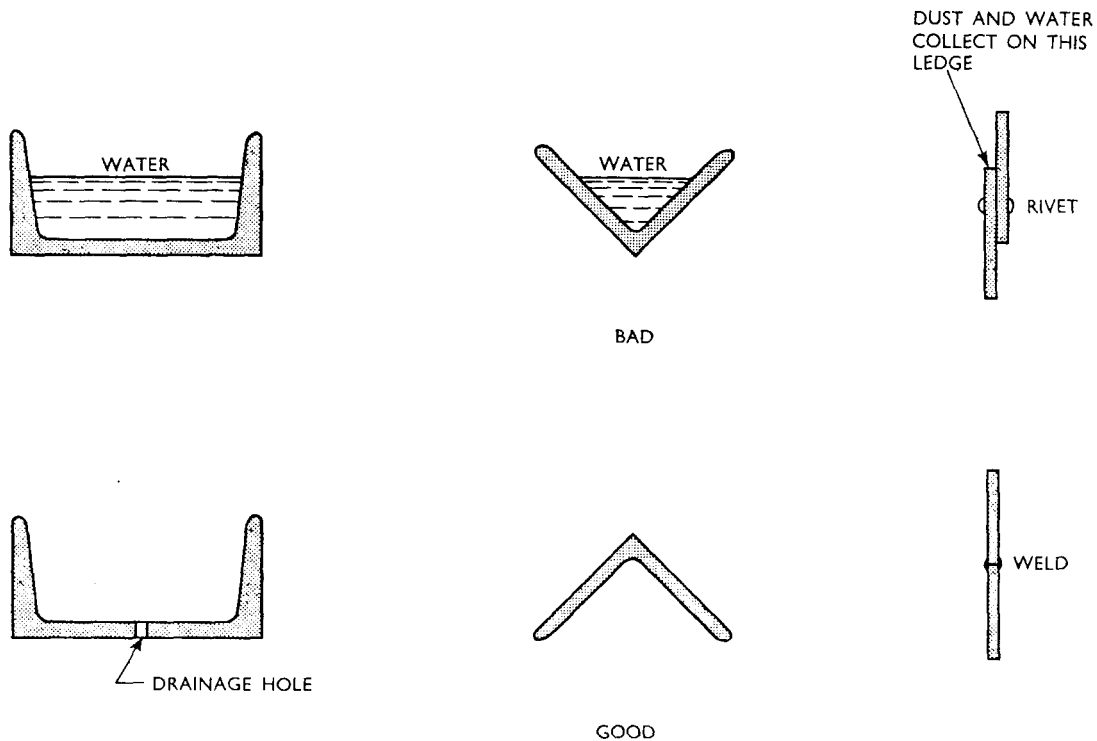
BAD

DRAINAGE HOLE

WELD

GOOD

Fig 10—Recommended Design Details to Reduce Atmospheric Corrosion
(*F.M. Reinhert, Product Engineering* 1951, 158 ; adapted by *J. C. Hudson,
Chemistry and Industry*, 1954, 641)

Thus, if a rivet is slightly cathodic to the adjacent plates, we have a condition that is safe—since any galvanic corrosion so produced is spread over a large anodic area ; the converse may be disastrous.

A cognate source of trouble arises from the presence of crevices between adjacent members (not necessarily dissimilar metals) in a structure ; frequently such crevices form a deliberate, but avoidable, part of the design. Conditions of rapidly moving (aerated) water, with certain reservations in respect of composition and treatment, are then favourable for the differential aeration effect —the adjacent exposed surfaces tending to become cathodic, a corresponding attack being thrown upon the sheltered walls of the crevice ; clearly, the aggravating condition of large cathode and small anode must necessarily here apply.

In atmospheric exposure crevices are again harmful, but for other reasons since the differential aeration mechanism of immersed corrosion can only exceptionally operate. Crevices not only afford lodgement for moisture and corrosive deposits from the atmosphere (Fig. 10), but moisture tends to be retained in the crevice long after the rest of the structure is dry. An important accessory consideration is that the volume occupied by a corrosion product is normally many times greater than that of the metal from which it is derived. The very considerable pressure so developed in a confined space may cause damage in the adjacent structure (e.g. snapping of rivets) or, by a progressive widening of the crevice, may lead to acceleration of the corrosion.

The galvanic order of the metals, as given by their electrode potentials, is likely to be modified to a greater extent (through the influence of surface films of reaction product) in atmospheric than in immersed corrosion. Moreover, a given potential difference is not so likely (because of the generally higher resistance of the electrolytic circuit) to produce dangerous corrosion currents. Nevertheless, dissimilar-metal contacts still call for vigilance in matters of

DE-SCALED   SCALE COVERED

BEFORE TEST
ⓧ

AFTER TEST

ⓧ AN IDENTICAL CENTRE-PUNCH MARK WAS APPLIED TO
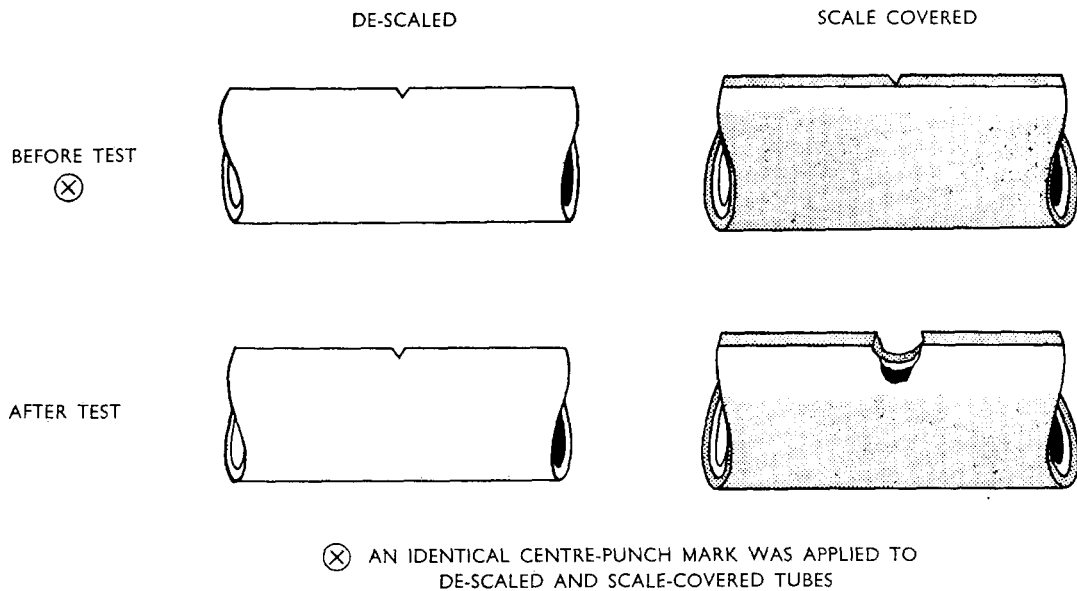DE-SCALED AND SCALE-COVERED TUBES

FIG. 11—INFLUENCE OF SCALE ON CORROSION OF STEEL CONDENSER TUBE
(20-DAY TEST IN C.R.L. ROTOR APPARATUS)

design since, in favourable circumstances, serious attack on the anodic member
may occur. Again, we have seen that in water systems the passage of relatively
electro-positive ions over a relatively electro-negative metal may bring about
serious localized corrosion ; the counterpart of this can also occur in atmos-
pheric corrosion, as for example when rain-water, falling over a copper or a
lead roof, is allowed to flow into an iron or galvanized iron gutter. Some
analogy with impingement attack may likewise be found when rain from a large
catchment area, whatever the material, impinges locally on a metallic structural
member.

(b) Surface Condition

In any given assembly, considerations of surface condition must be inti-
mately associated with those of design. Not only will the condition of the metal
surface—presence or absence of scale, degree of roughness or smoothness, etc.
—affect the initial rate and distribution of the attack ; it may determine the
whole of the subsequent course of corrosion. The influence of scale may be
profound, since, for reasons already discussed, intense localized attack may
be set up at discontinuities. FIG. 11 illustrates a laboratory experiment carried
out with sections of steel condenser tubes, with and without the presence of
surface mill-scale. Early failure of these tubes had been reported in service—
characteristically an almost clean-cut hole in a long length of unaltered tube.
The sections were all given an initial punch mark and rotated in a vessel con-
taining river water in which the original failures had occurred—with the results
diagrammatically shown. Freedom from this localized attack was achieved in
service by the use of completely de-scaled tubes.

The premature failure of paint coatings frequently arises from the presence
of underlying mill-scale or from its incomplete removal in the preparation of
the metal surface.

(c) Cathodic Protection

We now turn to a much more specialized modification of procedure—
illustrating par excellence the control of corrosion by control of the corrosion
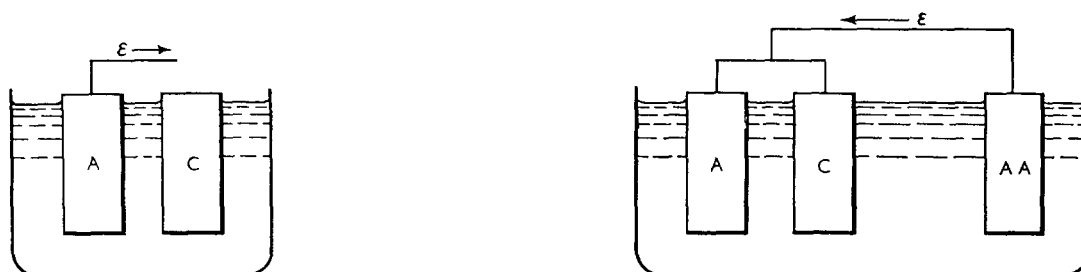mechanism—namely, cathodic protection. In our discussion of immersed

FIG. 12—CATHODIC PROTECTION : SCHEMATIC REPRESENTATION OF ANODES AND
CATHODES IN THE SAME SYSTEM

A—original anode
C—original cathode
AA—auxiliary (external) anode

corrosion we saw that in any assembly in which corrosion is taking place, we have anodes at which metal ions enter solution, and cathodes which, by accepting electrons from the anodes (via the metal circuit) receive protection. Sometimes the anodes and cathodes are so close together as to be indistinguishable, but sometimes they are spatially separated and the areas of attack and area of protection are clearly visible.

In the operation of cathodic protection, this mechanism is put to useful purpose by supplying electrons to the whole of the metal in contact with the electrolyte. Thus, if (FIG. 12) A and C represent schematically the anodes and cathodes of a system undergoing corrosion, the A zones corrode because they continually provide electrons to make good the deficiency of electrons in the C zones. If we now provide an external (auxiliary) anode AA (i.e. an external source of electrons) corrosion will cease if the supply of electrons from AA to C is equal to that previously forthcoming from A—in other words, if the original cathodes are polarized to the same electro-negative potential as the original anodes. Any further increase in the superimposed e.m.f. will further depress the joint potential of the original A and C areas, i.e. the whole structure will become more cathodically polarized. A sufficient cathodic current density may be impressed upon structures of iron or steel by the use of external anodes of magnesium, aluminium or zinc, the anode undergoing ' sacrificial corrosion '. Alternatively, insoluble anodes such as graphite (or anodes of scrap iron) may be employed, the necessary e.m.f. being obtained from external sources such as transformer-rectifiers or D.C. generators. For obvious economic reasons, cathodic protection is commonly employed as a second line of defence in conjunction with a protective (often a bituminous) coating, with the object of taking care of weak or damaged places in the coating. This serves as a reminder that the methods enumerated in Table II are not mutually exclusive.

The application of cathodic protection to buried or submerged structures now comprises an extensive and growing technology, the importance of which is becoming increasingly realized by civil, structural, mechanical and chemical engineers. No more than the foregoing brief statement of the underlying principle can be here included. A large body of authoritative opinion and experience on the application of cathodic protection in the field is now, however, available.

II. METHODS BASED ON MODIFICATIONS OF ENVIRONMENT

Broadly speaking, a given environment can be rendered less corrosive either by the removal of a harmful constituent, or by the addition of a substance that will act either directly or indirectly as a corrosion inhibitor.

(a) Deaeration of Water or Neutral Solution

As we have seen, the oxygen-absorption type of corrosion is dependent upon the supply of oxygen and may be prevented by its exclusion. Deaeration, therefore, presents a logical method of approach, which finds applications in service, particularly in boiler practice. Possible alternative methods of deaeration are as follows :—

(i) Mechanical

(ii) Chemical ; by passage of water over scrap iron or by the addition of an ' oxygen-scavenging ' chemical to the system.

(i) Mechanical—More Strictly Thermo-Mechanical

These methods depend upon the adjustment of temperature and pressure conditions so that dissolved gases are thrown out of solution, their expulsion being expedited by mechanical agitation. Although the principle is so simply stated, in practice the method involves the installation of elaborate and costly plant, the justification for which is in general to be found only in power stations, or similar steam-raising plant, where large quantities of feed water are regularly supplied to the system.

(ii) Chemical

The chemical method of approach consists in the removal of dissolved oxygen either by passage of the water over a large area of scrap (or ' expanded ') iron before entering the system, or by the addition to the circulating water of a chemical whose affinity for oxygen is much greater than that of iron ; in this way dissolved oxygen is removed before it has the opportunity to bring about the corrosion of the walls of the system. The scrap iron method is unduly slow in operation. Sodium sulphite (Na_2SO_3) is frequently employed as an oxygen-removing chemical ; since the product of the reaction (sodium sulphate) is also a soluble salt, the removal of oxygen necessarily results in an increase of dissolved salts in the system. In recent years, a new reagent has become available for de-oxygenation ; this is the chemical substance hydrazine, N_2H_4—available in the form of hydrazine hydrate ($N_2H_4.H_2O$), a water-white liquid. The attractiveness of this reagent to the boiler user lies in the fact that its addition gives rise to no additional solid matter in the boiler, the products of the reaction being nitrogen and water. Little recorded experience of its use, however, is yet available.

(b) Purification and Dehumidification of Atmosphere

From the principles discussed in the first article it follows that corrosive atmospheres can be rendered innocuous by (i) filtering out solid pollution, (ii) suitably absorbing gaseous pollution, or (iii) controlling the relative humidity so that it is consistently below the critical value. Apart from the removal of pollution at source, which must be regarded as the long range objective, it is evident that these measures are applicable only to relatively limited air spaces. Nevertheless, they must be taken seriously ; for example, in a shop in which fine steel surfaces are being prepared, air-conditioning might well be economically justified. In smaller enclosed spaces or containers, the humidity may be controlled by suitable desiccants ; alternatively, the use of ' vapour phase inhibitors ' (IIc, TABLE II) may become practicable.

(c) Use of Corrosion Inhibitors

The subject of corrosion inhibition is wide and complex, and there is a certain amount of danger (the danger of over-simplification) in attempting a simplified treatment such as is necessary in an omnibus discussion of this kind.

Inhibitors for Immersed Conditions

It will be remembered that corrosion under immersed conditions is made up of anodic and cathodic components and that it may be prevented by the suppression of either of these components. On this basis, two classes of corrosion inhibitors may be recognized, anodic and cathodic respectively. However, the distinction is not exclusive, because both components may be affected simultaneously.

The treatment of water for the removal of acidity and the conferring of an alkaline reaction protective towards iron and steel is probably the simplest example of the use of corrosion inhibitors. It is also a somewhat special one, since the protection is brought about by excess of hydroxyl ions which, as we have seen, are normally produced in the corrosion process itself—i.e. at the cathodic areas, where they exert supplementary protection ; by the addition of alkali they are also brought up to the anodes, where their presence in sufficient concentration ensures that the primary anodic product is ferrous hydroxide— a substance only very slightly soluble in dilute alkali. In this sense, therefore, sodium hydroxide (likewise sodium carbonate) is an anodic inhibitor.

Advantage may be taken of the alkali that is produced in natural waters during the corrosion process itself, by the addition of a substance that will produce an insoluble protective coating by reaction with the cathodic alkali. For example, zinc sulphate is sometimes added for that purpose and so constitutes a cathodic inhibitor. The calcium bicarbonate that is present in an ordinary hard water serves a similar purpose, since the carbonate that is precipitated by the alkali as a scale slows down the corrosion rate. On the other hand, too much scale may be objectionable for other reasons. Additions of sodium polyphosphates are often made to waters high in calcium bicarbonate in order to prevent undue precipitation of scale, the corrosion at the same time being substantially reduced, since the substance itself is film-producing. Sodium silicate (water glass) is effective in controlled amounts—particularly in hot water systems—in reducing the corrosion of mild steel, galvanized iron or brass ; a protective coating is laid down in which incipient corrosion product, as well as calcium and silicate ions, appear to take part.

The distinction between anodic and cathodic inhibitors may be illustrated by the graphical method used originally by Dr. U. R. Evans and his collaborators. FIG. 13 shows typical anodic and cathodic ' polarization curves ' for a corroding system, where A and C represent the initial electrode (anode and cathode) potentials before corrosion. Flow of current during corrosion brings about changes of potential (polarization), the anodes becoming more electropositive and the cathodes more electro-negative, to an extent depending upon the magnitude of the current density. The limiting conditions are represented by the intersection of the curves, where Op^1 represents the equilibrium corrosion potential and p^1P^1 the maximum value of the corrosion current. (The actual corrosion current may be less than this, depending upon the resistance of the circuit, but it cannot be greater). In (i) an approximately equal amount of polarization of anodes and cathodes is assumed. If now (ii) an anodic inhibitor be added to the system, the obstructive film formed at the anode raises the corrosion potential to Op^{11} and the corrosion current is reduced to $p^{11}P^{11}$. Conversely (iii), the addition of a cathodic inhibitor lowers the potential (Op^{111}) and the corrosion current is again reduced ($p^{111}P^{111}$).

Cathodic inhibitors are generally not so efficient as the anodic inhibitors (chromates, etc.) but they have the advantage of being ' safe '. This word is here used in the special sense that, if insufficient inhibitor is present, the situation is at least no worse than if no inhibitor were present at all. This arises from the fact that insufficient coverage of the cathodes will, in fact, increase the
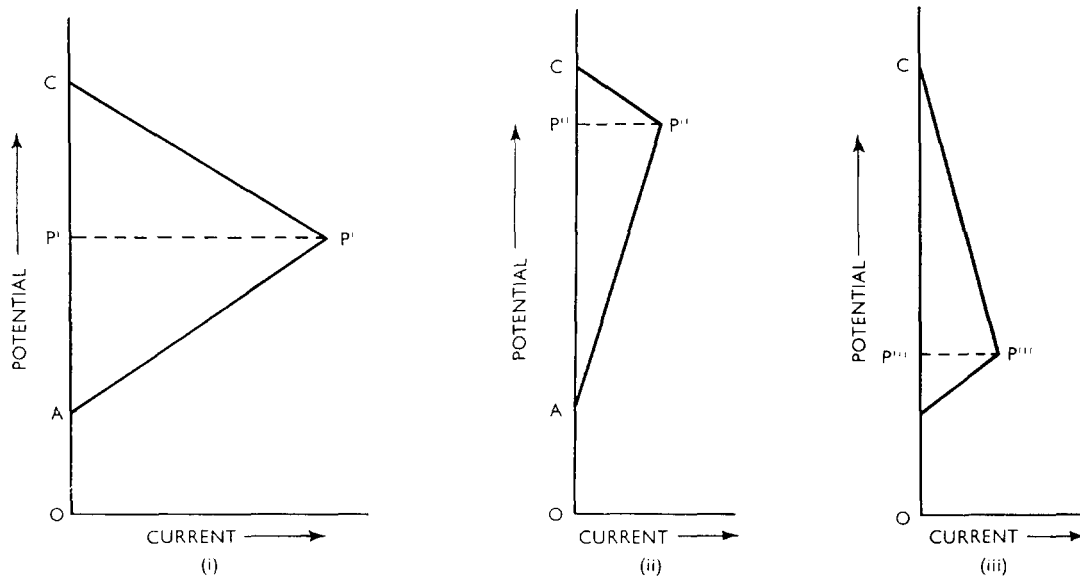
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Fig 13—Polarization Curves : Influence of Anodic and Cathodic Inhibitors

ratio between anode area and cathode area, and hence there can be no tendency to increased localization of attack.

The anodic inhibitors, e.g. sodium chromate, sodium nitrite, are characterized by a high degree of efficiency in that extremely small additions may prevent corrosion completely. Very much research has been carried out to elucidate the mechanism of the process. The film responsible for the inhibition has been removed from the substrate and examined by chemical and physical methods. It is certain that such inhibitors reinforce the protection afforded by air-formed films of oxide (i.e. by direct oxidation) ; radio-active tracers are now being employed by Chemical Research Laboratory, Teddington, and elsewhere to decide the respective contributions of oxygen and inhibitor. The effectiveness of these inhibitors is dependent upon the purity of the water ; chlorides are especially inimical, and in their presence higher concentrations of inhibitor are necessary for complete inhibition.
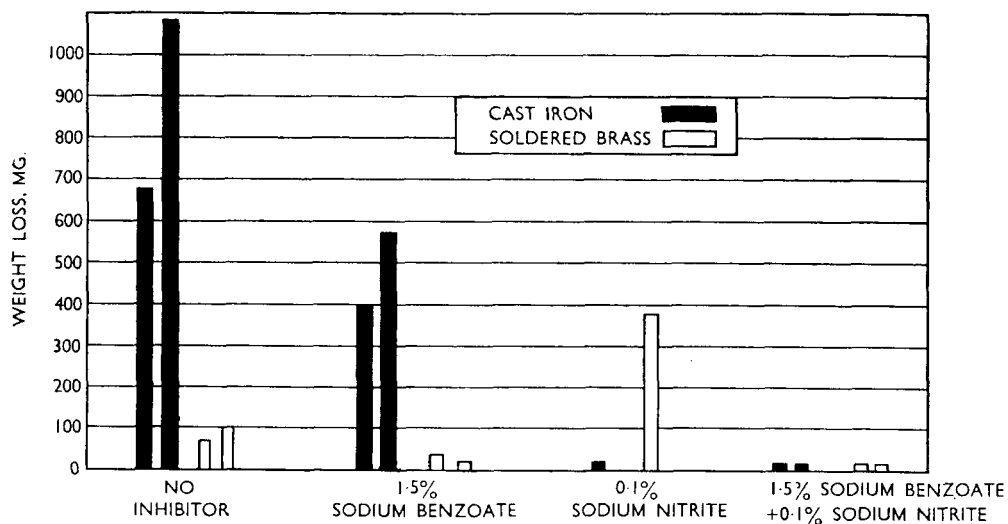

Fig 14—Effect of Sodium Benzoate and Sodium Nitrite on Corrosion of Cast Iron and Soldered Joints in 20 per cent Ethylene Glycol Solution (*Wormwell and Mercer, J., Applied Chemistry*, 1953, 24)
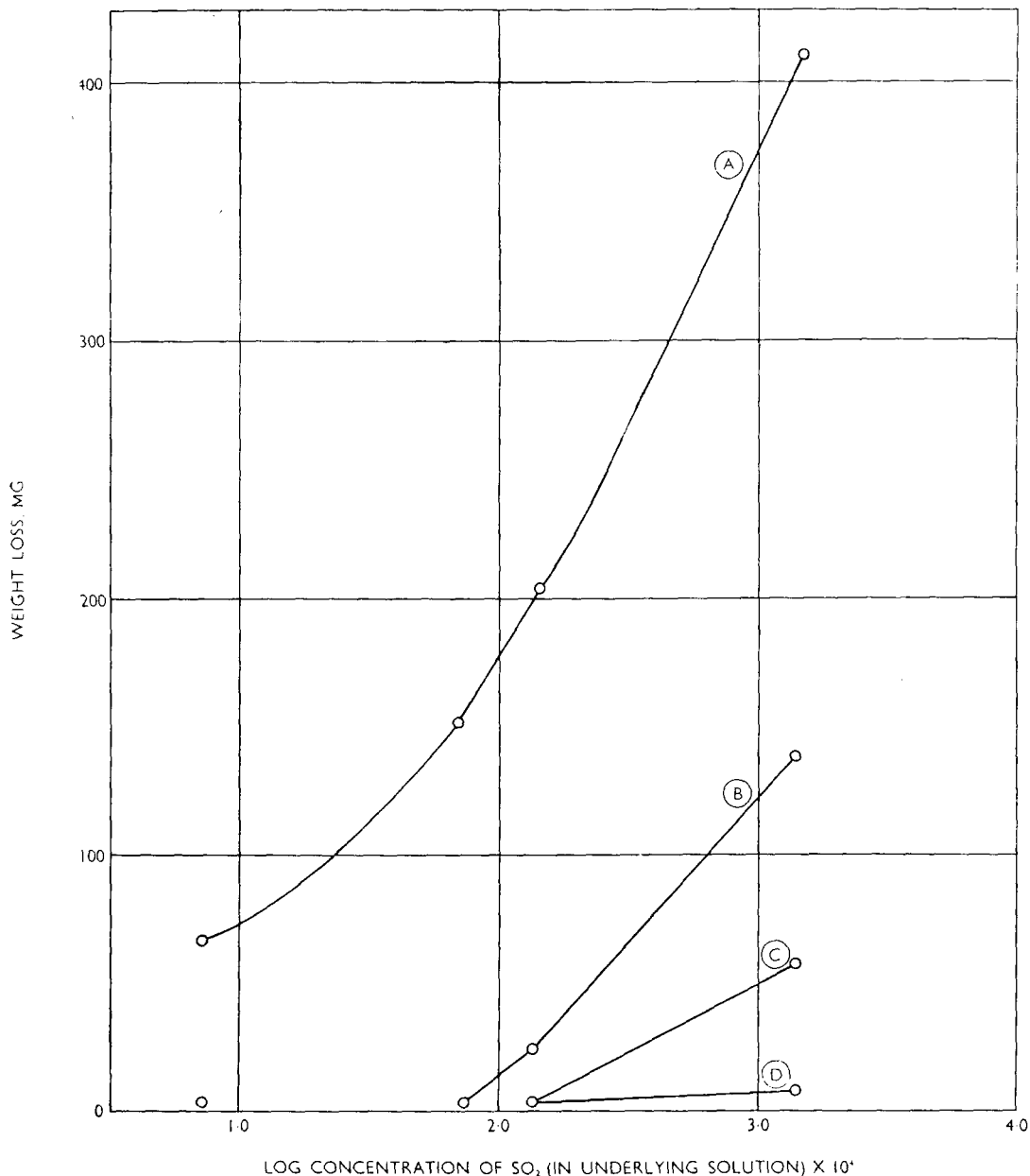
FIG 15—EFFECT OF VAPOUR OF ORGANIC CARBONATES ON CORROSION OF MILD STEEL
IN ATMOSPHERE CONTAINING SULPHUR DIOXIDE AND CONDENSING MOISTURE

A—control (no inhibitor)
B—25 per cent dibutylamine carbonate
C.D.—1 per cent and 3 per cent cyclohexylamine carbonate
(*Stroud and Vernon, J., Applied Chemistry*, 1952, 179)

Generally, anodic inhibitors fall into the category of ' dangerous ' inhibitors, using the word in the special sense already indicated. Thus, so long as sufficient inhibitor is present, protection is complete over the whole metal surface. If the minimum concentration is not reached, protection may still be maintained over most of the surface, and the total corrosion may be much less than in the complete absence of inhibitor ; on the other hand the localized penetration may be seriously increased. The position here is the converse of the one previously considered, since if the anodes are incompletely covered by the inhibitive film, the anode/cathode ratio is reduced, and the total attack may become concentrated on a greatly reduced area.

Sodium benzoate, a substance whose inhibitive properties have been discovered only in recent years at the Chemical Research Laboratory, appears to be unique in that, although an anodic inhibitor, it is ' safe ' ; i.e. insufficient inhibitor leads merely to general corrosion. On the other hand, it is not so efficient as chromate or nitrite, higher concentrations being necessary for complete protection.

From among the inhibitors available for use under immersed conditions, the choice in practice must depend upon the conditions of service. Present research is tending towards the use of ' mixed inhibitors ', e.g. the benzoate-nitrite combination (FIG 14) as developed at the Chemical Research Laboratory.

Inhibitors for Acid Solutions

The foregoing remarks have referred to the oxygen absorption type of attack in natural waters and neutral solutions. In acid solutions, in which corrosion proceeds by way of hydrogen evolution, the attack may be repressed by a purely cathodic mechanism if to the electrolyte is added, in small amount, a salt that will ' plate out ' on to the immersed metal surface an element having a sufficiently high hydrogen over-potential to impede the evolution of hydrogen. (Clearly the element must also be cathodic to the metal to be protected and the choice is therefore limited). More commonly (as in pickling solutions for the removal of scale from iron and steel) attack on the metal is prevented by the addition of certain organic nitrogen or sulphur bearing compounds (thioureas, etc.). As shown by Dr. Hoar, these function by suppressing either the anodic or cathodic component or both, and not necessarily only the cathodic reaction, as previously believed.

Inhibitors for Atmospheric Conditions

The limitations in the application of inhibitors to atmospheric conditions, as compared with those of immersion, will be sufficiently obvious. Within recent years, however, ' vapour phase inhibitors ' have been developed and hold much promise for the prevention of corrosion in enclosed air spaces. Earlier work on the restraining influence of carbon dioxide on the atmospheric corrosion of iron has already been mentioned ; now, a remarkable degree of suppression has been obtained under humid conditions (FIG. 15), even in the presence of substantial amounts of sulphur dioxide, by the combination of carbon dioxide with an inhibitive base, as in cyclohexylamine carbonate. By the impregnation of a suitable paper with sodium benzoate, corrosion-preventive wraps have been developed (E. G. Stroud and W. H. J. Vernon, *J. Appl. Chem.*, 1952, 2, 166) and are finding extensive application for the packaging of fabricated steel articles.