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CORROSION OF METALS AND THE EFFECT OF PROTECTIVE FILMS.

Various theories regarding the probable causes of corrosion have been briefly described in several issues of these papers, and sufficient has been said to indicate the extreme unlikelihood that the wastage of metals can be ascribed to any one single cause. The nearest approach to a common link between the different types of corrosion observed appears to be in the electrolytic theory, which maintains that differences of electrical potential of a very minute order can cause rapid destruction of the anodic part, *i.e.*, of the negative pole of an electrolytic cell.

The various influences which can result in the formation of such potential differences have provided a wide field for research and debate, as have also the protective methods that may be adopted to break up local electrolytic cells. One of the most interesting theories in this connection was referred to in Papers No. X, page 29, where it was stated that there is sound experimental evidence of the existence of naturally protective films upon the surface of condenser tubes, the inhibitive effect of these as regards corrosion being in some way dependent upon the nature of the tube material itself. Now this "film" concept in one form and another has been suggested by workers in other parts of the "corrosion" field, and it is the purpose of this paper to develop the ideas somewhat further, as it is in this direction that research is at present trending.

Oxide Films on Iron and Steel.

All metals on exposure to the air under suitable conditions rapidly become coated with a skin or film of oxide that in some cases acts as a complete preventive to further corrosion as long as it remains intact: the protective action may be due either to the imperviousness of the film to the corrosive influences or to the fact that the oxide is itself anodic to the underlying metal and thus further action proceeds at the expense of the film.

The skin formed on iron or steel on exposure to the air is, however, in general useless for the prevention of corrosion; the thick films which are produced at high temperatures are very prone to crack, and intensified action occurs along the lines of the fissures: the thinner films resulting from exposure at lower temperatures are rather more resistant. A better type of oxide film may be formed on steel by treating it with potassium chromate (say), but even this will not completely protect the metal from the action of sea water unless the chromate is added to the water at a sufficiently rapid rate to repair the film as fast as it is attacked by the chlorine in the water.

The formation of oxide films is quite unreliable in many cases as a preventative of corrosion, but their existence and action are

now accepted fairly generally as having a considerable bearing upon the actual location at which corrosion will occur ; an understanding of this matter is thus of some importance to the practical engineer.

Rapid corrosion of steel only occurs in ordinary waters if oxygen is present, but it is a curious fact that the action does not take place exactly at those parts of the surface where the oxygen is directly supplied ; in many cases the parts reached by the oxygen are the only ones that show no sign of corrosion. This apparent paradox may be explained satisfactorily by considering the effect of the oxide film, taking as an example the case of a piece of steel suspended vertically, half-immersed in salt water. The dry part of the specimen has a rudimentary oxide film upon it ; near the water line the oxygen of the air has relatively free access to the metal, thus maintaining the film in fairly good repair. The film, even when intact, is insufficient to protect the material entirely, but serves to divert the corrosion to the lower levels to which the healing supply of oxygen cannot find access.

It has been found that there is an actual difference in electrical potential between the upper well-aerated parts of the specimen and the lower parts where the film is in bad repair. This difference may, on occasion, amount to as much as half a volt, and in any case gives rise to a current flowing between the upper and the lower zones, the latter constituting the anodic area and suffering attack. The maintenance of this current depends upon the continuance of the oxygen supply to the upper area, ceasing if the supply is cut off.

An excellent practical example of this type of action recently came to notice in the case of a stainless steel impeller shaft (main circulating pump). It was found that where the shaft was exposed to the main stream of water around the impeller, pitting did not occur : the material in the way of the glands and bearings was, however, very heavily corroded. This selective action is exactly what might have been predicted on the above-mentioned theory, because the sea water in contact with the affected parts will not be aerated to the same extent as that around the impeller and adjacent shafting. Such differential aeration, with probability of consequent corrosion, is always to be anticipated in cases such as these where renewal of the supply of water to certain parts is rendered difficult by the presence of glands, etc. ; the oxygen in the semi-stagnant water attacks the surrounding materials, and thus the normal oxygen content of the water is reduced locally.

In passing, it may be remarked that the comparative immunity to corrosion of certain types of "stainless" steels is stated to be due to the existence of surface films, which are evidently either extremely tenacious or possess exceptional autohealing powers. The presence of such films on these steels has even been demonstrated, with some degree of assurance, but the laws controlling their formation and destruction are by no means well understood. It is, however, quite possible that the corrosion-resisting properties may be effected by mechanical removal of the film (due in this case

to friction of the glands and bearing), and that the differential aeration referred to may not be the main or sole cause of the pitting.

It should be realised that there appears to be a real difference between *rust* and the *oxide film* on iron (say) : rust is not the direct oxidation product of iron but is always formed by secondary reactions initiated by soluble corrosion products. The direct action of oxygen on iron is to produce a film of oxide which is invisible as long as it remains attached to the metal. This film tends to protect the metal. Rust on the other hand forms a loose covering which prevents the access of oxygen, which would keep the oxide-film in repair. Parts which become coated with rust, even if it is derived from other portions of the material, begin to suffer attack. Rust only serves to slow down corrosion if it covers the *whole* of the exposed surface : as has already been stated, rapid corrosion is engendered by the supply of oxygen to *some part* of the metal, so that *differences* in potential are set up.

The foregoing explains why in stagnant water rust begins at potentially weak places in the oxide film, *i.e.*, at sharp edges, surface defects, etc. The rust gradually extends till finally the corrosion becomes generally spread out and thus not dangerous. In rapidly running water the oxygen supply reaches the whole surface except possibly a number of weak points. Corrosion being confined to these becomes intense and relatively deep pits covered with rust are formed.

It may be well to record the fact that these invisible oxide films have been separated and made visible : this has been effected by dissolving the underlying metal. The currents set up between different parts of the same metal by variations in oxygen concentration have been definitely measured by galvanometer. The various products of corrosion have been identified by simple tests. In a word, the foregoing are not mere theories but are well established facts.

Metallic Coatings for Protection against Corrosion.

One obvious means of preserving metal from corrosion lies in covering the exposed surfaces with some other material which experience has shown to possess superior corrosion-resisting properties. This process has received a vast amount of attention and is the present subject of much research work. It may be of interest to consider briefly a few of the more important conceptions underlying modern progress in this particular field.

It will be convenient for the sake of argument to consider iron as the basic metal, to be protected by a skin of some other material. Now the remaining metals may be divided into two broad groups, the one cathodic (or positive) and the other anodic (or negative) to iron ; the former include gold, platinum, silver, and copper, all of which are fairly resistant to attack ; among the metals anodic to iron the most commonly used is zinc, but all such materials are more prone to attack than the iron itself.

Cathodic plating.

This type of coating should obviously be the most suitable for protection purposes, because of its own superior resistant qualities. Unfortunately it is impossible to ensure that any coating is entirely free from cracks and pinholes, while, even if they are originally perfect, there is always the danger that bending or abrasion may expose the underlying basic metal. If this occurs an electrolytic cell is formed with iron as the anode, which is then attacked; in most instances the action is much more violent than would be the case with the bare unprotected iron.

The only cathodic covering that is at present extensively used for protecting iron is nickel. This metal owes its virtues as a plating agent to its hardness, which resists abrasion; further, the E.M.F. of the Nickel-Iron couple is very low, so that even if the plating is punctured the rate of corrosion is slow.

The intense corrosion to be expected at a pinhole in a copper-plated steel article is well illustrated by the following experiment in which the relative rates of corrosion of (1) a steel specimen with a small copper central piece, and (2) a copper specimen with a small steel central piece were compared. It was found that the intensity of attack in the second case was twelve times as great as that in the first. The reason is as follows: the rate of corrosion depends to some extent upon the rate of oxygen supply to the cathodic area, that is to the copper plate; increasing this area means that the rate at which it can pick up oxygen is accelerated and since the effect is concentrated on the steel, it is clear that an increase of the copper area and a decrease in the steel area will greatly intensify the action upon the latter. The rapid pitting at the site of a pinhole in a cathodic skin can now be readily understood.

Anodic Plating.

When the metallic covering is anodic to the underlying material it is evident that in the event of any crack or pinhole occurring in the skin, the ensuing corrosion will be at the expense of the latter, while the basic metal will receive full protection. This protection will, however, only continue as long as the covering material lasts, and so it is evidently a matter of some moment to determine how quickly the skin or plating is attacked. A layer of sodium or potassium for instance, might be an ideal protective covering for iron as they are both strongly anodic to that material; unfortunately they might not last very long.

Let us consider the case of a zinc coating as a protector for iron. Experiments show that chalky water, while having little effect upon zinc, has a fairly marked rusting action on iron; it is thus highly beneficial to protect iron with zinc when exposed to the action of such waters. Salt waters on the other hand attack zinc even more readily than they do iron, so galvanising is of little use in such cases. It may be noted, however, that when zinc-coated steel is merely

damped by salt spray, alternated with drying in air, a film of corrosion product is built up on the zinc which is thereby comparatively well protected.

It is evident that to be effective as a protector to iron immersed in salt water any coating must be less subject to attack than is zinc under such circumstances, but must at the same time be at least mildly anodic to iron. Aluminium is an excellent example of a suitable plating material for this purpose, owing its own relative immunity to corrosion and to the fact that it rapidly becomes covered by a protective oxide film. Aluminium-coated iron also resists the attack of "hard" fresh water provided that the coat remains intact; should it become broken then rusting of the exposed iron will take place, because the aluminium is not attacked sufficiently vigorously in such waters to protect the iron. Thus aluminium-coated iron is untouched by the salt water but is attacked by the hard fresh water, although the latter is less corrosive than the former.

Conclusion.

It is not generally appreciated that the relative positions of two metals in the scale of electro-potentials is greatly affected by the presence or absence of oxide films upon them. The polarity of metals has been found to be greatly affected by these films; thus film-free chromium is anodic towards film-free iron, but chromium is often found to be cathodic to iron, because the film on the former raises it in the scale of potentials and is more ennobling than that on iron. Tin, lead, and aluminium are all metals that may be either anodic or cathodic to iron, depending upon the conditions.

It is evident that the correct choice of a metal for protectively coating any given base must depend upon the particular conditions that have to be encountered, and that many complex factors must be taken into account. It is, however, probable that the principles involved are now well understood; the pitfalls arise in their application.