CHAPTER IV

CORROSION OF BRASS
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General Account:

The term corrosion has been utilised to indicate a variety of phenomena by different authors. According to Evans\(^1\), 'corrosion may be defined as destruction by chemical or electrochemical agencies.' Speller\(^2\) considers corrosion as, 'the chemical action of certain external agencies on metal which causes their deterioration or destruction.' Bengaugh\(^3\) has defined two types of corrosion in brass - 'complete' and 'selective'. In complete corrosion, though the alloy may be attacked either generally or locally, it is wasted away as if it were a pure and a homogeneous metal. In selective corrosion only one ingredient (e.g. zinc) is lost.

Since copper and its alloys are extensively employed in condenser tubes, a vast amount of work has been done on the corrosion of copper and its alloys under different conditions. Noteworthy, in this respect, are the elaborate reports of the Corrosion Research Committee of the Institute of Metals covering
the period 1911 - 1928. The eight reports deal with all types of corrosion and offer a specially thorough study of corrosion in sea water.

The corrosion of metals and alloys is conditioned by a number of influences, such as composition of the metal, the dissolved substances present in the liquid in contact with it, temperature, stirring, dissolved oxygen, homogeneity, the previous mechanical and thermal treatment of the metal, the nature of its surface, and so forth. In considering the corrosion of any alloy, in practice, it must be remembered in many cases, that differences in operating conditions involving a great number of variables so alter the mechanism of corrosion that sweeping generalisations are extremely difficult, if not impossible.

The corrosion of brass has been extensively studied. The earliest observation is that of Calvert and Johnson⁴ who showed that an alloy of about equal weights of copper and zinc, immersed in concentrated hydrochloric acid gives up in a few days nearly the whole of zinc, leaving copper behind in a spongy state. Carnelley⁵ reported that the action of ammonium sulphate is slightly increased by the presence of potassium nitrate. Tilden⁶ suggests that, brass may be
boiled with a solution of salt for any length of time without alteration, provided air is excluded. He also observed that highly concentrated solutions did not act so vigorously as more dilute solutions presumably because concentrated solutions absorb oxygen less rapidly than dilute solutions. Venator found that a solution of sodium hydroxide attacks brass by dissolving only the zinc. Charpy states that the alloys with about 25% copper are attacked slowly because of the presence of $\text{Zn}_4\text{Cu}$. Lincoln studied the corrosion of brass and came to the conclusion that $\alpha$, $\alpha + \beta$ and $\beta$ brasses yield corrosion products of the same composition as the alloy. On increasing the percentage of zinc further in the alloy, the corrosion is markedly decreased and the corrosion product consists practically of zinc. Philip explains the corrosion of brass by assuming that the alloy is an agglomeration of minute couples of zinc and copper or alternatively of different phases of copper-zinc alloys. Edwards is also of the view that the metallic couples are of copper and $\text{Cu}_2\text{Zn}_3$, the latter being slightly anodic to copper. Gibbs studied the action of sea water and
came to the conclusion that the corrosive action of sea water results in the dissolution of copper by the dissolved salts, and in the dissolution of zinc by the dissolved gases. He considers that characteristics of copper and zinc when alloyed as in brass are altered, the characteristics of zinc being altered to a greater extent. In a 70/30 brass, copper is lost rather more rapidly than zinc under certain conditions. According to Bengough and Hudson\textsuperscript{13} the action of neutral or nearly neutral sea water is predominantly that of oxidation rather than electrochemical. Under some conditions, such as beneath certain deposits of basic salts of semipermeable nature and in other conditions when the oxidation is slow, zinc may be removed entirely along with some copper. From this, it is concluded that part of the copper is not associated with zinc in the formation of aggregates. The rest of the copper may be associated in the way suggested by Gibbs (loc. cit. p. 29). He considers that copper is redeposited rather than left in situ. According to Bengough and Hudson\textsuperscript{14}, the action of distilled water on brass in presence of air may be regarded as taking place in the following stages.
(1) The formation of a translucent tarnish consisting of an oxide. It is nearly uniform and not very porous to water or oxygen. A part of zinc passes into solution probably after being first oxidised; most of the copper oxide is found on the metal, but a trace is found in solution.

(2) The further oxidation of the tarnish, beginning at widely scattered patches and areas, forms a dark purple or black oxide and a basic salt of an amorphous nature.

(3) The commencement of local pitting. Reedy and Bertramfeuer\textsuperscript{15} consider that the high concentration of an electrolyte favours electrolytic corrosion and retards or inhibits complete corrosion. Similarly elevated temperature also favours electrolytic corrosion. Dissolved oxygen has no appreciable effect on electrolytic corrosion, but is essential to complete corrosion. Ions that combine with zinc and copper ions to form compounds of low ionization favour both electrolytic and complete corrosion. According to these authors, there is no specific influence of an anion except when complexes of low ionization are formed. Wurstemberger\textsuperscript{16}, while discussing selective corrosion of brass pointed out that in the case of solution of
sodium salts, particularly sodium chloride, there is a local accumulation of sodium hydroxide which causes local action. Evans\textsuperscript{17} considered the localized corrosion of copper and brass articles. Localization may be due to (a) preferential removal of copper salts from certain points, thus producing local concentration cells; (b) differential aeration, the points shielded from oxygen becoming anodic and (c) contact with conducting bodies or local removal of protective scale. Masing and Koel\textsuperscript{18} are of the opinion that the loss of zinc is due to the potential difference between brass and copper and may, therefore, be regarded as an electrolytic phenomena. Inamura\textsuperscript{19} studied the corrosion of copper 60/40 and 70/30 brasses by inorganic acids, bases and salts. He observed that corrosion proceeds at a steady rate over the whole period and the curves of loss in weight against time are straight lines. Rauch and Kolb\textsuperscript{20} found that corrosion of copper and copper alloys is maximum in 15-25\% potassium chloride. Equivalent chloride solutions behave similarly. Stager and Bier\textsuperscript{21} studied the corrosion of brasses (Cu 52-63, Zn 48-37) by 10\% hydrochloric acid, 5\% aqueous ammonia and 5\% sodium chloride. $<$ and $>$ brasses resist corrosion
well, while in $\alpha + \beta$ brass, the state of constraint causes greater dissolution of zinc, accompanied by a fragile and porous structure. Moore$^{22}$ studied the corrosion of brass in water adjusted to various pH. He found that the corrosion of brass appears to decline at pH 6.0 and is minimum at pH 10.0 and rises again. Piontelli and Peyronel$^{23}$ studied the process of dezincification of brass by means of metallographic, X-rays and electrochemical measurements. According to Holloman and Johnwulff$^{24}$ the corrosion of $\alpha$-brass occurs by the dissolution of the alloy as an entity. Dezincification occurs by the reduction of cupric ion to cuprous ion followed by the reduction of the latter to copper. The addition of Arsenic prevents the last reaction. Altorf$^{25}$ examined the corrosion of brass in mercurous nitrate, ammonium hydroxide, sodium hydroxide and gave the mechanism of intercrystalline and intracrystalline corrosion. Colegate$^{26}$ discussed the various forms and influencing factors of selective corrosion. Paololombardi$^{27}$ suggested that the sponge like copper surface is not a residue of the preferential solution of zinc but metal deposited by the solution.
REFERENCES

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23. Piontelli, R., and Peyronel, G., Chimica and Industria (Italy ) 1940, 22, 161-5.