XV. *Further researches on the preservation of metals by electro-chemical means.* *By Sir* Humphry Davy, *Bart. Pres. R. S.*

Read June 9, 1825.

In two papers read before the Royal Society, I have described the effects of small quantities of electro-positive metals in preventing the corrosion or chemical changes of copper exposed to sea water, and I have stated that the results appear to be of the same kind, whether the experiments are made upon a minute scale, and in confined portions of water, or on large masses, and in the ocean.

The first and preliminary experiments proved, that the copper sheeting of ships might be preserved by this method; but another and a no less important circumstance was to be attended to, how far the cleanness of the bottom, or its freedom from the adhesion of weeds or shell fish, would be influenced by this preservation.

The use of the copper sheathing on the bottom of ships is two fold: First, to protect the wood from destruction by worms:

And secondly, to prevent the adhesion of weeds, barnacles, and other shell fish. No worms can penetrate the wood as long as the surface of the copper remains perfect; but when copper has been applied to the bottom of a ship for a certain time, a green coating or rust, consisting of oxide, submuriate and carbonate of copper and carbonate of magnesia forms upon it, to which weeds and shell fish adhere.

As long as the whole surface of the copper changes or corrodes, no such adhesions can occur; but when this green rust has partially formed, the copper below is protected by it, and there is an unequal action produced, the electrical effect of the oxide, submuriate, and carbonate of copper formed, being to produce a more rapid corrosion of the parts still exposed to sea water; so that the sheets are often found perforated with holes in one part, after being used five or six years, and comparatively sound in other parts.

There is nothing in the poisonous nature of the metal which prevents these adhesions. It is *the solution* by which they are *prevented—the wear* of surface. Weeds and shell fish readily adhere to the poisonous salts of lead which form upon the lead protecting the fore part of the keel; and to the copper, in any chemical combination in which it is insoluble.

In general in ships in the navy the first effect of the adhesion of weeds is perceived upon the heads of the mixed metal nails, which consist of copper alloyed by a small quantity of tin. The oxides of tin and copper which form upon the head of the nail and in the space round it, defend the metal from the action of sea water; and being negative with respect to it, a stronger corroding effect is produced in its immediate vicinity, so that the copper is often worn into deep and irregular cavities in these parts.

When copper is unequally worn, likewise in harbours or seas where the water is loaded with mud or mechanical deposits, this mud or these deposits rest in the rough parts or depressions in the copper, and in the parts where the different sheets join, and afford a soil or bed in which sea weeds can fix their roots, and to which zoophytes and shell fish can adhere.

As far as my experiments have gone, small quantities of other metals, such as iron, tin, zinc, or arsenic, in alloy in copper, have appeared to promote the formation of an insoluble compound on the surface; and consequently there is much reason to believe must be favourable to the adhesion of weeds and insects.

I have referred in my last paper to the circumstance of the carbonate of lime and magnesia forming upon sheets of copper, protected by a quantity of iron above $\frac{1}{120}$ parts, when these sheets were in harbour and at rest.

The various experiments that I have caused to be made at Portsmouth, show all the circumstances of this kind of action, and I have likewise elucidated them by experiments made on a smaller scale, and in limited quantities of water. It appears from these experiments, that sheets of copper at rest in sea water, always increase in weight from the deposition of the alkaline and earthy substances, when defended by a quantity of cast iron under $\frac{1}{150}$ of their surface, and if in a limited or confined quantity of water, when the proportion of the defending metal is under $\frac{1}{4000}$. With quantities below these respectively proportional for the sea, and limited quantities of water, the copper corrodes; at first it slightly increases in weight, and then slowly loses weight. Thus a sheet of copper 4 feet long, 14 inches wide, and weighing 9 lb. 6 oz., protected by $\frac{1}{100}$ of its surface of cast iron, gained in ten weeks and five days, 12 drachms, and was coated over with carbonate of lime and magnesia: a sheet of copper of the same size protected by $\frac{1}{150}$, gained only 1 drachm in the same time, and a part of it was green from the adhering salts of copper; whilst an unprotected sheet of the same class, both as to size and weight, and exposed for the same time, and as nearly as possible under the same circumstances, had lost 14 drachms; but experiments of this kind, though they agree when carried on under precisely similar circumstances, must of necessity be very irregular in their results, when made in different seas and situations, being influenced by the degree of saltness, and the nature of the impregnations of the water, the strength of tide and of the waves, the temperature, &c.

In examining sheets which had been defended by small quantities of iron in proportions under $\frac{1}{250}$ and above $\frac{1}{1000}$, whether they were exposed alone, or on the sides of boats, there seemed to me no adhesions of confervæ, except in cases where the oxide of iron covered the copper immediately round the protectors; and even in these instances such adhesions were extremely trifling, and might be considered rather as the vegetations caught by the rough surface of the oxide of iron, than as actually growing upon it.

Till the month of July 1824 all the experiments had been tried in harbour, and in comparatively still water; and though it could hardly be doubted, that the same principles would prevail in cases where ships were in motion, and on the ocean; yet still it was desirable to determine this by direct experiment; and I took the opportunity of an expedition intended to ascertain some points of longitude in the north seas, and which afforded me the use of a steam boat, to make these researches. Sheets of copper carefully weighed, and with different quanties of protecting metal, and some unprotected, were exposed upon canvass so as to be electrically insulated upon the bow of the steam boat; and were weighed and examined at different periods, after being exposed in the north seas to the action of the water during the most rapid motion of the vessel. Very rough weather interfered with some of these experiments, and many of the sheets were lost, and the protectors of others were washed away; but the general results were as satisfactory as if the whole series of the arrangements had been compleat. It was found that undefended sheets of copper of a foot square lost about 6.55 grains in passing at a rate averaging that of eight miles an hour in twelve hours; but a sheet, having the same surface, defended by rather less than $\frac{1}{500}$ lost 5.5 grains; and that like sheets defended by $\frac{1}{70}$ and $\frac{1}{100}$ of malleable iron were similarly worn, and underwent nearly the same loss, that of two grains, in passing through the same space of water. These experiments (the results of which were confirmed by those of others made during the whole of a voyage to and from Heligoland, but in which during the return the protectors were lost) shows that motion does not affect the nature of the limits and quantity of the protecting metal; and likewise prove, that independently of the chemical, there is a mechanical wear of the copper in sailing, and which on the most exposed part of the ship, and in the most rapid course, bears a relation to it of nearly 2 to 4.55.

I used the very delicate balance belonging to the Royal Society in these experiments; the sheets of copper weighed between 7 and 8000 grains; and I was fully enabled to ascertain by means of this balance, a diminution of weight upon so large a quantity, equal to $\frac{1}{100}$ of a grain. It was evident from a very minute inspection of the sheet with the largest quantity of protecting metal, that there was not any adhesion of alkaline or earthy substances to its surface.

Having observed in examining the results of some of the experiments on the effects of single masses of protecting metal on the sheeting of ships, that there was in some cases in which sheets with old fastening had been used, tarnish or corrosion, which seemed to increase with the distance from the protecting metal, it became necessary to investigate this circumstance, and to ascertain the extent of the diminution of electrical action in instances of imperfect or irregular conducting surfaces.

With single sheets or wires of copper, and in small confined quantities of sea water, there seemed to be no indications of diminution of conducting power, or of the preservative effects of zinc or iron, however divided or diffused the surface of the copper, provided there was a perfect metallic connection through the mass. Thus, a small piece of copper containing about 32 square inches, was perfectly protected by a quantity of zinc which was less than $\frac{1}{4000}$ part of the whole surface; and a copper wire of several feet in length was prevented from tarnishing by a piece of zinc wire which was less than $\frac{1}{1400}$ part of its length. In these cases the protecting metal corroded with great rapidity, and in a few hours was entirely destroyed; but when applied in the form of wire and covered, except at its transverse surface, with cement, its protecting influence upon the same minute scale was exhibited for many days. A part of these results depend upon the absorption of the oxygen dissolved in the water when its quantity is limited, by the oxidable metal, and of course the proportion of this metal must be much larger when the water is constantly changing; but the experiments seem to show that any diminution of protecting effect at a distance, does not depend upon the nature of the metallic, but of the imperfect or fluid conductor.

This indeed is shown by many other results.

A piece of zinc and a piece of copper in the same vessel of sea water, but not in contact, were connected by different lengths of fine silver wire of different thickness. It was found that whatever lengths of wire of $\frac{1}{300}$ of an inch were used, there was no dimunition of the protecting effect of the zinc; and the experiment was carried so far as to employ the whole of a quantity of extremely fine wire, amounting to upwards of forty feet in length, and of a diameter equal only to $\frac{100}{98742}$ of an inch, when the results were precisely the same as if the zinc and copper had been in immediate contact.

Pieces of charcoal, which is the worst amongst the more perfect conductors, were connected by being tied together, and made the medium of communication between zinc and copper, upon the same principles, and with the same views as those just described, and with precisely the same consequences.

In my first experiments upon the effects of increasing the length or diminishing the mass of the imperfect or fluid conducting surface in interfering with the preserving effects of metals, I used long narrow tubes; but I found them very inconvenient; and I had recourse to the more simple method of employing cotton or tow for this purpose.

Several feet of copper wire in a spiral form were connected with a small piece of zinc wire of about half an inch in length. The zinc and a portion of the copper were introduced into one glass, and the coils of copper wire were introduced into other glasses, so as to form a series of six or seven glasses, which were filled with sea water, and made part of the same voltaic arrangement, by being connected with pieces of tow moistened in sea water.

It was found in these experiments, that when the pieces of tow connecting the glasses were half an inch in thickness, the preserving effect of the zinc in the first glass was no where diminished, but extended apparently equally through the whole series.

When the pieces of tow were about the fifth of an inch in thickness, a diminution of the preserving effects of the zinc was perceived in the fourth glass, in which there was a slight solution of copper; in the fifth glass this result was still more distinct, and so on till in the seventh glass there was a considerable corrosion of the copper.

When the tow was only the tenth of an inch in thickness, the preserving effect of the zinc extended only to the third glass; and in each glass more remote, the effect of corrosion was more distinct, till in the seventh glass it was nearly the same as if there had been no protecting metal. All the chemical changes dependent upon negative electricity were successively and elegantly exhibited in this experiment. In the first glass containing the zinc, there was a considerable and hasty deposition of earthy and alkaline matter, and crystals of carbonate of soda adhered to the copper at the surface where it was clean and bright; but in the lower part it was coated with revived metallic zinc. In the second glass the wire was covered over with fine crystals of carbonate of lime; and the same phænomenon of the separation of carbonate of soda occurred, but in a less degree. In the third glass the wire was clean, but without depositions; and the presence of alkaline matter could only be distinguished by chemical tests. In the fourth glass the copper was bright, evidently in consequence of a slight but general corrosion, but with a scarcely sensible deposit; in the fifth, the deposit was very visible; and in the seventh the wire was covered with green rust.

These results, which showed that a very small quantity only of the imperfect or fluid conductor was sufficient to transmit the electrical power, or to compleat the chain, induced me to try if copper nailed upon wood, and protected merely by zinc or iron on the under surface, or that next the wood, would not be defended from corrosion. For this purpose I covered a piece of wood with small sheets of copper, a nail of zinc of about the $\frac{1}{200}$ part of the surface of the copper being previously driven into the wood: the apparatus was plunged in a large jar of sea water: it remained perfectly bright for many weeks, and when examined, it was found that the zinc had only suffered partial corrosion; that the wood was moist, and that on the interior of the copper there was a considerable portion of revived zinc, so that the negative electricity, by its operation, provided materials for its future and constant excitement. In several trials of the same kind, iron was used with the same results; and in all these experiments there appeared to be this peculiarity in the appearance of the copper, that unless the protecting metal below was in very large mass, there were no depositions of calcareous or magnesian earths upon the metal; it was clean and bright, but never coated. The copper in these experiments was nailed sometimes upon paper, sometimes upon the mere wood, and sometimes upon linen; and the communication was partially interrupted between the external surface and the internal surface by cement; but even one side or junction of a sheet seemed to allow sufficient communication between the moisture on the under surface and the sea water without, to produce the electrical effect of preservation.

These results upon perfect and imperfect conductors led to another enquiry, important as it relates to the practical application of the principle; namely, as to the extent and nature of the contact or relation between the copper and the preserving metal. I could not produce any protecting action of zinc or iron upon copper through the thinnest stratum of air, or the finest leaf of mica, or of dry paper; but the action of the metals did not seem to be much impaired by the ordinary coating of oxide or rust; nor was it destroyed when the finest bibulous or silver paper, as it is commonly called, was between them, being moistened with sea water. I made an experiment with different folds of this paper. Pieces of copper were covered with one, two, three, four, five and six folds; and over them were placed pieces of zinc, which were fastened closely to them by thread; each piece of copper so protected was exposed in a vessel of sea water, so that the the folds of paper were all moist.

It was found in the case in which a single leaf of paper was between the zinc and the copper, there was no corrosion of the copper; in the case in which there were two leaves, there was a very slight effect; with three, the corrosion was distinct: and it increased, till with the six folds the protecting power appeared to be lost: and in the case of the single leaf, there was this difference from the result of immediate contact, that there was no deposition of earthy matter. Showing that there was no absolute minute contact of the metals through the moist paper; which was likewise proved by other experiments: for a thin plate of mica, as I have just mentioned, entirely destroyed the protecting effect of zinc: and yet when a hole was made in it, so as to admit a very thin layer of moisture between the zinc and copper, the corrosion of the copper, though not destroyed, was considerably diminished.

The rapid corrosion of iron and zinc, particularly when used to protect metals, only in very small quantities, induced me to try some experiments as to their electro-chemical powers in menstrua out of the contact, or to a certain extent removed from the contact of air, such as might be used for moistening paper under the copper sheathing of ships: the results of these experiments I shall now detail. A small piece of iron was placed in one glass filled with a saturated solution of brine, which contains little or no air; copper, attached by a wire to the iron, was placed in a vessel containing sea water, which was connected with the brine by moistened tow. The copper did not corrode, and yet the iron was scarcely sensibly acted upon, and that only at the surface of the brine; and a much less effect was produced upon it in many weeks than would have been occasioned by sea water in as many days.

With zinc and brine in the same kind of connection there was a similar result: but the solution of the zinc was comparatively more rapid than that of the iron, and the copper was rendered more highly negative, as was shown by a slight deposition of earthy matter upon it.

A solution of potassa, or of alkaline substances possessing the electro-positive energy, has nearly the same effect on saline solutions as if they were deprived of air; and when mixed with sea water impedes the action of metals upon them; but if used in quantity in combinations such as these I have just described, in which iron is the protecting metal, it destroys the result, and renders the iron negative. Thus, if iron and copper in contact, or fastened to each other by wires, be in two vessels of sea water connected by moist cotton or asbestos, all the various circumstances of protection of the two metals by each other may be exhibited by means of solution of potassa. By adding a few drops of solution of potassa to the water in the glass containing the iron, the negative powers of the copper in the other glass are diminished; so that the deposition of the calcareous and magnesian earths upon it is considerably lessened; by a little more solution of potassa the deposition is destroyed, but still the copper remains clean. The corrosion of the iron, which before was rapid, is now almost at an end; and a few drops more of the solution of potassa produces a perfect equilibrium: so that neither of the metals undergoes any change, and the whole system is in a state of perfect repose. By making the fluid in the glass containing the iron still more alkaline, it no longer corrodes; and the green tint of the sea water shows that the copper is now the positively electrified metal; and when the solution in the glass containing the iron is strongly alkaline, the copper in the other glass corrodes with great rapidity, and the iron remains in the electro-negative and indestructible state.

I began this paper by some observations upon the nature of the processes by which copper sheeting is destroyed by sea water, and on the causes by which it is preserved clean, or rendered foul by adhesions of marine vegetables or animals; I shall conclude it by some further remarks on the same subject, and with some practical inferences and some theoretical elucidations, which naturally arise from the results detailed in the foregoing pages.

The very first experiment that I made on harbour-boats at Portsmouth, proved that a single mass of iron protected fully and entirely many sheets of copper, whether in waves, tides, or currents, so as to make them negatively electrical, and in such a degree as to occasion the deposition of earthy matter upon them; but observations on the effects of the single contact of iron upon a number of sheets of copper, where the junctions and nails were covered with rust, and that had been in a ship for some years, showed that the action was weakened in the case of imperfect connexions by distance, and that the sheets near the protector were more defended than those remote from it. Upon this idea I proposed, that when ships, of which the copper sheathing was old and worn, were to be protected, a greater proportion of iron should be used, and that if possible it should be more distributed. The first experiment of this kind was tried on the Sammarang, of 28 guns, in March, 1824, and which had been coppered three years before in India. Cast iron, equal in surface to about $\frac{1}{80}$ of that of the copper was applied in four masses, two near the stern, two on the bows. She made a voyage to Nova Scotia, and returned in January 1825. A false and entirely unfounded statement respecting this vessel was published in most of the newspapers, that the bottom was covered with weeds and barnacles. I was present at Portsmouth soon after she was brought into dock: there was not the smallest weed or shell-fish upon the whole of the bottom from a few feet round the stern protectors to the lead on her bow. Round the stern protectors there was a slight adhesion of rust of iron, and upon this there were some zoophytes of the capillary kind, of an inch and a half or two inches in length, and a number of minute barnacles, both Lepas anatifera and Balanus tintinnabulum. For a considerable space round the protectors, both on the stern and bow, the copper was bright; but the colour became green towards the central parts of the ship; yet even here the rust or verdigrease was a light powder, and only small in quantity, and did not adhere, or come off in scales, and there had been evidently little copper lost in the voyage. That the protectors had not been the cause of the trifling and perfectly insignificant adhesions by any electrical effect, or by occasioning any deposition of earthy matter upon the copper, was evident from this—that the lead on the bow, the part of the ship most exposed to the friction of the water, contained these adhesions in a much more accumulated state than that in which they existed near the stern; and there were none at all on the clean copper round the protectors in the bow; and the slight coating of oxide of iron seems to have been the cause of their appearance.

I had seen this ship come into dock in the spring of 1824, before she was protected, covered with thick green carbonate and submuriate of copper, and with a number of long weeds, principally fuci, and a quantity of zoophytes, adhering to different parts of the bottom; so that this first experiment was highly satisfactory, though made under very unfavourable circumstances.

The only two instances of vessels which have been recently coppered, and which have made voyages furnished with protectors, that I have had an opportunity of examining, are the Elizabeth yacht, belonging to the Earl of DARNLEY, and the Carnebrea Castle, an Indiaman, belonging to Messrs. WIGRAM. The yacht was protected by about $\frac{1}{125}$ part of malleable iron placed in two masses in the stern. She had been occasionally employed in sailing, and had been sometimes in harbour, during six months. When I saw her in November she was perfectly clean, and the copper apparently untouched. Lord DARNLEY informed me that there never had been the slightest adhesion of either weed or shell-fish to her copper, but that a few small barnacles had once appeared on the loose oxide of iron in the neighbourhood of the protectors, which however were immediately and easily washed off. The Carnebrea Castle, a large vessel of upwards of 650 tons, was furnished with four protectors, two on the stern, and two on the bow, equal together to about $\frac{1}{104}$ of the surface of the copper. She had been protected more than twelve months, and had made the voyage to Calcutta and back. She came into the river perfectly bright; and when examined in the dry dock was found entirely free from any adhesion, and offered a beautiful and almost polished surface; and there seemed to be no greater wear of copper than could be accounted for from mechanical causes.

Had these vessels been at rest, I have no doubt there would have been adhesions, at least in Portsmouth or Sheerness harbours, where the water is constantly muddy, and where the smallest irregularity or roughness of surface, from either wear, or the deposition of calcareous matter, or the formation of oxides or carbonates, enable the solid matter floating in the water to rest. There is a ship, the Howe, one of the largest in the Navy, now lying at Sheerness, which was protected by a quantity of cast iron judged sufficient to save all her copper, nearly fifteen months ago. She has not been examined; but I expect and hope that the bottom will be covered with adhesions, which must be the case if her copper is not corroded; but notwithstanding this, whenever she is wanted for sea, it will only be necessary to put her into dock for a day or two, scrape her copper, and wash it with a small quantity of acidulous water, and she will be in the same state as if newly coppered.

At Liverpool, as I am informed, several ships have been protected, and have returned after voyages to the West Indies, and even to the East Indies. The proportion of protecting metal in all of them has been beyond what I have recommended, $\frac{1}{90}$ to $\frac{1}{70}$; yet two of them have been found perfectly clean, and with the copper untouched after voyages to Demarara; and another nearly in the same state, after two voyages to the same place. Two others have had their bottoms more or less covered with barnacles; but the preservation of the copper has been in all cases judged complete. The iron has been placed along the keel on both sides; and the barnacles, in cases where they have existed, have been generally upon the flat of the bottom; from which it may be concluded, that they adhered either to the oxide of iron, or the calcareous deposits occasioned by the excess of negative electricity.

In the navy the proportion adopted has been only $\frac{1}{250}$ of cast iron, at least for vessels in actual service, and when the object is more cleanness than the preservation of the copper.

It is very difficult to point out the circumstances which have rendered results, such as these mentioned with respect to Liverpool traders, so different under apparently the same circumstances, i. e. why ships should exhibit no adhesions or barnacles after two voyages, whilst on another ship, with the same quantity of protection, they should be found after a single voyage.* This may probably depend upon one ship having remained at rest in harbour longer than another, or having been becalmed for a short time in shallow seas, where ova of shell fish, or young shell fish existed; or upon oxide of iron being formed, and not washed off, in consequence of calm weather, and which consolidating, was not afterwards separated in the voyage. From what I can learn, however, the chance of a certain degree of foulness, in consequence of the application of the full proportion of protecting metal, will not prevent ship owners from employing this proportion, as the saving of copper is a very great object; and as long as the copper is sound, no danger is to be apprehended from worms.

It ought to be kept in mind that the larger a ship, the more the experiment is influenced by the imperfect conducting power of the sea water, and consequently the proportion of protecting metal may be larger without being in excess.

* The quality of the copper may be another cause.

I have mentioned these circumstances because they apply to ships already coppered, and because I have heard that a Liverpool ship, of which it was doubtful whether the copper was in a state such as would enable her to make another voyage to India with security, has, by the application of protectors of $\frac{1}{70}$, made this voyage,* without apparently any wear of her sheeting; and that she is now preparing with the same protectors to make another voyage.

In cases when ships are to be newly sheathed, the experiments which have been detailed in the preceding pages render it likely, that the most advantageous way of applying protection will be under, and not over the copper: the electrical circuit being made in the sea water passing through the places of junction in the sheets; and in this way every sheet of copper may be provided with nails of iron or zinc, for protecting them to any extent required. By driving the nail into the wood through paper wetted with brine *above* the tarred paper, or felt, or any other substance that may be employed, the incipient action will be diminished; and there is this great advantage, that a considerable part of the metal will, if the protectors are placed in the centre of the sheet, be deposited and re-dissolved: so there is reason to believe that small masses of metal will act for a great length of time. Zinc, in consequence of its forming little or no insoluble compound in brine or sea water, will be preferable to iron for this purpose; and whether this metal or iron be used, the waste will be much less than if the metal was exposed on the outside: and all difficulties with respect to a proper situation in this last case are avoided.

* The Dorothy.

The copper used for sheathing should be the purest that can be obtained; and in being applied to the ship, its surface should be preserved as smooth and equable as possible: and the nails used for fastening should likewise be of pure copper; and a little difference in their thickness and shape will easily compensate for their want of hardness.

In vessels employed for steam navigation the protecting metal can scarcely be in excess;* as the rapid motion of these ships prevents the chance of any adhesions; and the wear of the copper by proper protection is diminished more than two-thirds.

* I have mentioned in the two last communications on this subject some application of the principle; many others will occur. In submarine constructions—to protect wood, as in piles, from the action of worms, sheathing of copper defended by iron in excess may be used; when the calcareous matter deposited will gradually form a coating of the character and firmness of hard stone.