Life of Brass Condenser Tubes*

Results of a Study of the Actions of Certain Metals in Distilled and Sea Water, and Possible Protective Measures

By Drs. Guy D. Bengough and O. F. Hudson

THE fourth report of the Corrosion Committee, which was presented at the meeting of the Institute of Metals, is divided into three parts. In the first the authors, Dr. Guy D. Bengough and Dr. O. F. Hudson, discuss the actions that take place when certain metals and alloys corrode in distilled water and sea water. In the second they consider the behavior of condenser tubes in similar liquids and the variations in the behavior of different samples of tubes having nominally the same composition; and in the third they set forth a statement in some detail of the practical problems of corrosion.

After a brief consideration of the current theories of corrosion, the report discusses the difficulties in the way of making a true quantitative determination of the amount of corrosion, and shows that in certain cases they are almost insoluble with existing methods of analysis. Mere "loss of weight" measurements, unsupported by detailed examination, of scale and metals in solution, are regarded as being of little value in many cases, and it is thought they might advantageously be replaced by microscopic work.

NATURE OF ACTION.

The action of distilled water on metallic zinc, the authors conclude, is initially a process of chemical oxidation rather than of electro-chemical displacement. Normally metallic zinc is covered with a partially protective scale consisting largely of oxide or basic carbonate. Water containing carbon dioxide can attack or dissolve the oxidized layer, and a true metallic surface is then exposed to the action of the water. Where this takes place a peculiar form of oxide is formed on the surface; it probably contains zinc peroxide and exerts a catalytic action on the underlying metal. Being slightly soluble it passes into solution, and is afterwards largely precipitated as the ordinary hydroxide and carbonate. The precipitated hydroxide has a distinctly protective action on the metal beneath it, reinforcing the original scale and enabling it to resist the action of carbon dioxide. The action is thus localized. With very dilute acid, such as acetic, the action consists in the replacement of hydrogen by zinc, but the action is not severely localized, as with distilled water, there are no local accumulations of the products of corrosion, and consequently the action is more nearly uniform. There is no evidence that dissolved oxygen can act as a depolarizer; hydrogen is given off as gas. The action of sea water on zinc is also chemical rather than electro-chemical, and local action is again due to the local accumulation of certain products of corrosion. The principal action of distilled water and of sea-water on copper is also one of chemical oxidation.

The action of distilled water on 70:30 brass is considered to be the chemical oxidation of the copper and zinc and the partial solution of the oxidized products. Much of the zinc, in the presence of carbon dioxide, passes into solution, and part of the copper. The residue of both metals remains on the surface of the alloy as an oxide scale, and this becomes further oxidized and altered at certain spots which become covered with thick deposits of the products of attack. Such deposits are porous, and allow, and probably accelerate, local attack on the underlying metal. The attack is accompanied by redeposition of copper by displacement by the zinc either electro-chemically or otherwise, and precipitation of cuprite. There are signs of slight local dezincification at such places, but the attack over the general surface of the alloy is complete corrosion. The positions at which local attack and pitting take place are not determined by the variation in the electrical properties of the original metal, but by the conditions of the experiment. In the presence of dilute acids, such as hydrochloric and sulphuric, local action of the type described does not occur, since there is little or no local accumulation of oxidation products. On the other hand, the absence of carbon dioxide, retards the action. From the analytical data it appeared that the local action in the case of distilled water increased with time, while the rate of general corrosion over the whole specimen fell off. These facts suggest the fallacy of loss of weight test, since local action is more important practically than general corrosion.

The action of sea-water on brass has been studied

on the same lines as that of distilled water. The action is considered to be similar in type. Local pitting and dezincification are due to the accumulation of the products of corrosion. Under certain conditions redeposition of copper may occur. The rate of general corrosion is much greater than that in distilled water, and does not fall off so rapidly with time. At the ordinary temperature there is less tendency to local dezincification.

BEHAVIOR OF CONDENSER TUBES.

In studying the form of the surface of certain condenser tubes of 70:30 brass, the presence of a layer that differs in its behavior towards corrosive agents from the underlying metal has been identified in several different ways. In many cases this layer is probably richer in copper than the alloy beneath it. In such cases the tube may resist dezincification to a marked degree for long periods; in other cases the surface layer probably has nearly the same composition as the rest of the tube, and in such cases strong dezincification may take place in sea-water in the neighborhood of 50° C. Tubes from the same batch of manufacture usually resemble one another as regards the nature and properties of the layer, and tubes from different batches, even though made by the same maker, may differ. Thus one important factor as regards dezincification is the nature of the tube, but the kind of surface that best resists dezincification does not necessarily best resist other kinds of attack. Means of controlling the surface layer have not yet been worked out, but the problem does not appear to be insuperable.

In many cases local action may be initiated on condenser tubes by the action of certain bodies, which themselves appear to take no direct part in the action. Such bodies are sand, calcium carbonate, ferric hydrate, glass, clinker, and coke. The amount of action that takes place varies with the physical properties of the substance. The action is associated with the accumulation of products of corrosion, and may be largely assisted by them. The nature of this action is of well-marked type, and has been provisionally called oxide disintegration. It is usually characterized by intercrystalline oxidation. Actions of this kind are of great importance in many cases of corrosion on the practical scale.

PRACTICAL ASPECTS.

As a preliminary statement of the practical problem of the corrosion the authors propound that the ordinary 70:30 brass tube of commerce is not liable to any electrolytic action set up by anodic and cathodic areas inherent in its surface, even in the presence of good electrolytes such as sea-water. It is corroded, under normal conditions, by a slow chemical action, which produces a slight roughening of the surface, but no well-defined pitting. Unless this action were speeded up locally by factors independent of the tube, the life of a tube would normally be 15 to 20 years or more in the case of deep sea-water, and many types of neutral fresh water. If acid be present in the water in the proportions of only a few parts per 100,000, the speed of attack is greatly increased, the action being a general thinning of the tube. Neutralization is quite effective in stopping this increased action.

The following conditions are set forth as those under which a tube would have a normal life of 20 years. In practice tubes fail sooner because the normal slow roughening of the tube by chemical oxidation is locally speeded up by factors which are for the most part independent of the tube:—(a) Only clear water to enter the tube, or water that will not deposit suspended matter. (b) The water must be free from gases in suspension, and must not contain more than the normal amount of air in solution. (c) The water must be neutral or not more than very slightly alkaline. It must be free from ammonia and certain other specially harmful substances, which are, however, of comparatively rare occurrence in technical waters. (d) The temperature of the cooling water in the hottest part of the condenser should not exceed 35° C. (e) The speed of the water should be about 5 or 6 feet per second. (f) The steam should be properly distributed in the condenser, according to the best modern practice.

A water supply which varies considerably in composition at different times of the year involves special problems and must be excluded from the above statement at present.

EFFECT OF SCALE.

It is not uncommon to find a dozen or more different substances among the scale on a tube, and each of these substances will exert some influence, greater or less, harmful or protective, on the underlying tube. To a limited extent the nature of the scale on a tube can be modified, and it is probable that it is in this direction that work can be most usefully pursued in the endeavor to prevent certain types of corrosive action. In sea-water, estuarine water, and some other waters the scale contains calcium carbonate in larger or smaller amounts. The physical character and the distribution of this substance may be one of the most important factors in determining the nature and amount of the corrosive action that takes place.

The distribution and the effect on corrosion of this substance are, in the authors' experience, most nearly uniform when the tubes are maintained as cathodes in sea-water by some form of electrolytic protection. Under these conditions the layer is usually extremely thin and extends over the whole tube. It does not entirely prevent the disintegration of the underlying metal, but appears to slow down the rate considerably. When ordinary condenser tubes are used in sea-water, and certain other types of water, without any special electrolytic protection other than that afforded by the cast-iron water ends, a fairly continuous layer of calcium carbonate scale is found only for a distance of from 5 to 10 inches from each end of the tube. It usually appears to be coarser, thicker, and less uniform than that formed under the conditions already considered. It appears to retard corrosion, but to be less effective than the thinner, more uniform, and more compact layer, characteristic of continuous protection by a current generated outside the condenser. On the general surface of the tube farther away from the ends a continuous layer, more or less free from other substances, is not found as a rule, though isolated areas are sometimes covered with such a layer; but for the most part the calcium carbonate, if present at all, is mixed up with products of corrosion.

In the case of hard fresh waters, such as are used in the Northampton district, the carbonate scale may be of formidable thickness, especially with slow water speeds and low vacuum. Under such conditions it is coarse in structure and porous. It is not entirely protective, even when it is so thick as to interfere seriously with the efficiency of the condenser.

In certain cases, such as estuarine waters, where the nature of the water varies at different times of the year in accordance with the rainfall, it is probable that there is a continuous process of solution, deposition and resolution of the calcium carbonate of the scale going on in accordance with the chemical conditions set up at different periods by the varying composition of the water. Tubes that have been subjected to such conditions show discontinuous layers of carbonate scattered about the tube, which suggest that some such action has taken place. In such cases a rapid attack may be proceeding over certain areas of tubes which are free from scale, while other areas are largely protected.

The protective power of calcium carbonate may be considerable, but is not absolute even under the most favorable conditions yet investigated; moreover, it varies considerably in accordance with its physical condition. It has also been found in the laboratory that calcium carbonate, precipitated under certain conditions, may be very harmful and initiate corrosion in much the same way as does sand.

PROTECTIVE MEASURES.

The authors give a brief summary of their observations on the Cumberland method of electrolytic protection as applied at the power-station of the Brighton Corporation at Southwick. They say it seems clear to them that this process ensures a prolonged life for the tubes provided that they had not begun to corrode before it was applied. If severe corrosion has begun before the process is applied, or if it is applied imperfectly, it is by no means certain that it will be stopped by the process.

As it does not seem likely that the problem of preventing local pitting will be solved by improvements in composition, it may in certain circumstances be desirable to add to the resisting power of the tube by

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*Summary of report to Institute of Metals from *Times Engineering Supplement* (London).

Photography in Research

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the tube by the condensers of a No. 0 deliascope. An arc was found to be not only too intense but too variable in color and position. A gas-filled bulb with only one filament would be very desirable, while the Nernst or the new incandescent lamp as used for motion picture projection might answer well. It is best to absorb the heat from the light with a water cell. A prism illuminator was used with an achromatic objective and a compensating ocular, as these oculars give much better results than a Huyghenian.

MOTION MICROPHOTOGRAPHS.

All types of motion cameras are not readily adaptable to these special problems. Devices have been constructed for making motion pictures in various lines of research, notably at the Marey Institute in France. For my purpose I found the Bell and Howell camera an incomparable instrument. It is entirely of metal, compact and mechanically faultless. The rotating lens turret and the sliding base permit the focusing aperture to be moved to the exact position occupied by the film when recording.

As shown in Fig. 10 (omitted)¹ the camera and the stressing machine are clamped very firmly to a substantial table—a masonry pier would be more desirable—and the camera is then connected to the microscope by a black velvet sleeve to facilitate adjustments and to break the transmission of any vibration. A device for observing the action continuously by eye might be inserted but would result in some loss of definition. The microscope was first focused on a polished region at the base of the shoulder, shown in Fig. 9, where the stresses will be most intense.

Photographs of metals are usually at low power—one hundred or less. In making motion pictures the magnification was even lower in order to exhibit a sufficient field for study. This leads to more difficulty, because in the low magnification, the lines made by the crystal boundaries become so narrow that it is difficult to retain them in negative and positive with enough density to project well. It is possible to improve the sharpness of the image by using deep colored screens, preferably in the blue-green, thus eliminating other colors which might form color fringes. If this is done, panchromatic film is necessary. By

LIMITING RESOLUTION

Objective	Yellow line D			Green line E			Violet line H _γ		
	N.A.	λ = 5896 Å.U.		λ = 5269 Å.U.			λ = 4341 Å.U.		
1	.10	8,617		9,641			11,699		
2	.25	21,542		24,103			29,247		
3	.6	51,700		57,846			70,193		
4	.9	77,550		86,769			105,289		
Oilimmersion 1/4	1.4	120,638		134,974			163,783		

the accompanying table of resolving powers for transmitted light it is seen how much the working qualities of lenses are improved by increasing the numerical aperture and decreasing the wave length. Violet light is difficult to use, however, because the eye works very poorly in that region and it is quite impossible to focus the object, even with a magnifier. Sections of the film made in the present instance are shown in Fig. 11, while exposures of the same test made at higher powers with an ordinary metallographic microscope are shown for comparison in Figs. 12 and 13. In the results shown here the negative was made on positive film at the normal speed of 16 pictures per second, giving an exposure of 1/48 of a second, the negative film being too fast and not giving satisfactory contrast.

The little work which I have done in this field and the consideration of other special problems lead me to think that the motion camera with and without the microscope offers a means of research the value of which we can hardly predict. The field of application is as wide as human knowledge. Processes and reactions in the natural sciences and phenomena in the physical sciences will unfold many opportunities as we search for new facts. Special apparatus has been constructed whereby consecutive exposures can be made, each in one ten-millionth of a second. With such a tool, the transmission and reaction of sound waves might be quite readily photographed in motion.

One day some one may record the passage of electrons discharged across a vacuum. We can hardly set a limit.

Pressure Casting of High Tensile Copper Alloys

Two sets of copper alloys, prepared during the years 1915-1918 in the Metallurgy Department of the National Physical Laboratory in order to combine high tensile strength with great ductility, were described before the Institute of Metals by Dr. W. Rosenhain and Mr. D. Hanson. The requirements they had to meet involved extensive cold working, and they had

to be capable of being rolled into thin sheet which was required to have an excellent finish and to undergo further operations without cracking.

In the first series, in which it was desired to avoid the use of zinc, the copper was alloyed with aluminum or manganese, or both. One alloy of this series, containing 7 per cent. of aluminum but no manganese, attained in the "as rolled" condition a tensile strength only just under 40 tons per sq. in., with an elongation of 17.5 per cent., and after annealing a tensile strength of 27.5 tons and the remarkable elongation of 71 per cent. These results were closely approached by another alloy with 7 per cent. of aluminum and 1 per cent. of manganese; "as rolled" it gave 35.5 tons tensile and 28 per cent. elongation, and when annealed 29.3 tons tensile and 65 per cent. elongation. Similarly remarkable results were obtained with an alloy containing 6 per cent. of aluminum and 3 per cent. of manganese, and two with 5 and 7 per cent. of manganese without aluminum were interesting, though their figures were distinctly lower than those for the alloys containing aluminum.

In the second set it was required that no aluminum and not a high percentage of zinc should be used; the alloys were required to stand severe stamping and drawing operations in the form of thin strip less than 0.05 in. thick. None of them had such remarkable properties as some of those in the first set, but one containing 3 per cent. of manganese and 10 per cent. of zinc had in the cold-rolled condition a tensile strength of 47 tons with 3 per cent. elongation, and when annealed 23 tons tensile with 35 per cent. elongation.

Difficulties were encountered in casting the alloys of the first series owing to the presence of foreign matter floating on the surface of the molten metal, which, in spite of every care found its way in small quantities into the mould. Finally an adaptation of the pressure casting method patented by Mr. F. Tomlinson, of the Broughton Copper Company, was employed with considerable success. The principle consists in forcing the liquid metal, by means of externally applied air pressure, through a feeder tube communicating with the bottom of the mould and dipping into the molten metal nearly to the bottom of the crucible. It is necessary to use a previously heated feeder tube, through which the metal can be forced without splashing and without exposure to the atmosphere, the dross, charcoal, etc., being left in the crucible. The amount of metal in the crucible must be so adjusted that the mould is filled before the bottom of the feeder tube is exposed. When the metal approaches the top of the mould the rate of flow is gradually reduced till it is almost arrested. At this stage a crust is formed on the top of the ingot. As soon as this is sufficiently thick, the air-pressure is gradually raised to 30 lb. per sq. in. and is maintained at that value till the ingot is solid. A fairly hot mould must be used, else the metal is liable to be chilled in the narrow orifice through which it has to pass. Conditions should be so arranged that this orifice remains open until the whole of the ingot is solidified. In the experiments the mould was preheated in a special gas furnace in such a manner that the bottom of the mould was distinctly hotter than the top, the bottom temperatures being of the order of 500 to 600° C. Even during the short time necessary for casting, the manganese-copper alloys become covered with a thick black coating of oxide, which ruins the ingots; the addition of 0.25 per cent. of aluminum prevents oxidation and entirely removes this defect.—*Times Engineering Supplement*.

What is a Chemical Element?

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expected. Moreover, the period of eka-tantalum, as estimated from the range of its α-rays by Hahn and Meitner, makes it appear that in due course determination not only of the spectrum, but also of the atomic weight and complete chemical nature, of this element will be possible. It is only in this way that the open question whether the actinium series branches off as shown at uranium-II or at uranium-I can be settled.

As the figure shows, so far as the changes have been followed, they all result in the production of isotopes of lead ranging in atomic weight from 206 to 210, the main products being that of uranium, 206, and both thorium products in the two branches, 208. The conclusion that lead was the ultimate product of thorium was new, but the prediction that the ultimate products of both uranium and thorium are different isotopes of lead—the one with an atomic weight less, and the other with an atomic weight greater, than that of common lead, 207.2—has been completely confirmed by experiment, and it has also been shown that ionium has an atomic weight lower than thorium (compare *Nature*, July 19 and 26, 1917).

The older chemical analysis of matter distinguished only heterobaric heterotopes. The newer methods depending on radio-active change distinguish, not only heterobaric, but isobaric isotopes, and also isobaric heterotopes—that is, substances of different atomic weight and identical chemical character, of the same atomic weight and different chemical character. A glance at the chart will show many examples of all three kinds. Not only has the chemical element been robbed of its time-honored title to be considered the ultimate unchanging constituent of matter, but its title to be considered homogeneous has also vanished. The century that began with Dalton and ended with the discoveries by Becquerel and the Curies took the practical conception of the element it found extant, as that which could not be further resolved, and made of it the central conception of a theory of the ultimate constitution of matter. The element was first atomized, and then the atom and the element became synonyms, related as the singular is to the plural. Every one of the conceptions which associated the atom with the chemical element now has to be modified. Atoms of different chemical elements may have the same atomic weight; those of what the chemist and spectroscopist regard as the same element may have different atomic weight; and, most difficult to include of all to anyone today attempting to define the chemical element, even though the atoms all have the same weight, the element, nevertheless, may be an unresolvable mixture of fundamentally different isobaric isotopes. Present-day complete identity may conceal differences for the future of paramount importance, if ever transmutation is practically realizable at will. The goal that inspires the search for the homogeneous constituents out of which the material world is composed is now known to be, like infinity, approachable rather than attainable. The practical and necessary conception of the chemical elements, as understood before these discoveries, is, of course, unaffected. It had, and it has, a real significance as representing the limits of the spectroscopic and chemical analysis of matter, which remains, though it is now known to convey something very unlike the original and natural conception of the elements as the *l m n's* of the material alphabet.—*Nature*.

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special treatment before it goes into use. Such treatment, for instance, may be the production on the tube of a resistant scale by artificial means. Such a scale may consist of oxide, calcium carbonate, or a basic salt, or a mixture of these substances. The simplest, but not the most efficient, case of such a scale is an oxide scale produced upon the alloy by treatment in an annealing furnace in an oxidizing atmosphere, and a number of experiments have been made with tubes treated in this way.

The treatment in the case of 70:30 brass, lead, brass, or Admiralty alloy is to heat the finished tube in an oxidizing atmosphere for half an hour at a temperature of about 260 to 300° C. It is then put into use with the oxide scale on it—i. e., without pickling or further treatment. It has been found that this heat treatment does not affect the mechanical properties of the tube sufficiently to interfere with the making of a tight joint by the use of ferrules. (The heating periods and temperatures are different for metals or alloys other than those mentioned.) The process is known as the pre-oxidizing process. It is important that the tubes treated by this process should have a good surface, smooth and uniform. Harm may result if the heating temperature much exceeds the limits stated.

Tubes of various types of brass, treated in the way indicated, have given good results so far at Brighton, in comparison with ordinary tubes of similar composition, but it is not yet certain that such tubes will resist the active attack set up by certain deposits. A considerable number of treated tubes are under test in various parts of the country, under different sets of conditions, and the results of these tests will be reported in due course. Preliminary tests seem to show that treated lead, brass, and Admiralty tubes resist dezincification to a marked degree in ordinary seawater.

Finally, it must be emphasized that it is not likely that either tubes treated as described, or any other type of tube producible commercially, will be found satisfactory under all conditions. A tube and its treatment must be chosen to meet the particular conditions in which it will be used, but it is hoped that the number of types of tube and treatments required will be small. They may, perhaps, be eventually reduced to two, a copper type alloy and a selected brass alloy.

¹Details of the camera, microscope, etc., were illustrated in the SCIENTIFIC AMERICAN, for Oct. 26, 1918, p. 328.—EDITOR.