

# The Significance of Apparently Minor Factors in Corrosion Problems Affecting Condenser and Cooler Tubes\*

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## INTRODUCTION

It is not very easy to decide just what form a lecture of this type should take so that it can be of interest to the largest possible proportion of members. Corrosion of non-ferrous tubes, particularly in marine applications, has been the subject of many papers at different times over the past twenty-five years. Many of these papers are extremely valuable, and even papers published as long ago as 1903, for example that by Milton and Larke entitled "The Decay of Metals"<sup>(1)</sup>, can be read by a person keenly interested in the subject with very great benefit.

In more recent times there have been many very excellent papers published in the Institute's TRANSACTIONS and those of similar bodies, including those by Bradbury and Johnson<sup>(2)</sup>, the late Mr. Dickie<sup>(3)</sup>, Gilbert and May<sup>(4)</sup>, Gilbert<sup>(5)</sup>, Slater, Kenworthy and May<sup>(6)</sup>, details of which are given on page 372.

It has been decided to take a rather different line from that which has normally been taken, and the theme chosen is "The Significance of Apparently Minor Factors". The idea behind this is that there comes a time in most processes when a very small change makes a big difference in the result. It is a number of these points which are to be discussed and the course of the argument will transfer, therefore, from one type of corrosion to another with this thread running through it all as a connecting link. There is another aspect of this. The success or otherwise of non-ferrous tubes in service depends on a number of different factors, some connected with the actual alloy used, some with the manufacturing technique used for the tubes, others with the type of plant in which the tubes are fitted and, lastly and by no means least, with the way in which the plant is operated. It is hoped to show by examples that the best results can only be obtained when all the minor points connected with these various aspects of the problem have been carefully considered and properly evaluated.

With such a very wide field it is impossible to deal in very great detail with each of the different topics to be discussed, and this has, in fact, been one of the difficulties in preparing this paper, as there are very many places where there is a great temptation to digress from the theme and go into some topic in greater detail.

For very many years it has been standard practice to use non-ferrous, that is, copper-base alloy, tubes for ships' condensers and other marine purposes due to their general resistance to corrosion and excellent thermal conductivity. Certain types of corrosion were known to develop, however, when copper and brass were exposed to sea water under certain con-

ditions. One of the oldest and most perplexing of these was the phenomenon known as dezincification and this forms a suitable starting point.

It was observed that brass fittings, including condenser tubes and ferrules, exposed to sea water were liable to attack by dezincification. The attack could take one of two forms known, because of their appearance, as plug and layer type.

In layer type dezincification the whole of the brass surface exposed to sea water is uniformly attacked, giving the appearance, in the case of a tube, of a copper lining on the inside surface. A tube so attacked is shown in Fig. 1 (Plate A).

In plug type dezincification, attack takes place at a number of separate areas on the tube wall, giving the appearance of a brass tube with a number of copper plugs set in it. This type of attack is illustrated in Fig. 2 (Plate A). It is, perhaps, interesting to note that in the early days many people were inclined to believe that attack of this nature was not due to service corrosion but due rather to inferior tubes, suggesting that the plugs of copper were due to insufficient mixing of the copper and zinc during manufacture. It would be generally agreed today that dezincification is due to the use of inferior tubes, but inferior in their composition rather than in any deficiency in the melting or fabrication technique.

As long ago as 1890 steps were taken to try and cure this trouble by the addition of 1 per cent of tin in lieu of 1 per cent of zinc to the standard 70/30 alloy of those days. Mention of this fact was made by Vice-Admiral Oram in his 1914 Presidential Address to the Institute of Metals<sup>(7)</sup>, when he reviewed some of the steps already taken by that time to combat condenser tube corrosion.

Reference to dezincification is also made in Milton and Larke's paper referred to above. In this fifty-years-old paper, the authors refer to the "decay of brass and yellow metal balls in composite vessels and underwater fittings", and to the "decay of brazing metal in copper steam lines". It is, perhaps, interesting to note that the use of a type of brazing metal which will dezincify is still tolerated even today in some shipyards and in some ships. In the early days of the last war, very serious trouble was caused on many of the ships of the Royal Navy by the dezincification of so-called "bronze welds" used for joining together sea water pipelines. In actual fact, the material used was not bronze at all but a duplex structure brass, and the use of this material for sea water pipelines was therefore banned by the Admiralty<sup>(8)</sup>.

Before considering the question of dezincification, it is necessary to consider the types of brass formed when copper and zinc are alloyed together in different proportions. The result is fairly neatly summarized by the metallurgist on what is known as an "equilibrium diagram", as shown in Fig. 3. This indicates the melting points of the different alloys of copper and zinc, but also indicates when different phases are

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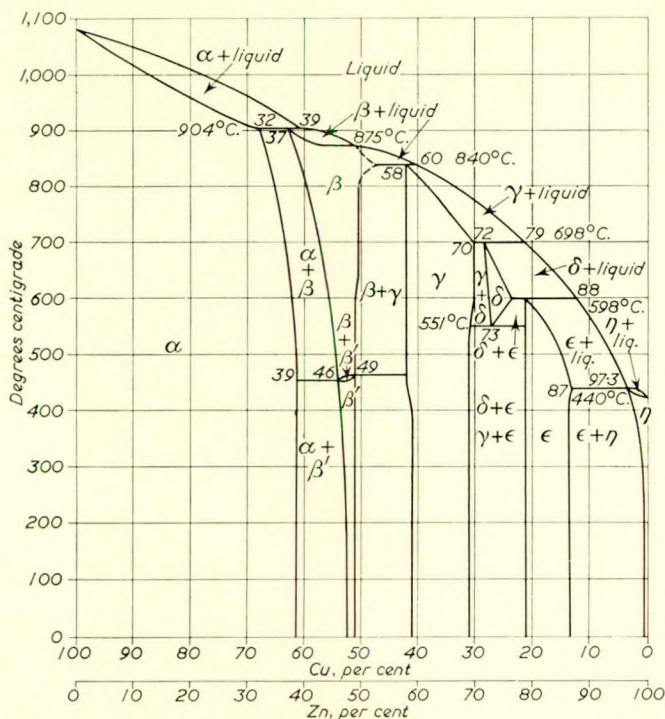


FIG. 3—Equilibrium diagram of the copper-zinc system

The freezing points for the complete range of alloys of copper and zinc are shown, together with any changes taking place after the alloys have reached the solid state. Alloys of copper and zinc containing less than 38 per cent zinc consist entirely of the alpha phase, but with increasing zinc content a proportion of the beta phase is present so that a 60/40 alloy at room temperature contains both alpha and beta phases.

present in the metal. It will be noted that on the diagram, from 100 per cent of copper down to approximately 62 per cent of copper, the material exists as one phase, known as the alpha phase. At a composition just below 62 per cent of copper, two phases exist, known as alpha plus beta. The properties of the alpha, or monophase, brass on the one hand and the alpha-beta, or duplex structure, brass on the other are very widely different, even though the difference in copper content is only sufficient to throw the material from one side of the line to the other. Fig. 4 (Plate A) shows a piece of alpha brass which has been polished and then etched with dilute acid. Under the microscope this material looks like a pure metal. The colour variations are due to the difference in orientation of the crystals, but there is only one phase present. Fig. 5 (Plate A) shows the structure of an alpha-beta brass, and here there are two distinct phases present. The significance of a small change in the copper content when the alloys contain about 62 per cent of copper is due to variation in behaviour of these two types of structure. An alpha-beta structure is readily hot worked whereas a monophase structure is not so easily hot worked. Duplex structure brass is used, therefore, for hot pressings, etc. In addition to the differences in mechanical properties, there is a very significant difference in the corrosion resistance of these two types of brass and it is that difference which is one of the things to be considered in this paper.

In 1910, the Institute of Metals set up a Corrosion Committee with the prime object of investigating the corrosion of marine condenser tubes, and considerable work was done by Bengough and his collaborators in an attempt to explain the mechanism of dezincification and a means of preventing it. The investigators came to the conclusion that the copper and zinc were simultaneously dissolved from the surface of the tube, and that by a series of electrochemical reactions the copper

was redeposited *in situ* as a porous, spongy mass. In the Seventh Report of the Corrosion Committee published in 1924<sup>(9)</sup>, Bengough and May reported the results of some tests which they had carried out on the effect of adding various constituents to a 70/30 brass. The tests had shown that the inclusion of a very small quantity of arsenic in the brass inhibited it against dezincification. The brass containing no arsenic was attacked by dezincification. The inclusion of 0.01 per cent of arsenic reduced the severity of the attack, and with 0.02 per cent of arsenic the attack was completely stifled. With this small quantity of arsenic, i.e. one part in five thousand parts of alloy, this difference can certainly be described as of apparently minor significance, and yet the difference in corrosion resistance of these two alloys is such that under some conditions one is corroded at an extremely rapid rate and the other is not corroded at all. In addition to arsenic, other elements also have an inhibiting effect, namely, antimony and phosphorus, but these are not so satisfactory as arsenic in this respect.

This discovery solved the problem as far as alpha brasses were concerned. With the duplex structure alpha-beta brass, however, the addition of arsenic was not effective in preventing dezincification, and even today there is no known inhibitor which, when added to a duplex alloy, prevents attack by dezincification. A duplex brass which has been attacked by dezincification is shown in Fig. 6 (Plate A). It can be clearly seen that this attack is preferential to the beta phase, with the islands of alpha as yet unattacked.

Nowadays, tube makers in Britain usually inhibit their monophase brass tubes with arsenic, and tubes complying with British Standard Specification 378 are required to contain not less than 0.02 per cent and not more than 0.06 per cent of arsenic. Throughout the world there is now relatively little uninhibited brass produced. There are, however, some places in America where it is claimed that they obtain better results with an uninhibited tube but, generally speaking, tube users prefer to have a material which is immune from dezincification.

Another type of corrosion which must be mentioned, in view of its importance, is corrosion erosion or impingement attack. It is not proposed to go into very great detail on this topic as it has been covered so ably by so many other people. It was, of course, this type of corrosion that interfered in no small measure with the operation of His Majesty's ships during the first World War<sup>(10)</sup>. This disease was recognized and was called "condenseritis", and is frequently referred to in all the classic books dealing with naval operations during the first World War, and even those dealing with the overall strategy.

Following the first World War this matter was vigorously investigated by a Corrosion Committee of the Institute of Metals and it was soon realized that the corrosion resistance of a metal was to a large extent dependent on the surface film formed. Without going into further detail at this stage, the outcome of this investigation was the development of aluminium-brass in which 2 per cent of aluminium was incorporated, and this was found to provide corrosion resisting properties which had never been seen before in non-ferrous tubes. It is interesting to recall that the early work with aluminium-brass tubes took place in 1928, which was after the influence of arsenic as an inhibitor against dezincification had been discovered, although its use was by no means general at this time. Some of the early aluminium-brass tubes were, therefore, non-arsenic and did not behave as well as they might otherwise have done.

This type of corrosion resistance involves a change in composition which is probably rather more than can be classified as minor. The main point is that 2 per cent of aluminium has been added to the brass, but in addition to this a change in the copper content has also had to be made. You will remember from the equilibrium diagram that there was a sharp difference between the alpha and the alpha-beta brasses at a particular copper content. Aluminium has the effect of behaving in the same manner as approximately 6 per cent of



FIG. 1—70/30 brass tube (arsenic-free) attacked by layer type dezincification

Uniform attack has developed from the inside surface, giving the appearance of a copper lined brass tube. The attack has penetrated approximately halfway through the wall of the tube. The tube shown was  $\frac{3}{4}$ -in. outside diameter  $\times$  18 WG.

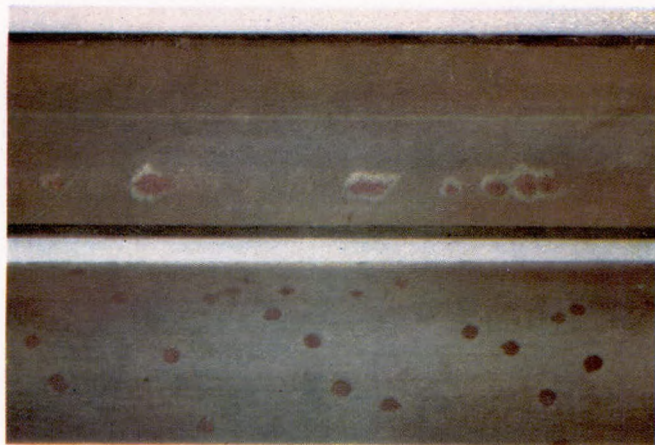


FIG. 2—Aluminum-brass tube (arsenic-free) attacked by plug type dezincification

The main body of the tube is free from attack by corrosion, but a number of small plugs of dezincification have developed from both the outside and inside surfaces of the tube. The plugs of porous copper completely penetrate the tube wall and will tend to fall out in service, resulting in perforation of the tube. The upper photograph is of the inside surface and the lower photograph is of the outside surface of a  $\frac{3}{4}$ -in. outside diameter  $\times$  18 WG tube.



FIG. 4—Photomicrograph showing the structure of alpha brass

A specimen of wrought 70/30 brass polished and etched to show the crystal structure. The material exists as a homogeneous alpha brass. Colour differences between groups of crystals are due to the different orientation of the crystals of the alloy.

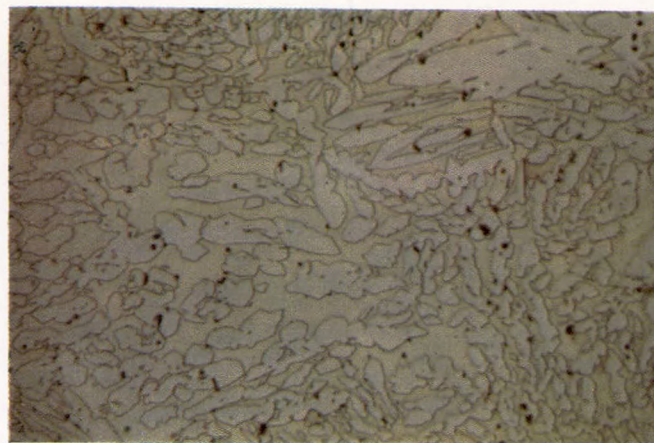


FIG. 5—Photomicrograph showing structure of a duplex brass

Specimens of wrought leaded 60/40 brass polished and etched to show the crystal structure. The two phases (alpha and beta) existing in this alloy can be distinguished on the photograph, the darker background showing the beta phase with islands of lighter coloured alpha phase embedded in it.

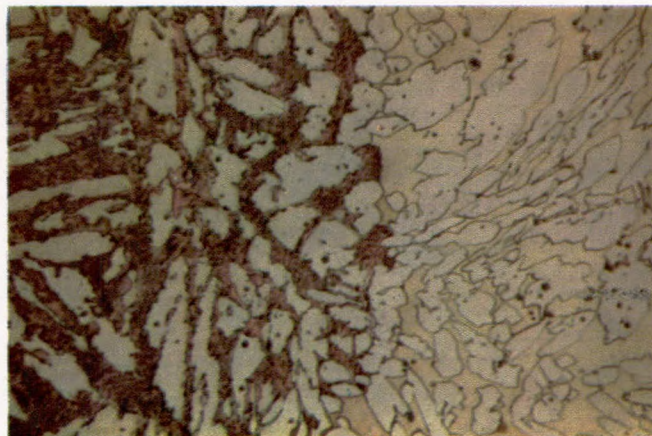


FIG. 6—Duplex structure brass attacked by dezincification

The specimen of duplex brass shown here is at a point where the alloy has been attacked by dezincification. The beta phase has been attacked and has been replaced by a mass of spongy, porous copper. The alpha has remained unattacked at this stage, and in the photograph the islands of unattacked beta alpha can be seen surrounded by the dezincified beta phase.



FIG. 7—70/30 brass generally attacked by corrosion erosion

The characteristic horseshoe shaped pits can be seen, all pointing in the same direction. The flow of water through the tube was from the left-hand side of the photograph, i.e. in the direction indicated by the open ends of the horseshoes. The original tube was  $\frac{3}{4}$ -in. outside diameter  $\times$  18 WG.

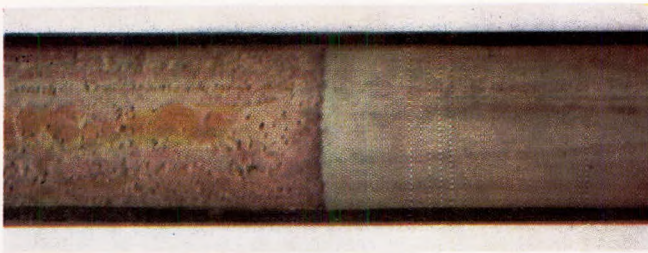


FIG. 8— $\frac{3}{4}$ -in. outside diameter  $\times$  18 W.G. aluminium brass tube after twenty years' service in a passenger liner

On the left-hand side of the photograph the tube is shown in the service condition, covered with a brown film. This film has been removed by acid cleaning over half the length of the tube to show the underlying metal surface, which is smooth and free from corrosion.

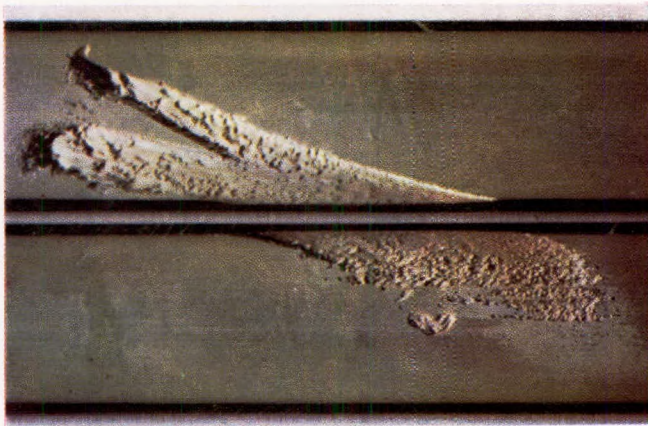


FIG. 9—A service failure due to an obstruction

Intense local attack has developed on the inside surface of the aluminium brass condenser tube. The bore of the tube has become partially blocked by the presence of a foreign body, thus increasing the local speed and turbulence at this point. The excessive turbulence created is sufficient to break down the protective oxide film, and rapid impingement attack develops in the violently turbulent area.

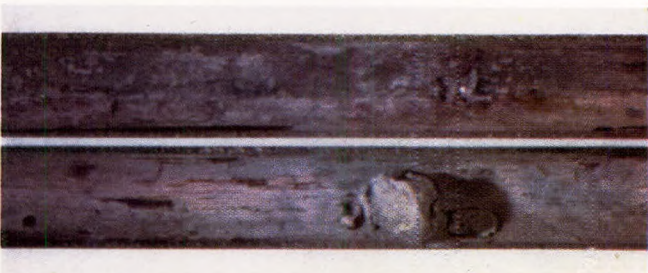


FIG. 10—Service failure due to an obstruction, with the obstruction in position

A failed tube which was sent for examination. On splitting the tube the partial obstruction, a small piece of pebble, was still in position in the tube. Severe local attack has developed on the surface of the tube, and the perforation can be seen in the opposite half section to that containing the pebble.

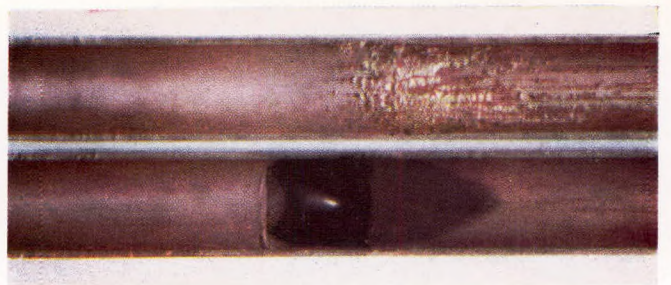


FIG. 12—Brass tube containing artificial obstruction

A laboratory experiment in which an ebonite obstruction of special shape and size was secured in the bore of a condenser tube. Aerated sea water was pumped through the tube at a known speed. The photograph shows the intense local attack which has developed immediately downstream of the obstruction, and the characteristic horseshoe shaped pits can be seen.

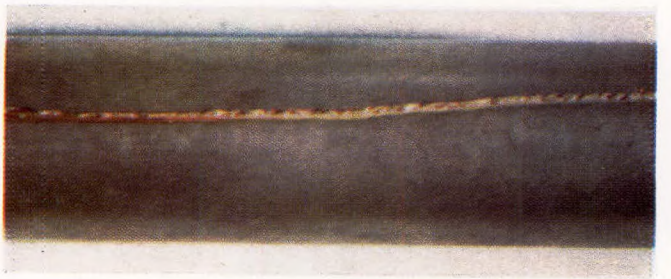


FIG. 13—Season cracked tube

Service failure due to unbalance stresses in the tube wall introduced during the manufacturing process. A typical longitudinal crack has been produced which completely penetrates the tube wall.

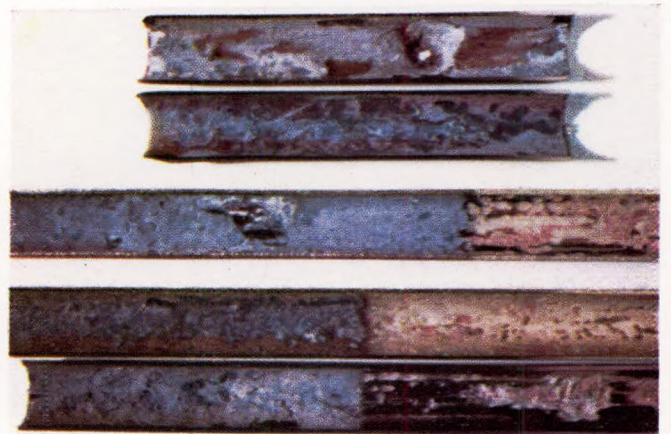


FIG. 24—Service failure by pitting attack

Examples of failed tubes which have failed due to severe pitting attack, the attack possibly being due to the condition of the tube prior to installation, as referred to in the previous illustration. The pieces shown are all half sections and the right-hand ends of the lower three have been acid cleaned.

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zinc, so that if 2 per cent of aluminium is added it is necessary to use a higher copper content in order to balance the apparently higher zinc content and still preserve an alpha brass. For this reason the final composition of an aluminium-brass is 76 per cent copper, 2 per cent aluminium and the remainder zinc.

In these days impingement attack, or corrosion erosion, is almost a thing of the past, but Fig. 7 (Plate A) illustrates a piece of brass tube which has been attacked in this way. One important characteristic to be noted in this case is the horseshoe shaped pits, and these always indicate the direction of flow of the water. It is just the same as when a receding tide flows round a pebble on the beach, the points of the horseshoe pointing in the direction of the flow of the water.

For comparison purposes, Fig. 8 (Plate B) shows a portion of an aluminium-brass condenser tube which was fitted in a ship over twenty years ago and which, until its removal, was in continuous service during that period. To all intents and purposes this tube is in as good a condition as the day on which it was installed. In actual fact, to be strictly accurate, the tube is better than when it was installed because it has developed to the full the optimum corrosion resistance which depends on film formation.

To come to another point in the consideration of this problem, which is really not concerned with composition. The problem of impingement attack was solved by the introduction of aluminium-brass tubes, and also, incidentally, cupro-nickel tubes, at about the same time. There were, however, a number of cases where isolated tubes suddenly developed extremely local areas of attack. This caused very much concern and conjecture at the time, and Fig. 9 (Plate B) shows a typical area of corrosion. The attacked area might occur anywhere throughout the length of a tube, and the whole of the remainder of the tube would be free from attack. This type of trouble usually occurred only on a small number of tubes. Careful comparison of analysis, mechanical condition and every other factor showed that these tubes were in every way similar to the tubes which were not attacked, and any tests carried out on portions cut from the tubes showed them to be perfectly normal in every way. The attack might lead to failure in a matter of only two to three weeks, and after the condenser had been running for several weeks or months it was unlikely that further trouble would arise. Eventually, it was realized that this local form of attack was due to partial obstructions in the bore of the tube. In many cases, the obstruction, or partial obstruction, causing the excessive local turbulence was still present in the tube at the time failure occurred. Fig. 10 (Plate B) shows a tube where this attack had developed and where the stoppage was still lodged in the bore of the tube when removed for examination.

The reason for this apparent very great difference in behaviour of tubes, therefore, was quite simply explained. It was nothing to do with the difference in tubes at all but merely to the difference in service conditions resulting from a pebble, a mussel, a bit of twig, a piece of coke, or some other obstacle lodging part-way down a tube. This type of minor difference arising in service, whether due to an actual service condition or due to design, is typical of a large number of factors, some of which are referred to later.

Fig. 11 illustrates the effect of a partial obstruction. Sea

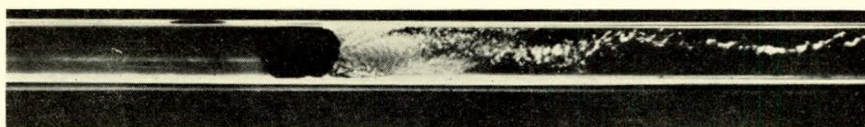


FIG. 11—Obstruction in glass tube

Aerated water passed through a glass tube containing a partial obstruction can be seen. Due to the turbulence of the water at the obstruction the large air bubbles are broken up into a large number of very small bubbles which bombard the tube at high velocity in the area of the obstruction and downstream for a short distance.

water is being pumped through glass tubes in which there is a partial obstruction. Approximately 3 per cent of air is added to the water, and the average speed through the glass tube in question was approximately 2ft. or 3ft. per sec. The intense turbulence immediately behind the obstruction can be seen and it is interesting, on the actual test apparatus, to listen with a stethoscope to the tube, when the violent bombardment by the air bubbles, which give rise to impingement attack, can be distinctly heard, and anyone who has seen a test of this kind carried out can no longer have any doubts as to the very severe nature of the conditions at these points.

Fig. 12 (Plate B) shows the result at a partial obstruction which has been produced artificially in the laboratory on a piece of aluminium brass tube. The very sharp and local nature of the attack is easily seen, and a careful examination shows some horseshoe shaped pits indicating the direction of flow. It is interesting to note in passing that the resistance to attack of alloys such as aluminium brass and the cupro-nickel alloys is now generally accepted as being due to the development on the surface of these alloys of a tough oxide, or hydrated oxide, film, and that these films achieve their optimum strength after some few days' exposure to moving sea water. If, therefore, areas of local turbulence arise in the very early life of a condenser tube, it is much more likely to be corroded than is the case if the obstruction becomes lodged after several months' service. With any alloy, however, a very bad case due to this type of obstruction could cause trouble even after a very long period of service.

We must now make a very brief reference to the influence of relatively small changes in composition in the case of the cupro-nickel alloys, which have been used since the early 'twenties. These were, initially, the 85/15 or 80/20 copper nickel type, and although they had some advantages they were far from being the complete answer. Later in the 'twenties the use of a higher nickel content alloy, namely 70/30 copper nickel, was tried and here again the results were promising but not entirely satisfactory. It was not for some considerable time that it was realized that, although the alloy was essentially a copper and nickel alloy, the presence of other elements made a remarkable difference to its corrosion resisting properties. These other elements were iron and manganese. This story is one of those referred to in which it would have been interesting to have gone into more detail; it is also a case where the practice in this country was years ahead of that anywhere else in the world, and some of the "behind the scenes" stories of developments during the late 'twenties and early 'thirties in connexion with this matter are an absorbing story. However, the fact is that the corrosion resisting properties of a pure 70/30 cupro-nickel are very much inferior to an alloy containing the same amount of nickel but with an addition of approximately 0.75 per cent each of iron and manganese. These amounts of iron and manganese convey film forming properties to the alloy which enable it to resist impingement attack. By 1933, further development had shown that an even higher addition of iron and manganese conferred on the alloy a remarkable resistance to abrasion, and the use of a 30 per cent nickel alloy with approximately 2 per cent each of iron and manganese proved to be the only satisfactory answer for condenser tubes at a number of generating stations which were built in situations where there was excessive solid matter carried in the cooling

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water. Two cases in particular were on the Bristol Channel and the River Mersey, where large quantities of sharp, heavy particles of sand are carried in the cooling water. These heavy particles shot-blast away the normal protective film which forms and ordinary cupro-nickel and aluminium-brass.

Whilst on the subject of cupro-nickel alloys and the very great significance of apparently minor changes in composition, reference should be made to the history of cupro-nickels since the early 'thirties. As already mentioned, the addition of iron to cupro-nickel was understood and practised in this country well before the last war. In other parts of the world the idea of deliberately adding iron to a cupro-nickel was not regarded with favour or as being necessary. The result was that in most other countries the behaviour of cupro-nickel alloys was not so good as that of British-made tubes. When the use of iron-bearing cupro-nickels had become standard practice here, it was a natural development to see if the same result would be obtained with a lower nickel-content alloy. As a result of this the 90/10 cupro-nickel alloy was tested with varying additions of iron and manganese and it was found that these additions did improve the resistance to impingement attack. During the early days of the war this latest information was passed to America and tests were made with the 90/10 cupro-nickel alloy. At that time the American 70/30 cupro-nickel did not contain sufficient iron and manganese to give the optimum corrosion resistance. When, therefore, a lower nickel content alloy came along which, from the outset, had the optimum addition of iron and manganese, it compared very favourably with the higher nickel content alloy then in use, which was more expensive. This is basically the reason for the great surge of preference for the 90/10 cupro-nickel alloy which has swept America in recent years. 90/10 cupro-nickel alloys containing iron and manganese have been used in this country

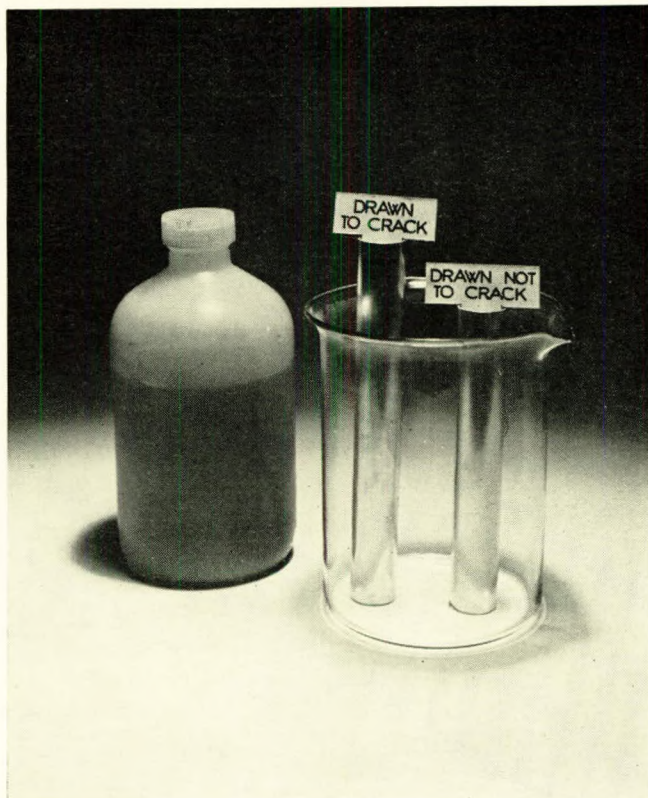


FIG. 14—Season cracking test (a) before immersion of specimens  
Two portions of the same, original tube, drawn by different drawing methods, are ready for immersion in 10 per cent mercurous nitrate solution.

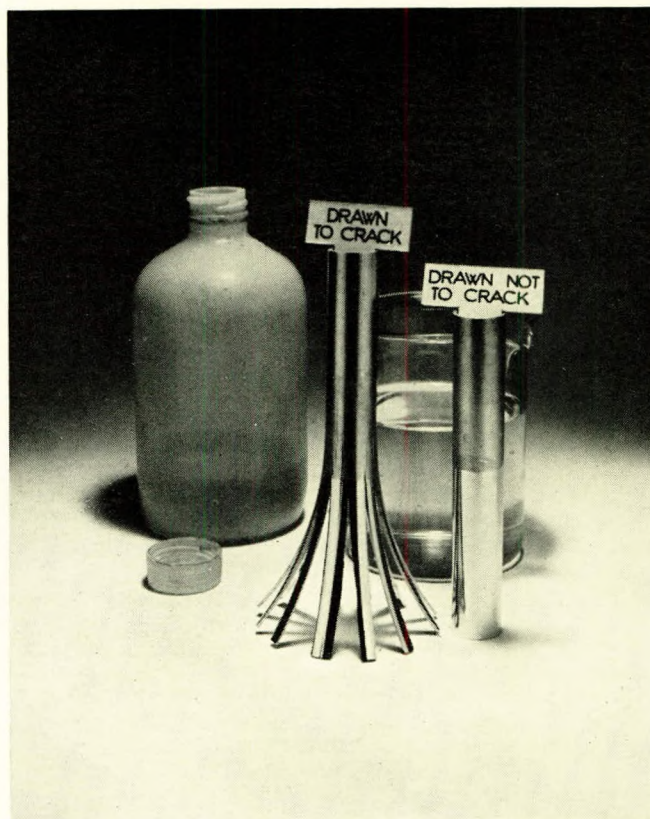


FIG. 15—Season cracking test (b) after immersion of specimens

After fifteen minutes' immersion in the solution the specimens are withdrawn. Each specimen has a layer of mercury deposited on the surface which acts as a rapid stress corrosion agent. The tube drawn to crack has failed by stress corrosion, resulting in numerous longitudinal cracks. The tube wall has also belled out due to the relief of the unbalanced compressive stresses. The tube drawn by normal methods has remained free from cracks.

for a very long time, in fact, since the 'thirties for some types of plant, but the authors do not consider this alloy at its best to be as good as the 70/30 cupro-nickel alloy at its best. This is another illustration of the importance of apparently minor factors, and in this particular instance the result has had almost international complications.

Up to now the matters referred to have been mainly variations in alloy composition. The behaviour of a tube in service does, however, depend on many other factors besides composition. Some of these points are very obvious and others not so obvious. One of the earliest and most obvious manufacturing shortcomings which was revealed in tubes, not only in ships' condensers but in other types of plant, was the question of season cracking. This type of failure was liable to occur suddenly without warning, and resulted in a substantial longitudinal crack appearing in the tube wall. This crack might extend only a few inches or from one end to the other of the particular tube concerned. A tube so attacked is shown in Fig. 13 (Plate B). It was soon established that this form of cracking was really a special case of stress corrosion cracking in which the stress was an unbalanced stress put in the tube as a result of an incorrect method of manufacture.

The undesirable stresses which may be present in a tube arise as a result of the methods of drawing; the type of drawing, and the reduction in size and thickness, etc., are all concerned. In order to illustrate the remarkable difference that merely the method of drawing can make, two pieces of tube which were originally part of the same tube were cut into two pieces and then drawn to finished size by two different

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drawing methods. The composition was, therefore, identical in both cases.

There is a very good test which illustrates when a tube is liable to fail by season cracking, in which the tube is immersed in a dilute solution of mercurous nitrate. The mercury liberated by chemical interchange on the surface of the brass tube acts as a very rapid stress corrosion agent and a tube which is liable to fail after a prolonged period in service can be cracked by a period of only a few minutes in this solution. Figs. 14 and 15 show tubes before testing and again after a period of only fifteen minutes in this solution. The correctly drawn tube has developed no cracks, but the one containing unbalanced stresses is very badly cracked and has been distorted by the stress.

Although the question of season cracking is a very important factor, the causes and cures are well understood and it is now largely a thing of the past, but there are still other factors where the effect of methods of manufacture can be very great indeed.

Most of the factors already referred to have been well known and covered to some extent in other papers. This next example is a matter which, so far as the authors are aware, has not previously been referred to. A few years ago they were investigating a few cases where rapid failure of condenser tubes took place under conditions where they would not normally have expected such rapid failure. After very careful investigation a peculiarity was observed which was present in all these

tubes, which could be attributed to a method of manufacture, and they accordingly started some laboratory experiments to test the proof of this observation. In giving the result of this laboratory test, it should be mentioned that there have been one or two other recent cases where practical experience has given further support to this theory. In order to eliminate as far as possible all variables except the one to be tested, they started with a single furnace melt of aluminium-brass and cast this in the usual way into a solid billet which was then extruded in the normal way into what is called shells. These various extruded shells were obviously all of the same composition, having all come from the same charge. The batch was then divided into four groups which were processed down to finished tubes by four different methods of manufacture. One group was run down in the ordinary way to give a control run. The second group was run down in a manner which would give a rather finer grain size than usual, the third group was finished by a method which would result in a very heterogeneous grain size, and the fourth group was run down to exhibit the peculiarities which they suspected might be important. The different grain sizes were included because in some quarters it has been suggested that grain size has an important bearing on corrosion results. When these tubes had been finished and inspected they were installed in a test condenser through which an estuarine water was pumped. After installation, the tubes were tested by the Probolog, which is an electronic instrument giving a trace indicating the condition of the tube. These traces are recorded on a strip of paper 2½ inches wide. Fig. 16 is a photograph of the charts of the nine tubes made in a normal manner. It will be seen that each trace is a straight line, as one would expect from a new tube. The bottom right-hand trace is of a standard tube containing artificial defects, which

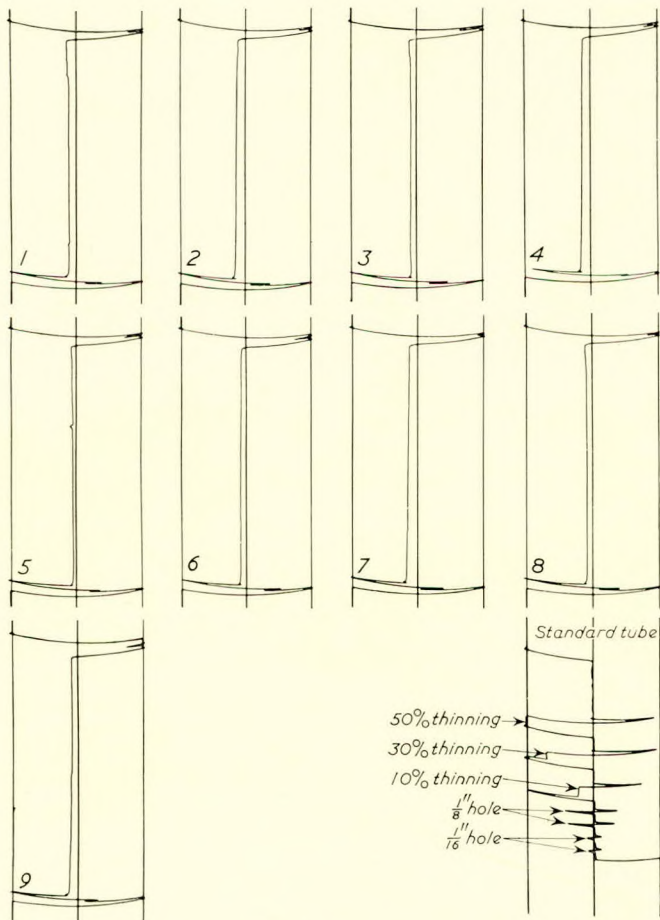


FIG. 16

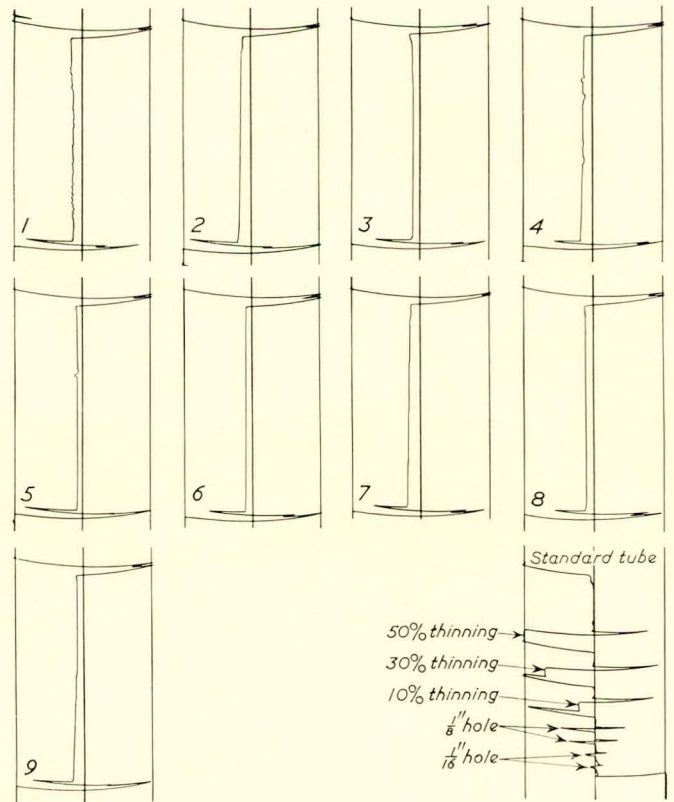


FIG. 17

FIGS. 16 (original) and 17 (after service)—Probolog charts of aluminium brass tubes drawn in the normal manner

The traces obtained for the nine tubes are shown prior to going into service, and after six months' service. It will be seen that there is little difference in the two sets of traces and that after six months' service these tubes are free from attack by corrosion.

## Significance of Apparently Minor Factors in Corrosion Problems

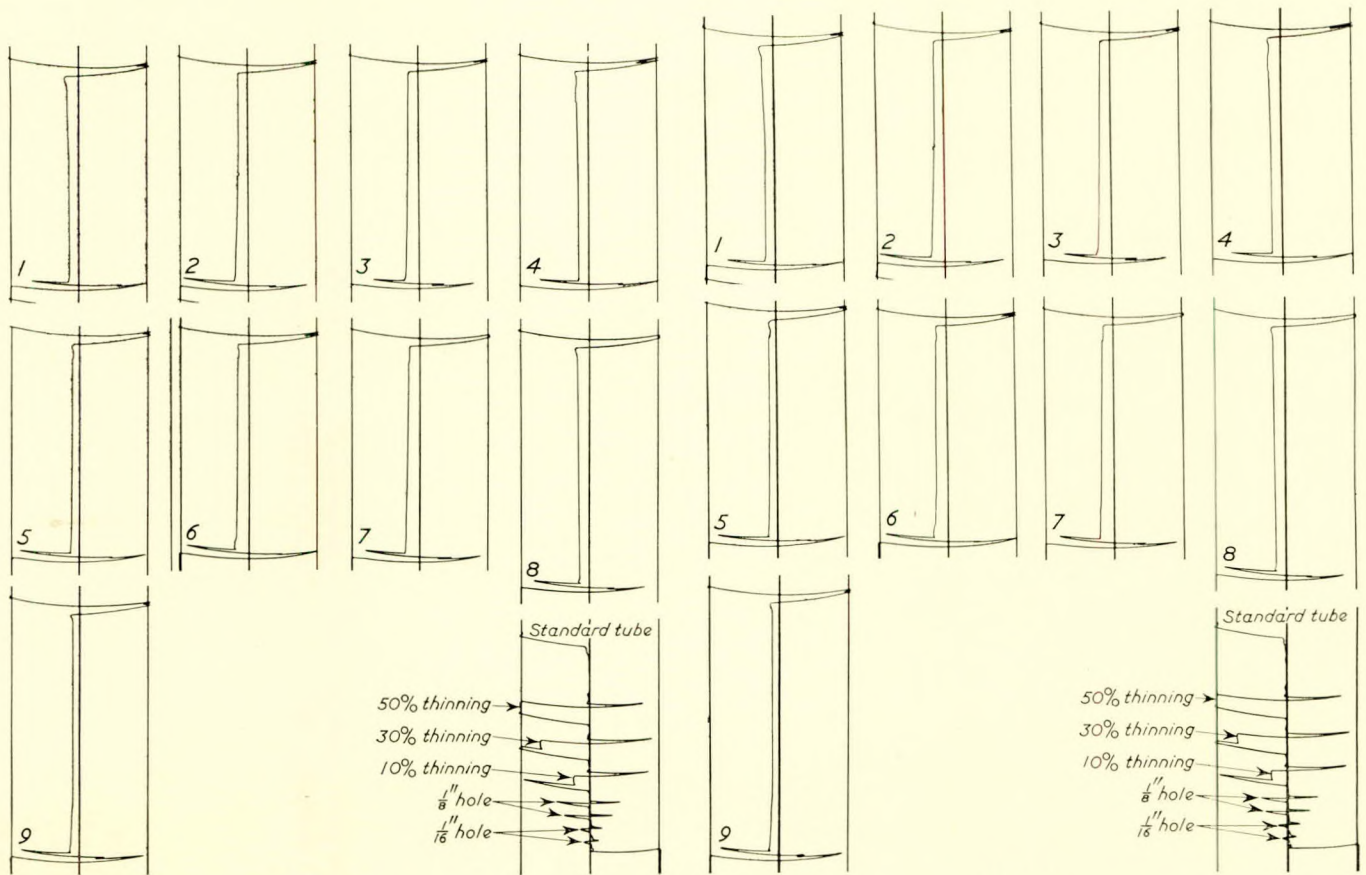


FIG. 18

FIG. 19

FIGS. 18 (original) and 19 (after service)—Probolog charts of aluminium brass tubes with a very fine grain structure

It will be seen that the two sets of traces are very similar in appearance and that no deterioration of the tubes has taken place during the six months' service.

is always included to calibrate the instrument and provide a check on the zero and amplification settings.

After the tests had been running for approximately six months the tubes were again examined by the Probolog. Fig. 17 shows the Probolog charts of the nine tubes made in a normal manner at the end of the test run. It will be seen that the traces are still essentially straight lines on the same standard setting of the instrument.

The particularly fine grain size tubes, before the test, are shown in Fig. 18, and after the test run in Fig. 19. Again, no corrosion of any consequence has taken place.

Fig. 20 shows the heterogeneous grain size tubes before the test, and Fig. 21 shows the traces given by the tubes after test, and again there has not been any corrosion.

Fig. 22 shows the fourth set of tubes before the test. The traces are all straight lines, but it will be noticed that they are displaced a little to the right of the centre line as they come from the machine. This indicates a slightly greater average thickness than the standard tube. The condition of the tubes after test is shown in Fig. 23 and it can be seen that corrosion has taken place throughout the length of all these tubes. The irregular nature of the trace indicates a general pitting type of attack, but it will also be noticed that the average centre line of the trace is displaced to the left, indicating a removal of metal sufficient to give the effect of a general thinning operation.

Fig. 24 (Plate B) is a colour photograph of a service failure due, it is thought, to this cause. The right-hand end of some of the pieces have been cleaned.

The small difference illustrated in this particular experiment is, as explained, nothing to do with the composition, micro-structure or hardness of the tubes. It is merely a surface phenomenon. The authors are at the present time trying to understand more about this although sufficient has already been learned to make them certain beyond any doubt that the final finishing operations from the last draw onwards are extremely important and that steps must be taken to ensure that the surface condition is entirely satisfactory. This particular type of apparently minor factor is of very great significance to all users of tubes as it is one which is not easily recognized as being of importance, and of which many tube makers are apparently unaware. It undoubtedly accounts for some of the very wide differences in behaviour which are sometimes reported of tubes of the same alloy made by two different makers.

There is a very similar case which has occurred in the ordinary domestic copper housing tubes supplied for water service pipes. A few years ago there was a very large number of rapid failures of some of these tubes when used with certain waters. These were particularly bore hole waters and the water from different districts behaved very differently in this respect. In some parts of the country copper tubes were liable to fail in a matter of eleven weeks although in the same district, and in some cases in the same building, other copper tubes had been in service for many years without any trouble. This also was a case in which different manufacturers' tubes behaved very differently, and eventually, as a result of some very sound work by The British Non-Ferrous Metals Research Association, it



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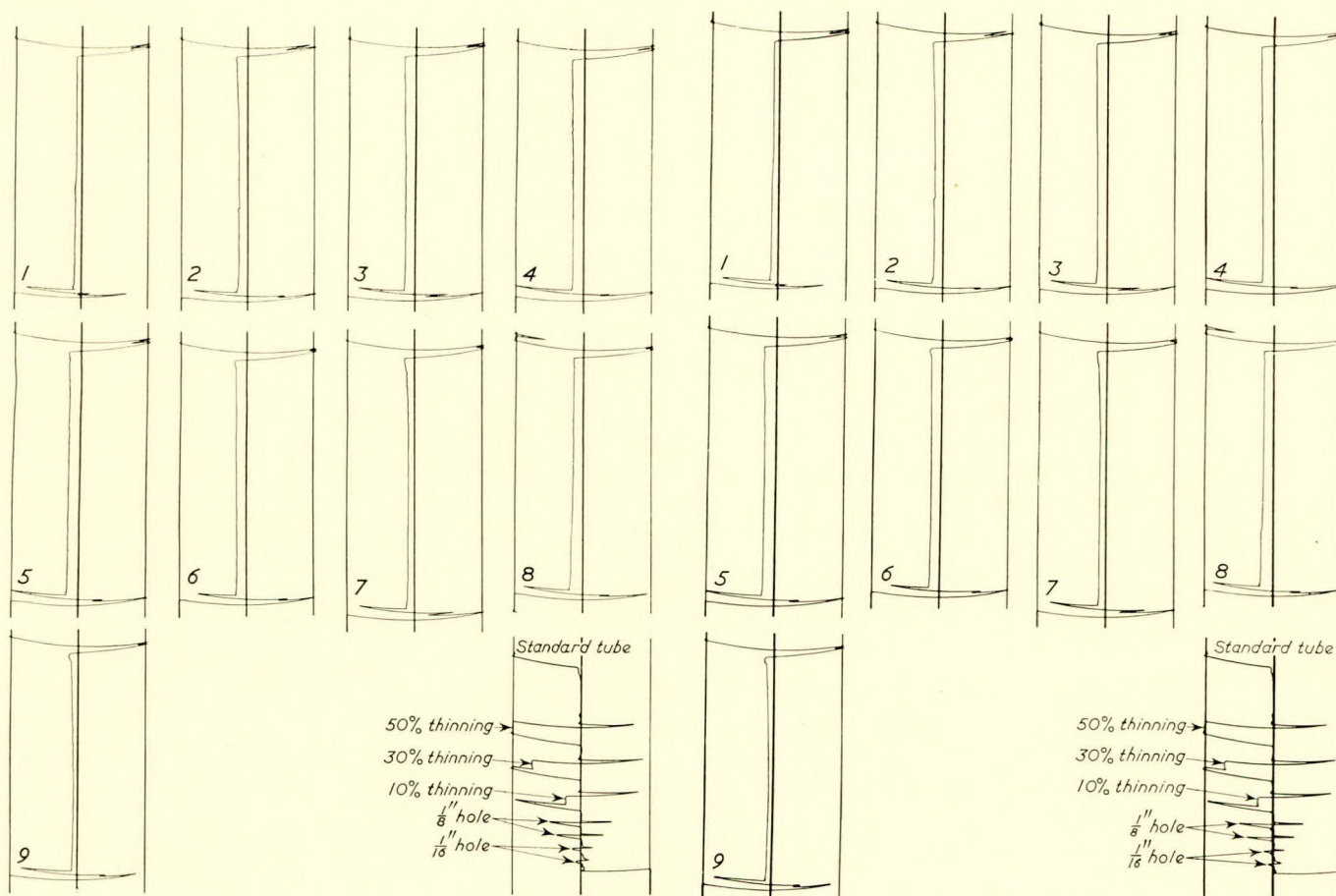


FIG. 20

FIG. 21

FIGS. 20 and 21—Probolog charts of aluminium brass tubes drawn with heterogeneous grain structure

Two sets of traces obtained are very similar in appearance and no corrosion has taken place during the six months' service.

was found that the type of tube which caused trouble did so not because of any particular composition or grain structure so much as the surface condition of the tubes. For example, if the tube was supplied with a cathodic film present on the inside due to the decomposition of the drawing oil in a bright annealing furnace, then, with these particular types of water, rapid pitting of the tubes took place.

Finally, a very brief reference should be made to the influence on the behaviour of non-ferrous tubes of design and operation of plant.

This particular aspect is one which, in their opinion as tube makers, is at least as important as any of the other matters already referred to. It is one which gives tremendous scope for improvement, particularly in the case of heat exchangers, evaporators, and the like, and very many cases of corrosion in these plants could be eliminated, and in many cases have been eliminated, by very slight modifications in design or operating conditions. This is a topic on which a full paper could very well be written, but only a few highlights can be mentioned on this occasion.

Figs. 25 and 26 illustrate some results which show how position in the plant can have a very remarkable effect on the behaviour of tubes, even though each tube in a condenser might be thought to be working under the same conditions.

Another of their experimental installations was on board a tug which operated in a very highly polluted water. In this tug the condenser was tubed with tubes of a number of different

alloys which they have examined regularly with the Probolog. Fig. 25 shows the Probolog traces for the ten 70/30 cupronickel tubes installed, and their positions are indicated in the diagram. This shows the conditions after the condenser had been in operation from May 1951 to November 1951 and it will be seen that there is little attack on any of the tubes except for one designated A8, on which there is a very severe area of attack. In November 1951 this single tube was replaced by another of the same alloy which gave a straight line trace on the Probolog. After a further ten months' service all the tubes were again tested by the Probolog and the results are shown in Fig. 26. It will be seen that this replace tube had developed an area of attack in exactly the same position as the previous tube, although the other tubes were not appreciably changed. In fact, it will be noticed that the particular tube A8 is at the top of the condenser and the area of attack is opposite the steam inlet. The engine in this instance is a reciprocating engine with a higher exhaust steam temperature than is usual in the case of a turbine. Their explanation of this corrosion (of which there is other evidence in support) is that the very slow rate of flow of the highly polluted water through the tubes is such that a stagnant layer is formed in contact with the tubes, and in the portions opposite the steam discharge this stagnant layer becomes much warmer than the average temperature in other parts of the condenser. The very great difference in behaviour, for example, between tube A8 and tube A5 shown above it on the diagram is due simply to a very

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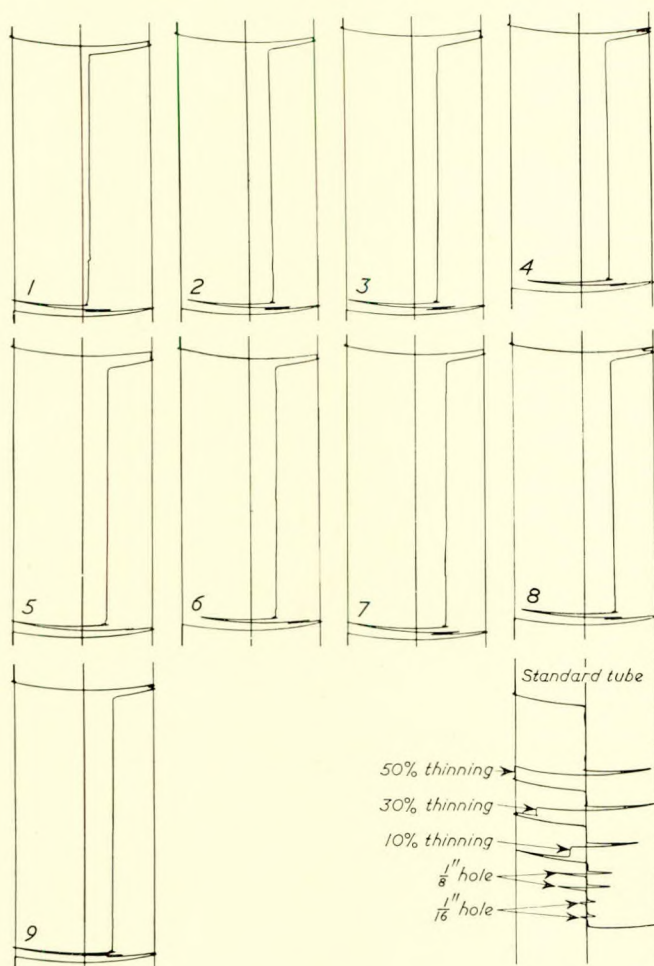


FIG. 22

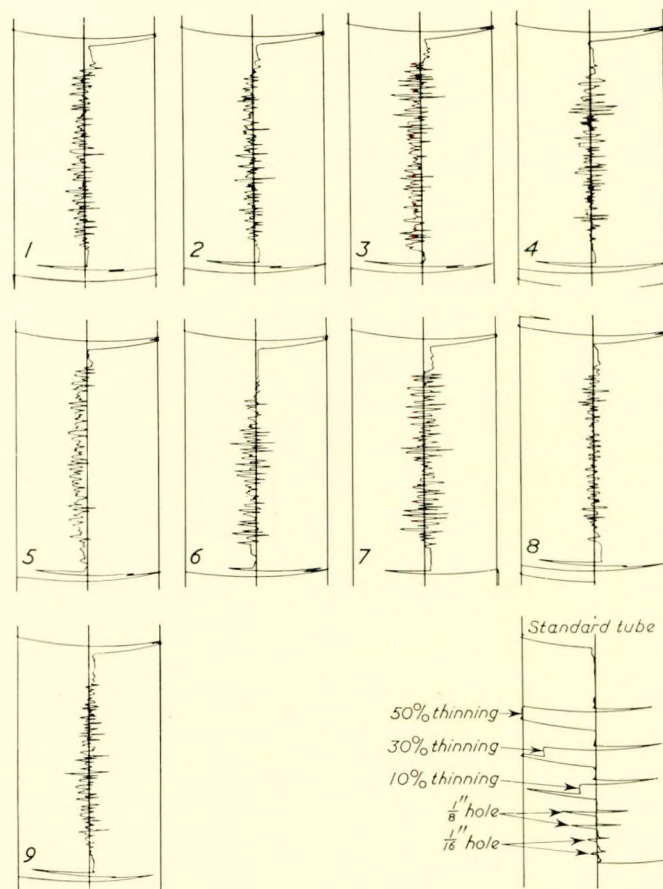


FIG. 23

FIGS. 22 (original) and 23 (after service)—Probolog charts of aluminium brass tubes made in special manner

It will be seen that there is a significant difference in the two sets of traces obtained. Before going into service each tube gave a straight line trace but after six months' service the traces have generally moved to the left, indicating general thinning, the number of small deflexions on each chart showing that pitting corrosion has taken place.

slight difference in surface temperature of the portion of the tube in contact with the cooling water. This example could be multiplied by other, similar cases, and to give a final example of an apparently minor factor they would like to mention briefly an entirely different type of corrosion, namely that due to incondensable gas attack.

When steam is being condensed in an evaporator, feed water heater, or even a condenser, the incondensable gases present in the steam are not usually readily dissolved in the steam at the condensation temperature. They do, however, particularly in the case of gases such as ammonia, readily dissolve in the condensate when it has been cooled a little below that temperature at which it actually condenses. If the plant is not designed so that all the vapour space is swept by vapour and the tube surfaces washed with condensate, any stagnant area in the plant may act as a sort of pocket in which the incondensable gas content of the vapour gradually increases, and in these circumstances the small amount of condensate which is present may dissolve these gases and form a very corrosive liquid. This type of thing frequently happens in an evaporator where the position and size of the vent is very important. Obviously, if the space which is blanketed by these incondensable gases is vented, not only are the incondensable

gases removed and prevented from doing any harm, but a surface which was not previously available for condensation then becomes available and the efficiency of the plant is thereby increased.

There have been many cases where severe corrosion of non-ferrous tubes due to these incondensable gases has been much reduced or even completely eliminated by simply modifying vents or opening up existing vents. Figs. 27 and 28 show two half sections of tube from a sugar evaporator. In this plant the tubes are fixed vertically. It will be seen that very rapid and locally severe corrosion has taken place where the condensate has hung between the top tube plate and the tubes. The tubes in this plant were 70/30 brass and lasted only one year. The interesting point about this story is that when this problem was investigated the use of some of the cupro-nickel alloys, which are more resistant to this type of attack, was suggested. It was also suggested that the vents which were at that time mid-way down the steam space should be moved to immediately underneath the top tube plate and on the opposite side to the steam inlet to ensure that no stagnant pocket of vapour could form. Cupro-nickel alloy tubes were installed for test along with 70/30 brass tubes, and one year later these were examined when it was found that there was

## Significance of Apparently Minor Factors in Corrosion Problems

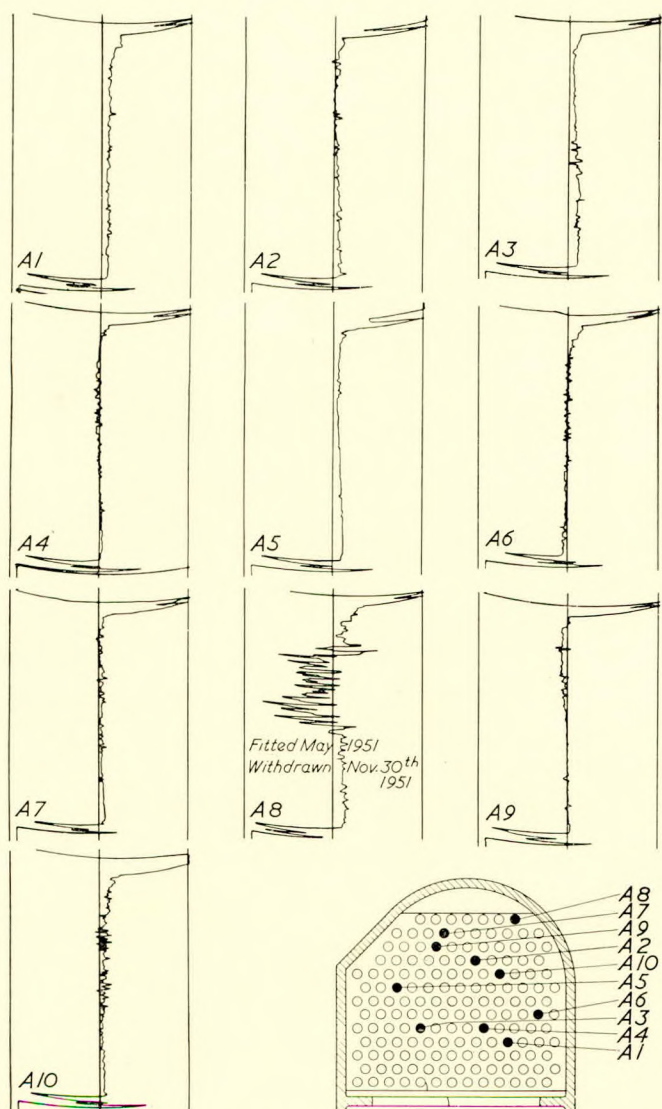


FIG. 25—Probolog charts of 70/30 cupro-nickel tubes installed in coastal tug: first period

The position of each tube in the condenser is shown on the diagram at the bottom right hand side of the photograph. After six months' service, severe attack has taken place on tube A8, the remaining tubes being free from corrosion. Tube A8 was replaced by a new tube of the same alloy after the examination.

no attack at all on the cupro-nickel tubes, nor was there any attack on the 70/30 brass tubes which had been installed at the same time, and which were similar in all respects to the tubes which had earlier been corroded to such an extent that they could not be used for a second year.

### CONCLUSION

The final point to be made is that in order to obtain the maximum service from non-ferrous tubes in any type of plant it is first necessary to select the correct alloy for the job. Secondly, it is essential that this should be fabricated into tubes by makers who are aware of the many pitfalls that may arise and who are very jealous of their reputation for a sound product. Thirdly, the design of the equipment, whether it be a condenser, feed heater, evaporator, or other type of heat

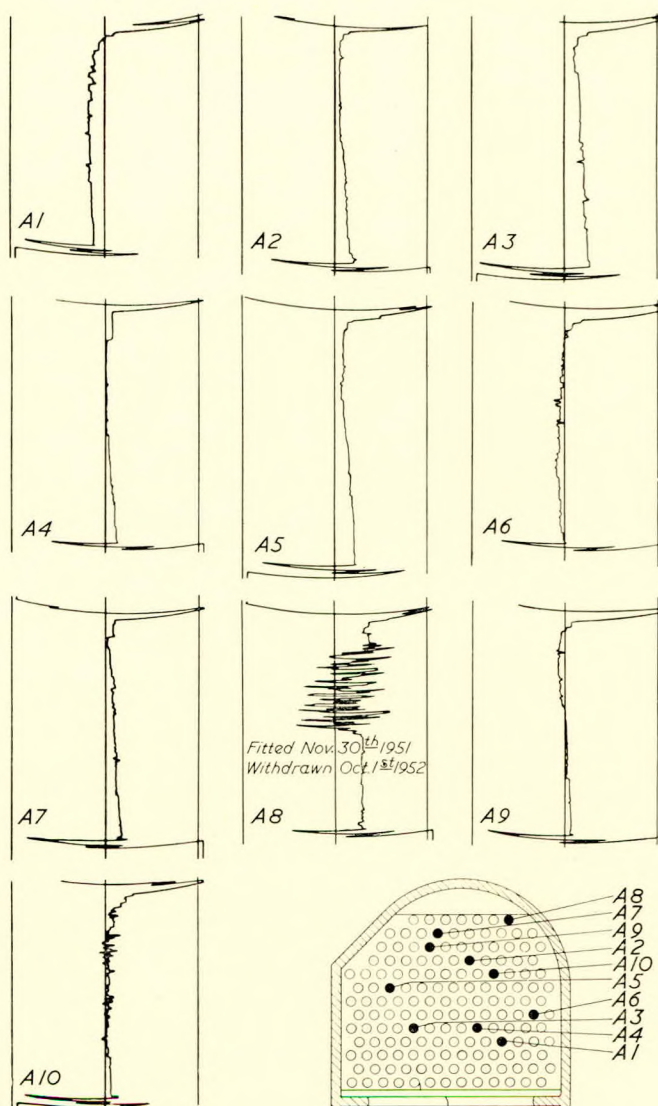


FIG. 26—Probolog charts of 70/30 cupro-nickel tubes installed in coastal tug: second period

Replace tube A8 has been attacked in a similar manner to the original tube A8 after a further ten months' service. The remaining tubes are still relatively free from attack by corrosion.

exchanger, must be carefully considered, and fourthly, the operation of the plant must be properly carried out. It is usual for best results to be obtained only by the combined efforts of metallurgists, fabricators, designers of plant and operators.

In this paper the authors have endeavoured to show that there is at all stages a number of apparently minor factors which can have an important bearing on the results obtained. The examples which have been used are by no means the only ones which could have been used, nor do they claim to be fully aware of all such factors. This is a matter on which a great deal of research has been carried out in the past, and they are sure that a future policy of research into this topic can only result in a better understanding of some of these factors and some of the hitherto unexplained things which have happened.

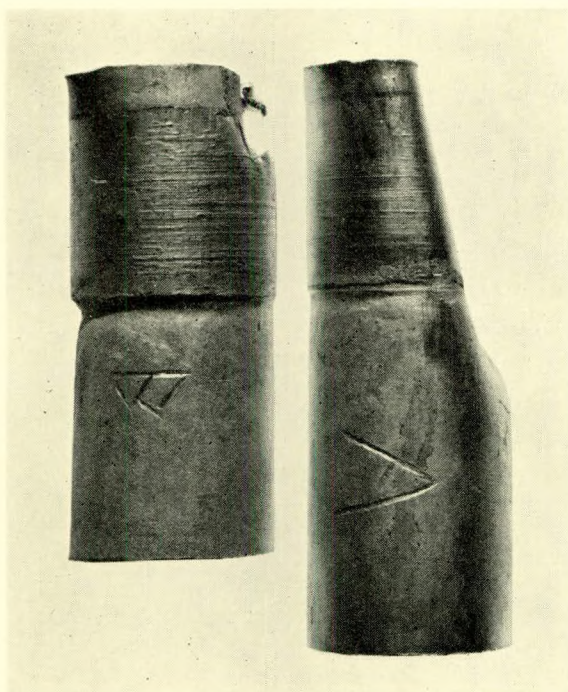


FIG. 27—Brass tube removed from sugar evaporator, outside surface

The photograph shows the severe thinning of the tube wall which has taken place just below the top tube plate due to the attack by incondensable gases. Except for the short distance near the top where corrosion has taken place, the tube wall is of the original thickness and is free from attack by corrosion.

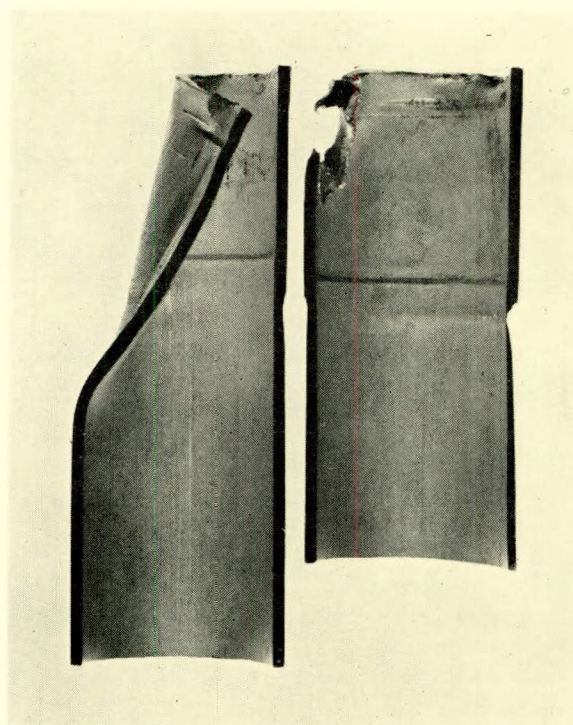


FIG. 28—Brass tube removed from sugar evaporator, inside surface

The photograph shows the severe thinning of the tube wall which has taken place just below the top tube plate due to the attack by incondensable gases. Except for the short distance near the top where corrosion has taken place, the tube wall is of the original thickness and is free from attack by corrosion.

REFERENCES

1. MILTON and LARKE. 1903. "The Decay of Metals". Proc.I.C.E., Vol. 64, p. 138.
2. BRADBURY, E. J., and JOHNSON, L. W. 1951. "Corrosion Resistant Materials". Trans.I.Mar.E., Vol. 63, p. 59.
3. DICKIE, W. H. 1952. "High Power Single Screw Cargo Liners". Trans.I.Mar.E., Vol. 64, p. 167.
4. GILBERT, P. T., and MAY, R. 1950. "Materials for Use in Ships' Condensers and Other Seawater-carrying Systems". Trans.I.Mar.E., Vol. 62, p. 291.
5. GILBERT, P. T. 1954. "The Resistance to Failure of Condenser and Heat Exchanger Tubes in Marine Service". Trans.I.Mar.E., Vol. 66, p. 1.
6. SLATER, I. G., KENWORTHY, L., and MAY, R. 1950. "Corrosion and Related Problems in Sea Water Cooling and Pipe Systems in H.M. Ships". Jnl.Inst.Met., Vol. 77, Part 4, p. 309.
7. ORAM, H. J. 1914. Presidential Address. Jnl.Inst.Met., Vol. 11, p. 38.
8. HOLT, N. G., and CLEMITSON, F. E. 1948. "Notes on the Behaviour of H.M. Ships during the War". Trans. I.Mar.E., Vol. 60, p. 207.
9. BENGOUGH, G. D., and MAY, R. 1924. Seventh Report to the Corrosion Research Committee. Jnl.Inst.Met., Vol. 32, p. 81.
10. JELLICOE. 1919. "The Grand Fleet". Cassell and Co., Ltd.