Dec. 3, 1940. F. M. BARRY 2,224,095

TUBE FOR HEAT EXCHANGING APPARATUS

Filed Feb. 15, 1940

Fig. 1.

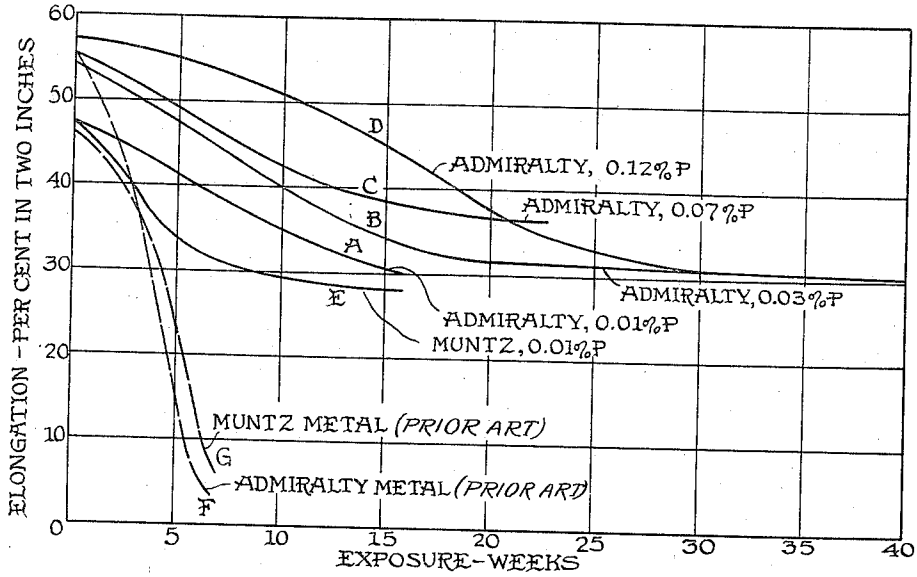
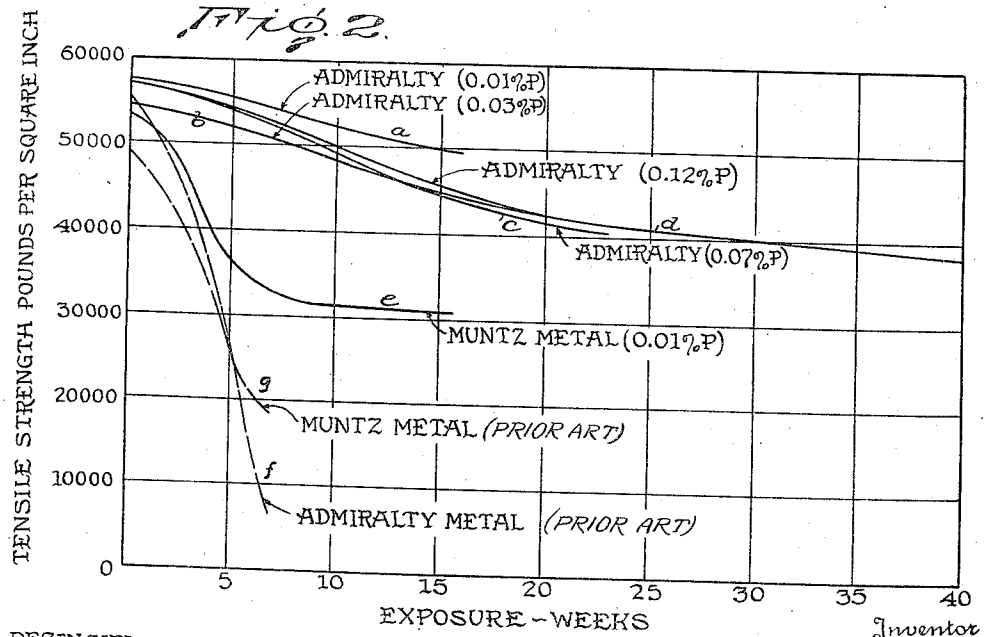


Fig. 2.



DEZINCIFICATION-RESISTANT PHOSPHORIZED ZINC-COPPER ALLOY

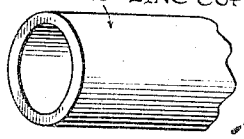


Fig. 3.

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TUBE FOR HEAT EXCHANGING APPARATUS

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Application February 15, 1940, Serial No. 319,158

5 Claims. (Cl. 138—47)

This invention or discovery relates to improvements in tubes for heat exchanging apparatus; and comprises, as an element in condenser systems or the like for use with aqueous fluids in which the solution pressures of copper and zinc are high, a conduit or tube resistant to dezincification and composed of an alloy like admiralty metal containing 0.001 to a maximum of 0.2 per cent phosphorus in uniform distribution through the metal, and the balance substantially all copper and zinc with a small proportion of tin and usually with a small proportion of modifying metals; said tube exhibiting a markedly lower solution pressure in contact with such fluids and being capable of developing a protective film on the surface thereof in contact with moisture, protecting the tube from dezincification; all as more fully hereinafter set forth and as claimed.

Copper-zinc alloys (brasses and bronzes) have found extensive use in conduits for use in heat exchangers, etc., in installations where the use of steel tubes is not feasible. Such alloy tubes give good service with many waters, but in some installations the phenomenon known as dezincification is encountered. A tube which has failed as a result of dezincification exhibits a weak, porous structure, partly or entirely composed of copper, and often showing characteristic lamina.

Dezincification of tubes is associated with waters in which zinc, and to a less extent copper, has an abnormally high solution pressure. In ordinary water zinc exhibits a small solution pressure while that of copper is negligible. But in some aggressive waters the solution pressure of copper and of zinc may be very high, relatively speaking.

Dezincification is that form of brass corrosion which results in the formation of soluble copper and zinc compounds with redeposition of the dissolved copper at corroded areas, and resulting in a loss of zinc. The action may occur locally (plug type dezincification) or over broad surfaces (layer type dezincification). As corrosion progresses the tube wall is eventually transformed into a porous, spongy mass of copper, of characteristic appearance. Dezincification is favored by (1) high operating temperature, (2) brackish, acid and other contaminated circulating waters, (3) sluggish or stagnant waters, (4) certain types of permeable scale formations, (5) moisture-contaminated petroleum vapors especially at elevated temperatures. The higher zinc content alloys are the more susceptible of this type of corrosion; those alloys containing less than 15 per cent zinc being essentially free under normal conditions of service.

The durability of brass tubes depends partly on the establishment and maintenance of an inert protective film in contact with water, with of course maintenance of massive non-corroded metal under and supporting the film. The constitution of the film depends on the character of the alloy and of the liquids to which the tube is exposed, and on other things. Often in condenser tubes the film is composed of oxides or hydrated oxides of both the alloyed metals, together with lime, etc., from the water. Hard waters are rarely aggressive to copper-zinc tubes, because of the scale formed thereby on the tubes. Dezincification is in part associated with a breakdown, or non-formation, of a suitable protective film. The same is true of other types of corrosion (concentration-cell action, galvanic type corrosion), etc. but a film which adequately protects brass condenser tubes from certain other types of corrosion may leave the brass wide open to the dezincification type of corrosion.

Dezincification, an end result not developed in other type of corrosion, is of outstanding importance in condenser tubes.

I have discovered that in copper-zinc alloy tubes the solution pressure of the copper and of the zinc can be effectively restrained by the presence of a minimal amount of phosphorus in solid solution therein. Dezincification is inhibited. Tubes of copper-zinc alloys and in particular admiralty metal, which is an alloy of 70 per cent copper, 29 per cent zinc and 1 per cent tin, can be markedly improved as regards resistance to dezincification by incorporation in the alloy of a small proportion of phosphorus. The proportion added is minute, ranging from 0.001 per cent to 0.2 per cent, and is uniformly distributed throughout the metal. A proportion of 0.03 per cent seems to give best results. Tubes made of this alloy in service in contact with moisture under conditions which would ordinarily produce dezincification, develop a thin film containing phosphorus which effectively protects the body of the metal against this type of corrosion. The effect of the added phosphorus is out of all proportions to the amount employed. Incidentally, the new alloys are characterized by a finer grain structure upon annealing which is reflected by an enhanced surface smoothness. This is an additional factor in prolonging the life of the tubes.

In the tubes of the present invention, dezincification is practically obviated though the general

corrosion resistance of the tube is not markedly different from that of tubes of similar alloys but containing no phosphorus. On the other hand there are some substances which if added to admiralty metal for condenser tubes suppress dezincification well enough, but accentuate corrosion at the grain boundaries of the alloys, so that the tubes are apt to fail sooner than ordinary tubes even though no appreciable dezincification take place. In general considerations regarding corrosion of brasses as ordinarily understood are of no help in determining the dezincification resistance of the brass. While any substantial amount of phosphorus is not regarded with favor in brasses and bronzes, except in those intended for special purposes (such as springs, for example), I find that in the presence of a mere trace of phosphorus, insufficient to affect the physical properties of the brass materially, dezincification is substantially inhibited. A very small amount of phosphorus is sufficient to achieve this result. About 0.03 per cent is a good optimum. The proportion of phosphorus can be increased up to a maximum of about 0.2 per cent without substantial degradation of the physical properties of the alloy, but usually the desirable proportion of phosphorus is much less than 0.2 per cent.

The reason for the action of these minimal additions of phosphorus is not known, but the solution pressure of the alloy of copper and zinc is effectively restrained. The film formed on the alloy tubes in service contains phosphorus.

The invention is especially useful for improving admiralty metal tubes but is also useful with other copper-zinc alloys. In general, copper alloys containing more than 85 per cent copper exhibit little tendency to dezincification and the addition of phosphorus is not so necessary. On the other hand, alloys with less than about 60 per cent copper find little use in the installations described. Muntz metal which finds considerable use in condenser tubes, etc. is improved by phosphorus additions as described and so are high copper alloys (85 per cent copper, 15 per cent zinc) and copper-zinc alloys containing other modifying elements than tin, such as aluminum brass which contains copper, zinc and a small amount of aluminum; often in proportions 76 Cu, 22 Zn and 2 Al.

In preparing a condenser tube according to the invention, a suitable copper-zinc alloy melt is prepared and phosphorus in the form of a copper phosphorus alloy is incorporated in the melt, or at any other suitable stage of operations, in such proportion that the finished tube contains phosphorus in the specified proportions. The phosphorus-containing alloy is wrought into tubes in the ordinary way.

In the accompanying drawing there are presented charts illustrative of the improvement in dezincification resistance achieved in the invention. In the drawing

Fig. 1 is a diagram showing the effect upon dezincification resistance, of exposure of articles made of the alloy of the invention to a standard corroding solution, as measured by ductility,

Fig. 2 is a diagram corresponding to test data similar to Fig. 1 but in terms of tensile strength, and

Fig. 3 is a perspective view of an alloy tube according to the invention.

Referring to the drawing, Figs. 1 and 2 correspond to corrosion tests on specimens of the new alloys with various phosphorus contents and exhibit the resistance to dezincification achieved thereby. In making the tests, specimens of the several alloys were kept in an aggressive aqueous liquid, at a temperature of 120° F., for various lengths of time. For the sake of concreteness a 1 per cent copper chloride solution was employed as the aggressive liquid. Such a solution gives, at an accelerated rate, results quite comparable to those obtained with aggressive waters over longer periods of time. Dezincification strictly speaking is measured by the loss of the zinc content of an alloy, but two other parameters, ductility and tensile strength, are rather closely related to loss of zinc and were used for the comparative tests.

Fig. 1 shows, in curves A, B, C and D the effect on ductility of exposure for various lengths of time of test specimens of admiralty metal containing 70 parts copper, 29 parts zinc, 1 part tin, and phosphorus in the proportions, by weight on the alloy, of 0.01, 0.03, 0.07 and 0.12 per cent, respectively. Curve E shows the effect for phosphorized Muntz metal (60 parts copper, 40 parts zinc and 0.01 part phosphorus). Curves F and G are for ordinary non-phosphorus-containing admiralty and Muntz metals of the prior art and are shown for the sake of comparison.

The curves show that the new alloys retain a usefully high ductility over prolonged exposure to the aggressive liquid. The ductility drops at first, probably due to corrosion, rather than dezincification, but soon reaches a constant relatively high value around 30 per cent elongation in two inches. Dezincification is effectively inhibited. By contrast, ordinary admiralty and Muntz metals lose practically all their ductility within the first few weeks.

Fig. 2 presents tensile strength data for the same set of alloys exposed to the same corrosive solution at the same temperature. The curves, *a*, *b*, *c*, *d*, *e*, *f* and *g*, correspond to curves A to G of Fig. 1 except that tensile strength is the quantity measured. The phosphorized alloys retain a high tensile strength (above 30,000 pounds per square inch) indefinitely, while ordinary Muntz and admiralty metals very soon lose all useful tensile strength.

Fig. 3 shows a portion of a heat exchanger tube embodying the invention.

The flattening off of the curves for the phosphorus-containing alloys is indicative of the formation of a protective film. The film varies with the character of the aggressive bath; but the relations indicated hold qualitatively for a wide variety of aggressive liquids. Quite comparable results are obtained in actual condenser tubes exposed to a wide variety of aggressive fluids; moist oil refinery vapors, sewage, carbonate waters, etc. etc.

This application is a continuation-in-part of my prior application, Serial No. 278,457, filed June 10, 1939 for Copper base alloys.

What I claim is:

1. In a heat exchanging conduit exposed to dezincification-producing conditions in contact with moist corrosive fluids and made of an alloy of copper 58 to 85 per cent and the balance zinc and tin, the tin being present in a proportion up to approximately one per cent of the alloy, means for inhibiting dezincification therein consisting of a quantum of phosphorus present in the finished alloy, in the proportion 0.001 to 0.2 per cent of the alloy.

2. The conduit of claim 1 wherein the proportion of phosphorus is 0.03 per cent.

3. The conduit of claim 1 wherein the alloy

contains approximately 70 per cent copper, 29 per cent zinc and the balance tin and phosphorus.

4. The conduit of claim 1 wherein the alloy contains approximately 60 per cent copper and 39 per cent zinc and the balance tin and phosphorus.

5. In a heat exchanging conduit exposed to dezincification-producing conditions in contact with moist corrosive fluids and made of an alloy of copper substantially 76 parts per hundred, zinc substantially 22 parts per hundred and aluminum substantially 2 parts per hundred, means for inhibiting dezincification therein consisting of a quantum of phosphorus present in the finished alloy, in the proportion 0.001 to 0.2 per cent of the alloy.

FREDERIC M. BARRY.