United States Patent [19]

Costas

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[45] **Aug. 19, 1975**

[54] **SILICON BRASS RESISTANT TO PARTING CORROSION**

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[73] Assignee: **The Anaconda Company,** New York, N.Y.

[22] Filed: **Mar. 19, 1974**

[21] Appl. No.: **452,618**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 434,613, Jan. 18, 1974, abandoned, which is a continuation of Ser. No. 222,508, Feb. 1, 1972, abandoned, which is a continuation-in-part of Ser. No. 887,927, Dec. 24, 1969, abandoned.

[52] **U.S. Cl.** ..... **148/32;** 75/157.5; 148/32.5; 148/11.5 R; 148/12.7

[51] **Int. Cl.** **C22c 9/10;** C22f 1/08

[58] **Field of Search** ..... 75/156.5, 157.5, 160; 148/11.5 R, 32, 32.5, 12.7

[56] **References Cited**

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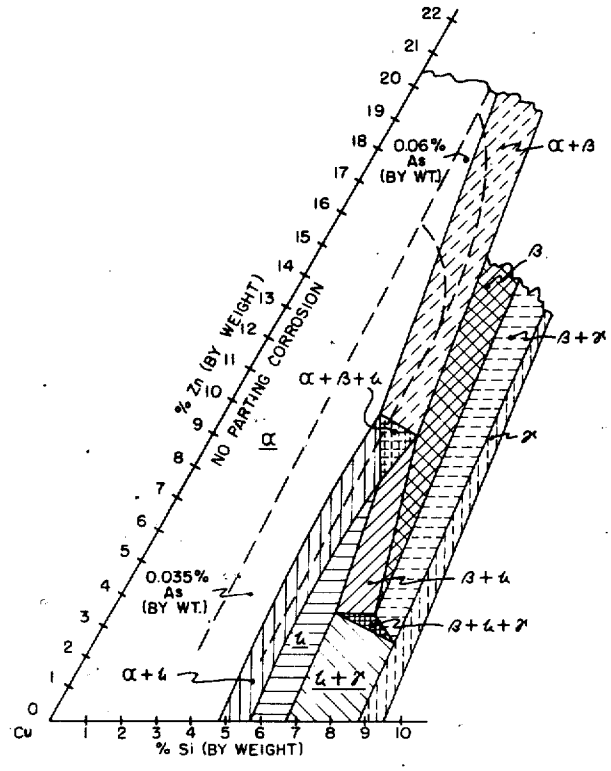
Primary Examiner—C. Lovell

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[57] **ABSTRACT**

This disclosure relates to silicon brass alloys in which corrosion resistance is obtained by the addition of a small amount of an inhibitor, such as arsenic, to provide an alloy which when properly heat treated has substantial resistance to parting corrosion in waters which contain corrosiive ingredients such as are found in many public water supplies.

2 Claims, 4 Drawing Figures



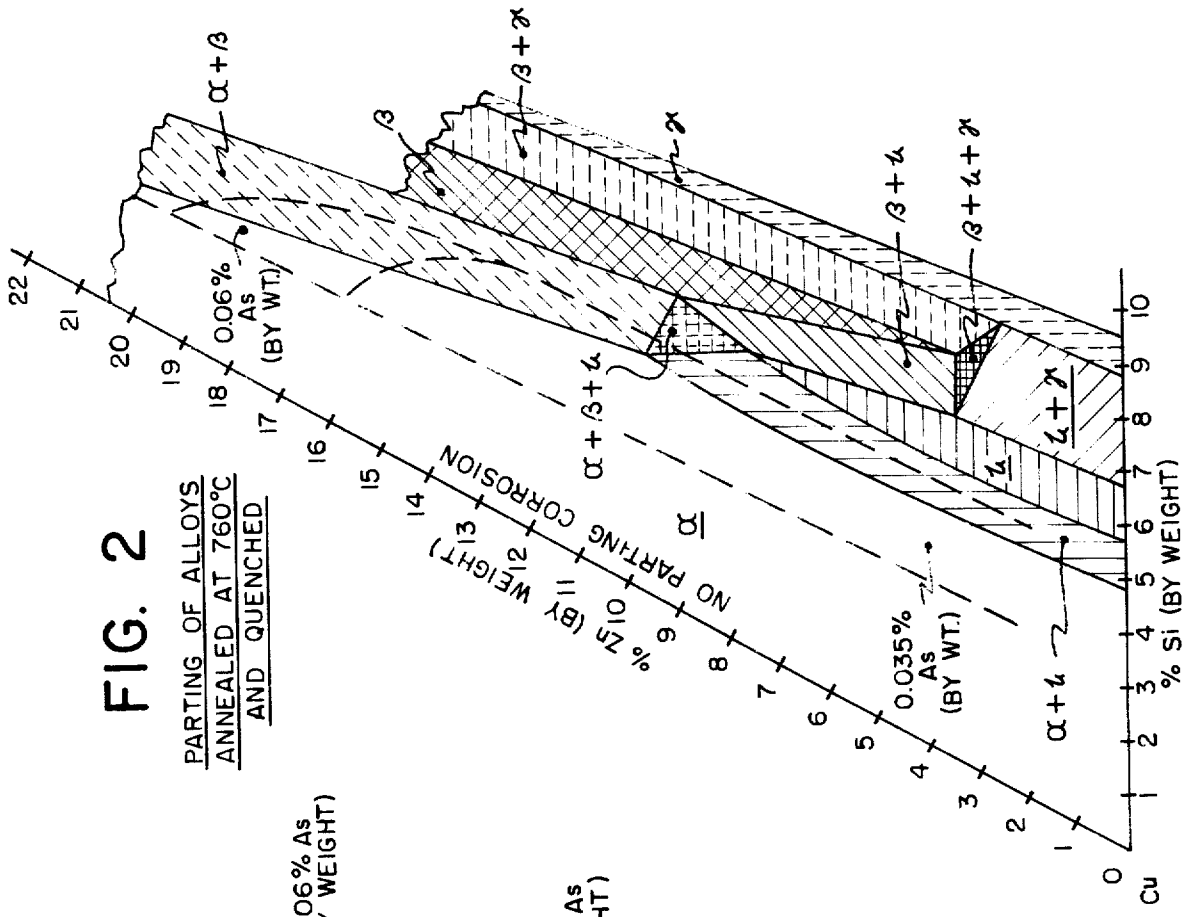


FIG. 2

PARTING OF ALLOYS ANNEALED AT 760°C AND QUENCHED

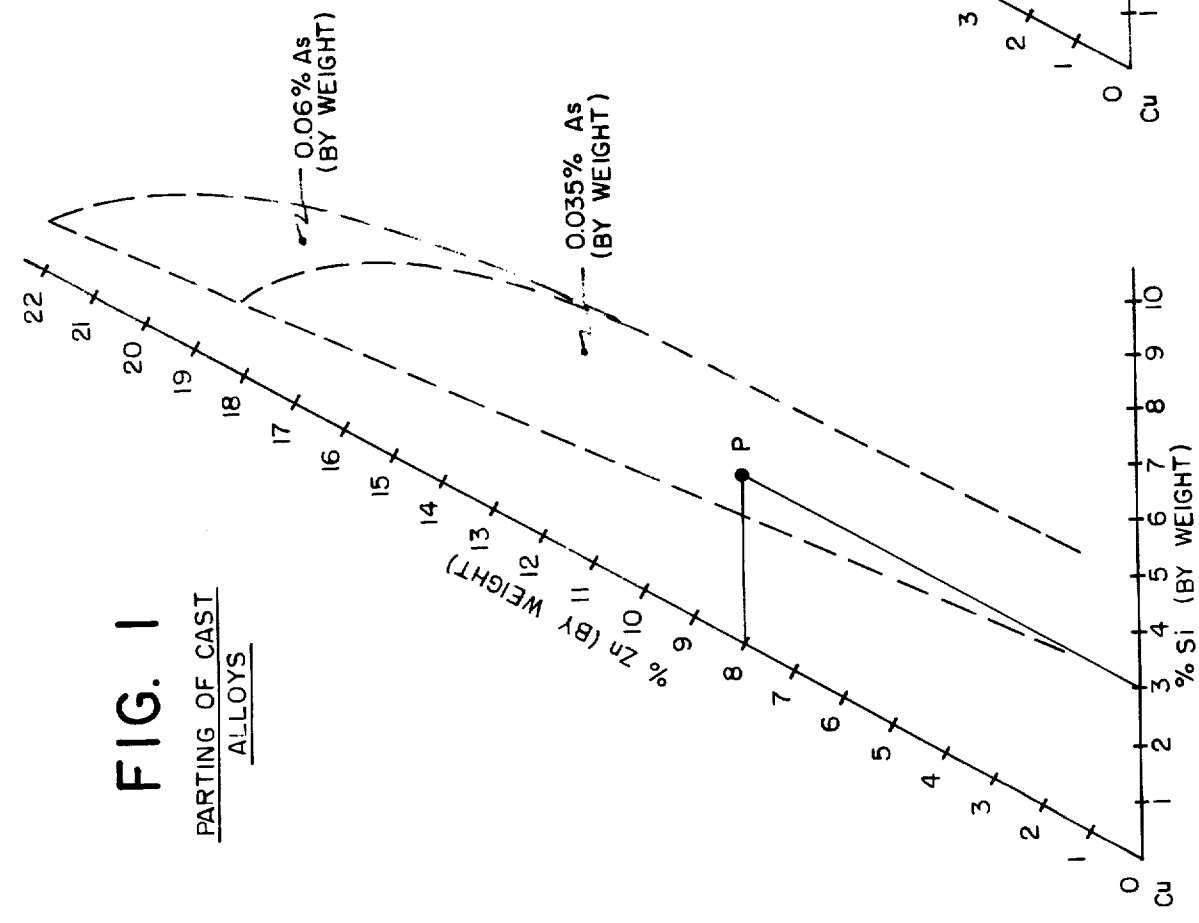


FIG. 1

PARTING OF CAST ALLOYS

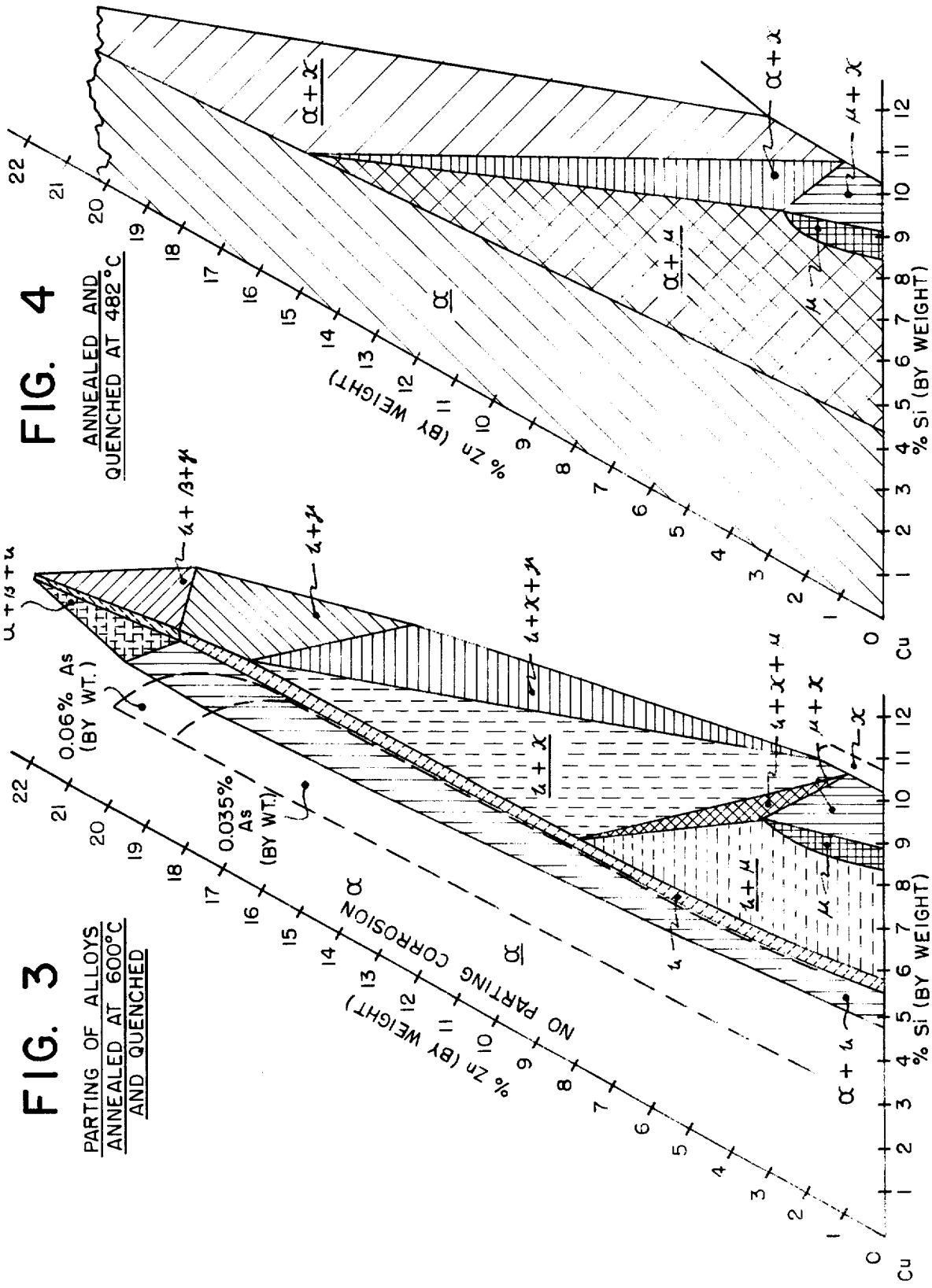


FIG. 4

ANNEALED AND QUENCHED AT 482°C

FIG. 3

PARTING OF ALLOYS ANNEALED AT 600°C AND QUENCHED

SILICON BRASS RESISTANT TO PARTING CORROSION

RELATED APPLICATION

This application is a continuation-in-part of my application Ser. No. 434,613 filed Jan. 18, 1974 now abandoned, which was a continuation of application Ser. No. 222,508 filed Feb. 1, 1972 now abandoned, which in turn was a continuation-in-part of my application now abandoned Ser. No. 887,927 filed Dec. 24, 1969.

BACKGROUND OF THE INVENTION

The addition of silicon to brasses increases the mechanical strength of the alloys making them more suitable for use as valve stems and other objects which are subjected to tensile and bending forces. Other desirable features of these alloys are machinability and their freedom from galling or seizing in operation.

However, the resistance of silicon brasses to the corrosive action of many waters and other corrosive fluids has not been satisfactory. For example, in some public water systems valve stems have failed within 1 to 2 years due to parting corrosion. This type of corrosion can be thought of as a leaching out of alloying agents leaving copper behind in a porous and weakened condition. This process of parting corrosion is usually referred to as "dezincification" when it occurs in the common copper-zinc brasses.

The problem of dezincification in valve stems has been recognized for years and it was particularly severe when high zinc alloys, such as manganese bronze with 40 percent zinc, were used. To combat this problem, manufacturers of valves turned to the silicon brasses which can contain from 5 to 22 percent zinc and over 0.5 percent silicon, but usually the range of 12 to 20 percent zinc and 2.5 to 4.5 percent silicon has been used. This approach is based on the premise that the lower zinc content would deter dezincification and to some extent it has been successful. However, the parting corrosion problem is again becoming serious because of lower water quality as a consequence of the increasing demand for water due to increased population and industrial needs.

As a reaction to this corrosion problem, the trend once again is towards lower zinc levels. The disadvantages of smaller zinc contents are (1) increased cost of alloys and (2), what is more important, decreasing the zinc does not necessarily eliminate parting corrosion. I have discovered that parting corrosion in silicon brass is not solely a function of zinc content but rather of both zinc and silicon.

Another approach has been the addition of arsenic, antimony, or phosphorus inhibitors which is known to reduce parting corrosion in single phase copper-zinc brasses, but the use of such inhibitors had been found to be ineffective for twophased copper-zinc brasses. Since most silicon brasses depend upon multiphase structure to produce high mechanical strength, the benefits of these inhibitors would not have been predicted, nor would such additions have appeared promising. Furthermore, it has not been appreciated that silicon additions aid parting corrosion of even alpha phase, the primary structure, and therefore no prior attempts to negate the effect of silicon have been made.

SUMMARY OF THE INVENTION

Copper-zinc alloys containing small amounts of silicon in the range of 1 percent to about 2.5 percent silicon, depending on zinc content, are resistant to parting corrosion. However, when the silicon content is increased for strength purposes above these levels to amounts in the range of greater than about 2.5% to about 7 percent, depending on zinc content, parting corrosion will occur. To overcome the corrosion disadvantage of higher silicon levels, arsenic, antimony or phosphorus will provide the alloy with substantial immunity to parting corrosion, whether the alloy is single or multiphased, if proper heat treatment is performed on cast or wrought material.

Broadly stated, the present invention comprises a silicon brass alloy whose thermal history is controlled in such a manner that the alloy includes substantial quantities of alpha and zeta phases and consists of about 3 to 20 percent zinc, about 2.5 to 6 percent silicon, from about 0.030 percent up to the percentage of solid solubility in the alloy of one or more elements of the group consisting of arsenic, antimony and phosphorus, and the remainder copper. Optionally, an amount of lead to provide good machinability may be added to the alloy.

The principal of operation of the present invention is the selection of proportions of copper, zinc, silicon and inhibitors within ranges depicted by areas bordered by dashed lines on the Figures. The dashed-lined areas disclose the alloys which under commercial conditions of heat treatment are protectible by inhibition addition. These areas of the Figures show the alphazeta phase for alloys held at temperature for short periods of time prior to quenching while the solid-line phase boundaries show the phases, including the alpha-zeta phase as indicated, obtained when the alloys are held for long periods, such as days, at selected temperatures to permit an equilibrium condition to be reached.

The upper end of the range of inhibitor is the percentage just below that at which the inhibitor will start to precipitate and form compounds that may have deleterious effects. While percentages above about 0.10 percent are not generally required, the addition of amounts of inhibitors above 0.10 percent does not adversely affect the alloy until the percentage of solid solubility is passed.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1, 2 and 3 of the drawings show parting corrosion behavior for three different alloy conditions plotted on the copper-rich corner of the ternary alloy system of the present invention. FIG. 4 shows the phases formed when the alloy is cooled from a temperature below 500°C.

DESCRIPTION OF THE PREFERRED EMBODIMENT

FIGS. 1, 2 and 3 show the copper-rich corner of the ternary system of copper, zinc and silicon and whether an alloy having a particular composition undergoes parting corrosion with, or without, an inhibitor present in a specific water, and under electrochemical conditions that will be described below. The areas defined by the dashed lines denote compositions which were tested and found to suffer parting corrosion in the absence of an inhibitor. For example, in FIG. 1 it is seen that an alloy P, whose composition is 8 percent zinc, 3 percent silicon, and balance copper, and cast using normal commercial procedures, would suffer parting corrosion. However, in accordance with my invention, the

addition of at least about 0.03 percent inhibitor provides substantial immunity to parting corrosion.

The solid lines of FIGS. 2, 3 and 4 are the equilibrium phase boundaries as determined by Horace Pops (Trans. Met. Soc., AIME, 230, 813–820, 1964). The significance of these diagrams is that they define the phases that would exist if the alloys were allowed to remain at these temperatures for long periods of time such as days or weeks depending on the temperature. No equilibrium phase boundaries are shown in FIG. 1 since cast alloys are generally produced under non-equilibrium conditions.

In commercial operations, the alloys of this invention are cast, then heated and further processed by extrusion and drawing. Such treatments do involve high temperatures, such as 500° to 750°C, but the length of time of treatment is generally only a few hours in duration and equilibrium is never attained. Thus, it is quite common to find, for example, alpha and zeta phases existing in alloys where only alpha would be predicted from the phase diagram. However, the phase diagram provides an excellent base on which to describe metallurgical phonomenon.

In FIGS. 2 and 3 it will be noted that the area bounded by the dashed lines involved three phases, alpha, beta, and zeta. However, beta in this region of composition is stable only at high temperatures and attempts to retain it by very rapid quenching fail; it quickly transforms to a mixture of alpha and zeta. On the other hand, alloys consisting of alpha or alpha and zeta at these higher temperatures can be quenched so that these same phases remain intact at room temperature. Thus commercial alloys quickly cooled or quenched from above about 500°C commonly consist of alpha and zeta phases even though only alpha or alpha and beta would be predicted from the phase diagram.

Below about 500°C, depending on the composition, zeta phase is no longer stable and transforms either into mu or chi as shown in FIG. 4. In the temperature range of 400°-500°C, the kinetics of the transformation of zeta are fast enough to produce significant amounts of mu or chi in minutes. These phases cannot be protected from parting corrosion, even with inhibitors present, and so they are highly undesirable from the corrosion resistance standpoint. Alpha, of course, can be protected by inhibitor as has been known for years. The unexpected discovery that zeta phase can also be inhibited is the basis for this invention. Thus, with proper inhibitor addition and temperature control, silicon brass alloys manufactured either in the cast or wrought form can be made resistant to parting corrosion so long as only alpha and zeta phases exist in the final state.

The parting corrosion test used to develop the data herein employed an electronic potentiostat, an instrument which allows corrosion reactions to occur under carefully defined electrochemical parameters. This test more closely parallels actual service conditions than past procedures using hydrochloric acid or copper chloride solutions which are extremely aggressive and not therefore typical of conditions found in water distribution systems.

The tests were carried out under an argon cover for 24 hours at zero millivolts referenced to a saturated calomel electrode. Cylindrical specimens were 10 millimeters in diameter and about 20 millimeters long. Room temperature test water was used, but, if no parting was detected, the test was again run at 52°C and, if still no parting was found the specimen was categorized as showing no parting. These tests were found to correlate well with actual experience with a variety of uninhibited alloys which had been in service for years in aggressive potable waters. Where an alloy specimen passed both the room temperature and 52°C test, it can be predicted that it would perform well in service in a corrosive water condition. The potentiostatic tests were carried out using a test water having similar composition and characteristics of Colorado River water which is an aggressive potable water used in large quantities in the Southwestern region of the United States. The composition of the test water and Colorado River water is set out in the following table.

TABLE I

	Test Water	Colorado River Water
Total Dissolved Solids	680–730 ppm	650 ppm
Total Hardness ($CaCO_3$)	122–170	125
Alkalinity	110–122	109
SO_4	286–293	214
Cl	92–104	80
NO_3	2	0.5
Ca	46–48	32
Mg	1–13	11
Na	170	172
K	5	4
Conductance (micromhos/cm)	1000–1100	1021
pH	7.8–8.1	8.35

In compiling the corrosion data set forth on FIG. 1, alloys having the ranges of zero to 24 percent zinc, 1 to 6 percent silicon, up to about 0.06 percent of an inhibitor and with the remainder copper were cast into specimens which were then rapidly cooled to room temperature. Each specimen was thereafter tested to determine if the test water would cause any detectable parting corrosion. The criterion for determining the occurrence of parting was metallographic examination. The following table includes the composition of a number of specimens tested and states whether parting corrosion was detected.

TABLE II

Composition of Cast Alloys and Results of Parting Corrosion Test

	Parting						
Cu	74.01	77.4	78.87	82.71	93.54	95.51	94.10
Zn	24.64	18.9	17.22	13.41	3.63	—	—
Si	1.35	3.4	3.91	3.87	2.83	4.49	5.72
Pb	—	090.24	—	—	—	—	—
As	—	090.02	0.01	0.01	—	—	0.056
	No Parting						
Cu		79.23	78.69	82.74		86.54	89.07
Zn		17.45	17.45	13.34		8.68	6.28
Si		3.23	2.81	3.88		4.74	4.61
Pb		—	—	—		—	—
As		0.05	0.05	0.03		0.03	0.04

Lead was added to some of the specimens since valve stem brass usually includes this element to improve machinability. Lead was found to have no effect on the corrosion properties of the alloys of the present invention when added in quantities as required to give good machinability. For example, up to about 1.5 percent lead may be added to the alloys.

The corrosion data depicted in the ternary phase diagrams of FIGS. 2 and 3 was obtained in the same manner as described in obtaining data for the diagram of FIG. 1, except that the cast specimens were swaged, encapsulated, annealed at 600°C for 10 days and 760°C for 5 days and then quenched. Compositions of some of the specimens tested and the results of the tests are set forth below in Table III.

TABLE III

			Parting			
Cu	77.1	77.9	78.0	79.30	82.79	89.03
Zn	19.2	20.3	19.52	17.34	13.37	6.38
Si	3.4	1.83	2.50	3.35	3.83	4.59
Pb	0.24	—	—	—	—	—
As	—	—	—	0.005	0.005	—
			No Parting			
	Cu	76.96	78.79	82.58	89.07	
	Zn	19.66	17.24	13.47	6.28	
	Si	3.32	3.93	3.90	4.61	
	Pb	—	—	—	—	
	As	0.06	0.03	0.05	0.04	
		Cu 82.06	Cu 82.11			
		Zn 19.94	Zn 13.82			
		Si 3.96	Si 3.98			
		P 0.04	Sb 0.088			

The effect of annealing specimens at 760°C was to require the use of more inhibitor at the higher zinc and silicon contents to provide immunity to parting corrosion, as illustrated by the upper dashed area on the Figures. Annealing at 600°C reduced the requirement of using a larger amount of inhibitor until the zinc content reached over 19 percent. Other samples were annealed at various temperatures between 550°C and 760°C and it was found that the immunity to parting obtained was substantially as illustrated on FIGS. 2 and 3. If, however, alloys are annealed or slowly cooled below about 500°C, mu and chi phases will occur which are highly susceptible to parting. These phases, as mentioned earlier, cannot be protected by an inhibitor, thus it has been found essential to quickly cool castings or wrought material from over 500°C to prevent these phases from forming.

Field tests in public water supplies in major cities in the U.S. have provided further evidence of the advantages of the present alloys. A cast ASTM B 198, CDA 875 alloy, having 14% zinc, 4.5 percent silicon, 0.4 percent lead, and the remainder copper was compared with the same alloy plus 0.05 percent arsenic. In addition, wrought ASTM 391, CDA 697 alloy, heated to about 650°C and quickly cooled, having 18 percent zinc, 3 percent silicon, 1.1% lead and the remainder copper was compared with a similarly treated alloy containing 0.05 percent arsenic. The results are given in the following table:

TABLE IV

	Corrosion Rate (Millimeters per year)			
	ASTM B 198 (CDA 875)		ASTM 371 (CDA 697)	
Site	Non-Inhibited	Inhibited	Non-Inhibited	Inhibited
Washington, D.C.	1.6	0.06	0.4	0.06
Cleveland, Ohio	1.1	0.04	0.4	0.1
Pasadena, Cal.	0.4	0.05	0.2	0.06
Philadelphia, Pa.	0.6	0.1	0.3	0.1

Metallographic examination revealed that in the cast alloy, zeta phase was heavily attacked in the non-inhibited form whereas the inhibited counterpart was only superficially affected. In the wrought 697 alloy, both alpha and zeta suffered parting corrosion without an inhibitor present but when inhibited, this form of attack virtually disappeared.

I claim:

1. A silicon brass alloy resistant to parting corrosion consisting essentially of about 3–21 percent by weight zinc, an amount of silicon in the range of about 2.5 to about 7 percent, said amounts of zinc and silicon being sufficient to produce a structure consisting of alpha plus zeta phases in the brass, from about 0.030 percent up to the percentage by weight of solid solubility of one or more elements of the group consisting of arsenic, antimony and phosphorus remainder essentially copper, said alloy having been rapidly cooled to room temperature from a temperature in the range of 500°c to 760°C and consisting of alpha plus zeta micro structure.

2. The alloy of claim 1 having about 0.06% by weight arsenic as the element.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,900,349

DATED : August 19, 1975

INVENTOR(S) : LOUIS P. COSTAS

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 56, "twophased" should read --two-phased--

Column 2, line 29, "alphazeta" should read --alpha-zeta--

Column 4, line 54, "090.24" should read --0.24--

Column 4, line 56, "090.02" should read --0.02--

Column 6, line 40, "500°c" should read --500°C--

Signed and Sealed this

twenty-third Day of *December 1975*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks