

1

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PROCESS FOR ELECTROCHEMICALLY CLEANING AND BRIGHTENING COPPER ALLOY AND BRASS STRIP

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ABSTRACT OF THE DISCLOSURE

A process for cleaning copper alloy strip is provided comprising soaking the strip in an electrolyte solution of polyphosphate and organic hydroxycarboxylic acid, and making the strip the anode in an electrochemical cell, the electrolyte in said cell being a solution of polyphosphate and organic hydroxycarboxylic acid.

The usual process for cleaning and brightening copper alloy strip either in process or at finish gauge involves immersing the strip in solutions of sulfuric acid, sulfuric acid plus chromic acid (or sodium dichromate) or, in some cases, sodium cyanide. These solutions are very corrosive, toxic and present problems in disposal when they are spent. Furthermore, strip treated with these solutions is frequently not cleaned uniformly and will often develop stains rapidly after cleaning.

It is an object of the present invention to provide a process for cleaning copper alloys and brass strip rapidly and completely to produce an attractive uniform surface while dissolving only a miniscule quantity of metal.

It is another object of the present invention to produce a "passive" surface on these alloys which has some resistance to tarnishing.

Another object of the present invention is to avoid the use of toxic, corrosive, or expensive chemicals and alleviate the problems of corrosion and the danger of handling toxic chemicals.

It is another object of the present invention to provide a solution which can be regenerated continuously and, therefore, never need to be dumped, and, thus, ease the problems of waste disposal and stream pollution.

The foregoing objects are achieved in a two-step process.

The first step is a soaking operation in which the stained strip is exposed to the electrolyte solution. The electrolyte soaks through the stains and appears to soften the stain.

The second step is an electrochemical step in which the strip is made the anode in a cell with controlled flow. A small quantity of metal under the stain dissolves so that the stain or oxide is no longer attached to the metal. Then a reaction occurs between the electrolyte and the anodic layer which forms an extremely thin, transparent, passive layer on the metal.

The strip then leaves the bath and is rinsed, dried and coiled.

The electrolyte which is used in both the soaking and electrochemical steps is a solution of polyphosphate and organic hydroxycarboxylic acid. The pH of this solution should be adjusted to be between 6.0 and 9.0 with 8.0 as a preferred operating value. The electrochemical cleaning process does not proceed when the pH exceeds 9.0 and the polyphosphates are not sufficiently stable below pH 6.0.

Any polyphosphate including pyrophosphate, tripoly-

2

phosphate, tetrapolyphosphate, etc., can be used for this solution, but the sodium pyrophosphate is preferred.

The concentration of polyphosphate should be between 50 and 90 grams per liter of anhydrous phosphate radical. For anhydrous tetrasodium pyrophosphate, this is approximately equivalent to a range of 75 to 140 grams per liter. The preferred concentration of sodium pyrophosphate is approximately 100 grams per liter.

The hydroxycarboxylic organic acid for the solution includes citric, tartaric, glycolic, gluconic, and sugar acids. Citric acid is preferred. Because pH adjustment is necessary, it is desirable to add equal weights of citric acid and sodium citrate. If this is done, then the pH will need little or no adjustment. The concentration range of citric acid and sodium citrate is from 10 grams to 60 grams per liter each. The exact concentration chosen is based on other process requirements as discussed below.

The electrolyte temperature should be in the range of 40–80° C. Low temperatures are undesirable because the voltage requirements are higher and pyrophosphate tends to crystallize out at lower temperatures. On the other hand, high temperatures produce excessive evaporation and require excessive heat inputs to maintain temperature. The preferred operating temperature range is 60–70° C.

The soaking time requirement is dependent largely upon the type of stain present. Heavy or dense stains require soak times up to 60 seconds, while light stains need only 2–10 seconds. Most industrial strip can be cleaned adequately with less than 30-second soaks.

The electrochemical step in the process is critical to produce a satisfactory surface. The electrolyte must flow past the strip during treatment at a uniform velocity determined by the equations given below. The current density J of the anodic treatment must be set between the limits shown by these equations:

$$J \text{ max.} = .53(V_f - V_s)(Ct/10) \quad (1)$$

$$J \text{ min.} = .36(V_f - V_s) \quad (2)$$

where $J \text{ max.}$ is the maximum current density in amps per square inch; $J \text{ min.}$ is the minimum current density in amps per square inch; V_f is the fluid velocity in feet per second and may vary from 2 to 15; V_s is the strip velocity in feet per second and may vary from 0 to 10; and Ct is the concentration of sodium citrate and citric acid in the electrolyte expressed in grams per liter.

In these equations, the velocity terms represent vectorial quantities and so the velocity difference shown must be the magnitude of the vectorial velocity difference. Furthermore, these equations apply only to well-developed turbulent flow and so appropriate corrections must be made when considering any other flow regime situation. Wall shear is the important criteria in these relations.

If the current density exceeds the maximum set by these equations, then a brown or red stain or deposit will appear on the metal surface and the metal will not be clean. On the other hand, if the current density is too low, then the metal surface will be etched and cleaning will again be unsatisfactory. In the range specified, the cleaning rate is optimum and the metal acquires a bright, passive surface.

For some alloys, the minimum current density is lower than that shown. This group of alloys includes the alloys of copper and tin, and also of copper and aluminum. For these alloys, the minimum current density is about one-third the value calculated from Equation 2.

The citrate is consumed by an electrochemical oxidation reaction in this process. This reaction is necessary to produce the desirable cleaning and passivation which results from this process. However, it is necessary to add

citrate to the bath to make up that consumed in the reaction.

The voltage requirement of this process is dependent upon a number of factors including: the cathode material, cathode-anode ray ratio, alloy being cleaned, current density, electrolyte temperature, and composition and resistances in the external circuitry.

More specifically, this voltage is given by an expression of the form:

$$V = V_o + \left(\frac{aP}{g} + bw + c \right) J \quad (3)$$

where V is the applied voltage in volts; V_o is a constant voltage determined by the alloy in volts; a , b and c are constants and may vary respectively from 0.01 to 2.0, 0.01 to 1.00, and 0.1 to 3.0; p is the electrical resistivity of the alloy and is from 10 to 100 ohms mil ft. for copper and copper alloys; g is the gauge of the strip; w is the width of the strip; and J is the current density in amps per square inch.

The constants a and b are determined by the external circuit and C is determined by the electrochemical cell parameters.

The treatment time in the electrochemical portion of the process is dependent upon the nature of the stain present and upon the current density used. This treatment time is therefore given by Equation 4:

$$t = m/J \quad (4)$$

where t is the treatment time in seconds; m is the extent of treatment in coulombs per square inch; and J is the current density in amps per square inch.

For most industrial strip, m is approximately 5 coulombs per square inch, although in cases of heavy stains, annealing oxides, etc., m should be increased to values between 10 and 20 for adequate cleaning.

This process will dissolve copper and other alloying elements into the electrolyte. As time goes on, the electrolyte will become less effective because of these heavy metals in solution. Therefore, it is desirable to keep the copper concentration of the electrolyte below 3 grams per liter and other alloying element concentrations below 5 grams per liter total.

This can be accomplished by plating these elements out in a regeneration cell composed of cathode starter sheets and stainless steel anodes. The electrode sheets should be hung vertically in this regeneration and should be at least two feet long in the vertical direction. The current density in this regenerator should be maintained between about 1 and 20 amps per square foot and will vary according to the concentration of heavy metals in the electrolyte.

The zinc content of the metal deposited on the cathodes will be given by Equation 5:

$$Zn = 7.5 (J_r - 4) \quad (5)$$

where Zn is the present zinc in the deposit; and J_r is the regenerator cathode current density in amperes per square foot.

Equation 5 holds when the zinc content of the electrolyte is about 3 grams per liter and the copper content is 1.5 grams per liter and the temperature is 50–60° C., and the current density is between 4 and 10 amps per square foot. If the copper concentration of the electrolyte exceeds 1.5 grams per liter, the copper content of the deposit would be greater than predicted, and if it falls below 1.5 grams per liter, current efficiency of the cell would fall off. If the zinc content falls below the 3 grams per liter, the zinc content of the deposit would be lower than predicted. This behavior can be used to control the electrolyte composition accurately while recovering the heavy metal values from the electrolyte.

If zinc is not present in the electrolyte, heavy metals, for example, including Fe, Pb, Sn, Ni, Co and Mn can be removed from the solution by operating the regenerator at current densities of 1 to 20 amperes per square

foot. However, most heavy metals can be removed with current densities of 2 to 6 amps per square foot with heavy metal concentrations up to about 5 grams per liter.

The following examples illustrate the invention without limiting its scope:

Example I.—Cleaning an alloy 260 brass strip

An apparatus was constructed to treat coils of brass strip.

The strip was first immersed in a tank with an immersive length of about 7 feet. Then the strip passed over a 3-foot diameter roller on which the electrochemical treatment was carried out. A curved stainless steel cathode, 30 inches long, was placed over the roller so that the distance between the cathode and the strip was $\frac{5}{16}$ inch uniformly over its length and width. The electrolyte was pumped from a nozzle in this cathode-anode space, such that its velocity was opposed to that of the strip.

A volume of 200 liters of electrolyte consisting of 100 grams per liter anhydrous sodium pyrophosphate, 10 grams per liter each of sodium citrate and citric acid was made up and heated to 60° C. A 1-inch wide strip of alloy 260 brass with a dull grey stain on its surface was threaded through the apparatus. The strip speed was adjusted to 100 feet per minute and the solution flow adjusted to 50 gallons per minute. This corresponded to a flow velocity of 7.3 feet per second. The current was adjusted to 132 amperes at 8.9 volts corresponding to current density of about 4.4 a.s.i. and a treatment of 6.7 coulombs per square inch. The voltage relationship values for Equation 3 were $p=37$ ohms mil ft., $g=8.5$ mils, $w=1.00$ inch, $V_o=0.3$ volt, $a=0.11$, $b=0.24$ and $c=103$.

The strip acquired a bright, lustrous surface.

However, when the current was increased above 170 amperes (5.0 a.s.i.), the surface became covered with brown stains.

When the current was decreased below 91 amperes (2.8 a.s.i.), the surface became etched and matte in appearance. The strip was rinsed, dried and coiled after treatment.

Example II.—Cleaning an alloy 230 strip

An alloy 230 strip, 2.1 inches wide, with a severe water stain on its surface, was placed in the apparatus described in Example I.

The electrolyte was identical to Example I.

The voltage relationship values for Equation 3 were $p=37$ ohms mil ft., $g=10.8$ mil, $w=2.10$ inches, $V_o=0.6$ volt, and a , b , and c as given in Example I.

The strip speed was adjusted to 40 feet per minute and the electrolyte flow rate was adjusted to 35 gallons per minute (or 6.5 ft. per sec.). The current was set at 215 amperes (3.4 a.s.i.) and the extent of treatment was 13 coulombs per square inch. A voltage of 6.2 volts was required for this current.

The strip was cleaned completely and acquired a lustrous, attractive surface after treatment.

Example III.—Cleaning an alloy 260 strip in a high citrate electrolyte

An apparatus was constructed with a pre-immersion soak length of three feet and a system of five nozzles, each with a 1-inch long cathode.

A black, heat-stained strip of alloy 260 brass, 2.5-inches wide, was treated in this apparatus at 50 feet per minute, with 500 amperes (22.7 a.s.i.), and a treatment of 20 coulombs per square inch, 17 volts were required for this treatment and 37 gallons per minute total flow was passed, i.e., 7.4 gallons per minute, through each nozzle (or 8.0 ft./sec.).

This treatment produced a bright, lustrous finish and complete removal of stain.

Example IV.—Regeneration of electrolyte

Electrolyte containing 100 grams per liter of sodium pyrophosphate, 10 grams per liter each of sodium citrate and citric acid was prepared and heated to 60° C.

Copper ion at 1.5 grams per liter and zinc ion at 3.0 grams per liter were added to this bath.

Stainless steel anode and a copper cathode each 28 inches long were placed in this bath.

The zinc content of the cathode deposit was measured at various current densities.

| Current density (amps per sq. foot) | Zn content of cathode deposit, percent |
|--|---|
| 4 | 5 |
| 6 | 20 |

Example V.—Stain resistance of treated metal

An alloy 230 strip cleaned by the process of the present invention in a 100 grams per liter sodium pyrophosphate, 10 grams per liter each of sodium citrate and citric acid, electrolyte at 70° C. with 3 a.s.i. current density and 10 coulombs per square inch treatment, rinsed and dried, was prepared.

A stain test was performed in which panels were cooled to 40° F. and then exposed to an environment at 100° F. with a relative humidity of 95% for 3 days.

Panels cleaned in sulfuric acid developed a dark, matted appearance and were given an appearance rating of 33%.

The panels treated with the process of the present invention showed a brighter, more uniform appearance and were given an appearance rating of 63%.

It is to be understood that the invention is not limited to the illustrations described and shown herein which are deemed to be merely illustrative of the best modes of carrying out the invention, and which are susceptible of modifications of form, size, arrangement of parts and detail of operation, but rather is intended to encompass all such modifications which are within the spirit and scope of the invention as set forth in the appended claims.

What is claimed is:

1. A process for cleaning copper alloy strip comprising:

(a) soaking the strip in an electrolyte solution consisting essentially of a polyphosphate and an organic hydroxycarboxylic acid, and

(b) making the strip the anode in an electrochemical cell, the electrolyte in said cell being a solution consisting essentially of a polyphosphate and an organic hydroxycarboxylic acid having a pH of from 6-9 and being maintained at a temperature in the range of from about 40° C. to about 80° C., and wherein said strip is subjected, as the anode to an

electric current for a sufficient time so that 1-30 coulombs per square inch flow through said strip.

2. A process according to claim 1 in which the pH of the solution to be used in step (a) is between 6.0 and 9.0.

3. A process according to claim 1 in which the polyphosphate in steps (a) and (b) is selected from the group consisting of pyrophosphate, tripolyphosphate, and tetrapolyphosphate.

4. A process according to claim 3 in which the polyphosphate is sodium pyrophosphate.

5. A process according to claim 1 in which the concentration of polyphosphate is between 50-90 grams per liter.

6. A process according to claim 1 in which the hydroxycarboxylic acid is selected from the group consisting of citric, tartaric, glycolic, gluconic, and sugar acids.

7. A process according to claim 6 in which the acid is citric acid.

8. A process according to claim 1 in which the temperature of the electrolyte is maintained in step (a) in the range of approximately 40-80° C.

9. A process according to claim 8 in which the temperature is approximately 60-70° C.

10. A process according to claim 1 in which the soaking time in step (a) is 2-60 seconds.

11. A process according to claim 1 in which the current density J is maintained within the range J_{\max} and J_{\min} , in which $J_{\max} = .53(V_f - V_s)(Ct/10)$ and $J_{\min} = .36(V_f - V_s)$.

12. A process according to claim 1 in which the electrolyte is electrochemically regenerated.

13. A process according to claim 12 in which the current density is maintained in the range of 1 to 20 amps per square foot.

14. A process according to claim 13 in which the regeneration solution contains zinc and the zinc content of the metal deposited on the cathodes is given by the equation $Zn = 7.5(J_r - 4)$, where Zn is the percent zinc in the deposit; and J_r is the regenerator cathode current density in amperes per square foot and is in the range of approximately 4 to 10.

15. A process according to claim 14 where the copper content of the regeneration is at least 0.5 gram per liter.

References Cited

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