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MATERIAL FOR AND PROCESS OF PICKLING COPPER OR ITS ALLOYS

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This invention relates to the pickling of metal articles and has particular application to the acid pickling of copper and copper-containing alloys for the purpose of removing scale and producing a bright finish.

It is common practice to remove the oxide scale from articles composed essentially of copper and copper alloys, such as brass and bronze compositions, by dipping them in aqueous solutions of sulfuric or muriatic acid. Although these acids are adapted to remove certain scales, such as black cupric oxide scale and the oxides of alloying elements such as zinc and tin, they do not adequately remove any cuprous oxide scale, which is red and tends to leave the surface with an undesirable red coloration. Moreover, they do not act on copper rich surface areas, which are frequently formed as a result of preferential volatilization of the alloying element during annealing, and in general they tend to preferentially dissolve the alloying elements of the alloy instead of the copper, which further contributes to the poor or unsatisfactory color of the alloy.

To overcome the objectionable features of acid pickling baths of the above type, resort has been made to the use of aqueous solutions of ferric salts, such as ferric sulfate and ferric chloride, either alone or in combination with mineral acids, such as sulfuric or muriatic acid. Thus, solutions containing such salts are not only capable of removing scale in a satisfactory manner, but they tend to avoid the production of a reddish or copper rich surface and to remove any surface areas predominantly red in color resulting from the annealing or other heat treatment to which the metal is generally subjected. However, these baths also are objectionable, in that they tend to produce surfaces of a dull or dirty appearance, and at best do not form a smooth, shiny, natural appearing surface such as is required in the trade.

It is accordingly an important object of the invention to provide a pickling bath for copper or its alloys which not only removes oxide scales satisfactorily, but avoids the formation of red colorations and produces bright and smooth surfaces having an appearance which is more natural to the copper or alloy than that produced by mineral acids and/or ferric salts.

A further object of the invention is to provide a bath for pickling copper or its alloys which is capable of removing the dull or dirty appearance obtained as a result of preliminary pickling of the metal in other pickling baths.

Still further objects and advantages of the invention will appear from the following description and appended claims.

The invention relates in general to the pickling of copper or its alloys with acid reacting aqueous baths containing ferric salts, to which there has been added a substance capable of supplying organic anions, particularly aliphatic anions, either directly or by interaction with other ingredients of the bath. More specifically the invention is directed to the pickling of copper or its alloys with aqueous solutions of ferric salts, such as ferric sulfate or ferric chloride, containing relatively small amounts of organic acids, salts or esters, which act in combination with the ferric salts not only to remove scale, but to remove or prevent discoloration and produce a smooth and bright, natural appearing surface on the metal.

The copper alloys which may be successfully treated in accordance with the invention include such alloys as cartridge brass, high brass, low brass, leaded brass, red brass, rich low brass, the bronzes, gilding metal, and nickel silver. High nickel alloys, such as constantan, cupro-nickel, and Monel metal, and alloys containing silicon or beryllium, such as silicon brass, silicon bronze, and beryllium copper, may also be treated, but require somewhat larger amounts of pickling agents than the other copper alloys.

The organic agents which may be used for the purposes of this invention include a wide variety of acids, or their salts or esters. Among the substances which have been found to be most suitable may be mentioned such organic acids as citric, tartaric, acetic, adipic, lactic, glycollic, gluconic, succinic, malonic, dl malic, formic and benzoic acids, and their equivalent salts or esters. These substances are readily soluble in water, and in some instances are capable of producing the desired results when used in exceedingly small amounts. In general they are employed in amounts varying from about .1 to 10%, although in special instances, such as when cream of tartar is employed, it is possible to use as little as .001%. Preferably, however, they are used in amounts varying from .1 to 3%, as larger amounts do not show any appreciable increase in effectiveness.

The amount of ferric salt employed in the pickling operations may be widely varied. For example, it is possible to use anywhere from 1 to 50%. However, it is preferable from the standpoint of economy to use solutions containing not more than 10% of the ferric salt, ex-

cept in the case of high nickel or silicon alloys of copper, when amounts as high as 20% may be required. Solutions which are appreciably stronger than this are too viscous for quick drainage. Exceedingly weak solutions on the other hand require constant replenishment.

Although it is possible to obtain highly satisfactory results by pickling the metal in a single bath containing a ferric salt and one or more of the above organic addition agents, it is frequently desirable to employ a preliminary pickle, particularly when the surface of the metal being treated is covered with a relatively heavy scale. This preliminary pickle, commonly called a "pre-pickle", may consist of an aqueous solution of either mineral acid, preferably sulfuric or muriatic acid, or a combination of such an acid with a ferric salt, preferably ferric sulfate or chloride. By using a pre-pickle such as the above the descaling action is enhanced, and it is possible to employ a reduced quantity of the primary pickling or brightening agent.

The reagents used in the preliminary pickle may be present in quantities varying from about 1 to 50%. However, it is preferable to use the mineral acid in amounts varying from 5 to 15%, and the ferric salt in amounts varying from 5 to 20%. In the case of certain alloys, particularly those having silicon oxide scales, it is necessary to use hydrofluoric acid in the pre-pickle, which may be present in amounts varying from .1 to 5% together with a suitable amount of ferric salt.

A further understanding of the invention will be obtained from the following examples of baths suitable for the treatment of different alloys:

Example I

A low brass containing 85 parts of copper and 15 parts of zinc and having a scale which was unusually hard to remove was subjected for about 2 minutes to an aqueous pre-pickle containing 10% sulfuric acid at a temperature of 125° F. It was then pickled for about 5 minutes in an aqueous solution containing 9% of ferric sulfate and 0.1% of cream of tartar at 160° F. The metal, following the above treatment, had all of its scale removed and at the same time had a smooth and bright surface and an appearance entirely natural to brass.

Example II

The same kind of brass as in Example I was pre-pickled for about 2 minutes in an aqueous solution containing 10% sulfuric acid and 9% ferric sulfate at 125° F., and then pickled for about 2 minutes in an aqueous solution containing 9% of ferric sulfate and 3% of acetic acid at room temperature. Substantially the same beneficial results as in Example I were noted.

Example III

A high brass containing copper and zinc in the ratio of about 2 to 1 and having a scale which was relatively easy to remove was prepickled for about 2 minutes in a solution containing 10% of sulfuric acid and 9% of ferric sulfate at a temperature of about 140° F. and then immersed for about 2 minutes in a solution containing 9% of ferric sulfate and 0.5% of citric acid at room temperature. The brass treated in this manner was thoroughly descaled, and in addition had a smooth, bright, natural appearing surface.

Example IV

A high brass of the kind described in Example III was subjected for about 2 minutes to a preliminary pickle in an aqueous bath containing 10% of sulfuric acid at 140° F. and then pickled for about 3 minutes at room temperature in an aqueous solution containing 9% of ferric sulfate and 3% of acetic acid. The resulting brass was entirely free of scale and had a smooth, bright and natural appearance.

Example V

A sample of nickel silver was pre-pickled for about 2 minutes in an aqueous solution containing 10% of sulfuric acid and 9% of ferric sulfate at a temperature of about 140° F., and then immersed for about 4 minutes in an aqueous pickling bath containing 9% of ferric sulfate and .5% of adipic acid at room temperature. After treatment in the above manner the alloy was free of scale and had a smooth bright and natural appearance.

Example VI

A sample of silicon bronze was subjected for about 1 minute to the action of an aqueous pre-pickle containing 18% of ferric sulfate and 2% of hydrofluoric acid at 160° F., and then pickled for about 3 minutes in an aqueous solution containing 9% of ferric sulfate and 1% of cream of tartar at 160° F. The alloy treated in the above manner was smooth and bright and had an appearance natural to bronze.

It should be understood that the above examples are illustrative only, and that wide variations may be made not only in the amount and kind of pickling or brightening agents used, but in the time of treatment and temperature of the bath. Different alloys require different amounts of pickling or brightening agents, and different immersion periods and bath temperatures, depending on the nature of the alloy and the kind of annealing or other treatment to which it has previously been subjected. In general, however, it is not necessary to employ more than about 20% of the ferric salt and about 3% of the organic acid or other brightening agent in the primary pickling bath, as larger amounts do not appreciably increase the effectiveness of the baths and in the case of the ferric salts they frequently result in solutions which are too viscous for efficient drainage.

The use of a preliminary pickle is not always necessary, as frequently satisfactory results may be obtained with a single immersion in baths containing ferric salts and organic acid or like brightening agents. When a preliminary descaling bath is employed, however, it is usually not necessary to employ more than about 10% of the mineral acid and/or the ferric salt, except in the case of silicon-containing alloys and high nickel alloys, which require somewhat larger amounts of ferric salts and, in the case of silicon alloys, a small amount of hydrofluoric acid.

The temperature of the bath may be varied between its freezing and boiling points, i. e., maintained at any intermediate point therebetween. Although in general more marked results are obtained by increasing the temperature of the bath, and also the time of immersion, it is usually not necessary to employ a temperature much above about 160° F., and in the case of high brasses and other easily pickled copper alloys it is sufficient to employ room or only slightly elevated temperatures. Moreover, baths

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containing certain of the agents, such as acetic acid, should not be heated in any case.

The time of immersion of the copper or alloy in the baths may be varied from a few seconds, in the case of easily pickled stock, to 30 minutes or more, as required. In general, however, it is not necessary to immerse the stock for more than about 4 or 5 minutes, and when agitation of the bath is resorted to, even less time is usually sufficient.

By using pickling baths such as those described herein in the pickling of copper or its alloys, it is possible not only to thoroughly remove oxide scale, but to remove predominately reddish areas resulting from preferential volatilization during annealing and to prevent general red coloration resulting from preferential dissolution during pickling. Moreover, the baths or solutions of this invention tend to produce smooth and shiny surfaces which have an appearance natural to the particular alloy being treated.

It is believed that the beneficial brightening effects resulting from the addition of the organic acids, esters or salts is related to the ability of these substances to form complexes with metallic ions. The exact cause of the effectiveness of the organic addition agents in improving the action of pickling baths containing ferric salts is unknown, however, and it is not intended to predicate the invention on any theory or belief such as the above.

Where reference is made herein to the per cent of substance or agent employed in the bath, this is intended to mean the number of grams present or added per 100 cc. of solution. Also, where use is made of the term "primary pickling bath," it is to be understood that this refers to the baths containing ferric salts and organic addition agents of the type described, i. e. to those baths which may be used either alone or subsequent to a preliminary pickle to obtain the objects and advantages of the invention.

It is also to be understood that the invention is not limited in its application to the details described herein, since the invention is capable of other embodiments and of being practiced or carried out in various ways. Also it is to be understood that the phraseology or terminology employed herein is for the purpose of description and not of limitation, and it is not intended to limit the invention claimed herein beyond the requirements of the prior art.

I claim:

1. An aqueous acid reacting bath for pickling copper or its alloys containing water-soluble ferric ions and organic anions.

2. An aqueous acid reacting bath for pickling copper or its alloys containing ferric ions and organic aliphatic anions.

3. An aqueous bath for pickling copper or its alloys containing a ferric salt and an organic aliphatic acid.

4. An aqueous acid reacting bath for pickling copper or its alloys containing a ferric salt and a salt of an organic aliphatic acid.

5. An aqueous acid reacting bath for pickling copper or its alloys containing ferric sulfate and organic anions.

6. An aqueous bath for pickling copper or its alloys containing ferric sulfate and citric acid.

7. An aqueous acid reacting bath for pickling copper or its alloys containing ferric sulfate and cream of tartar.

8. An aqueous bath for pickling copper or its alloys containing ferric sulfate and acetic acid.

9. The method of pickling copper or its alloys which comprises subjecting the same to the action of an aqueous acid reacting bath containing water-soluble ferric ions and organic anions.

10. The method of pickling copper or its alloys which comprises subjecting the same to the action of an aqueous acid reacting bath containing a ferric salt and organic aliphatic anions.

11. The method of pickling copper or its alloys which comprises subjecting the same to the action of an aqueous acid reacting bath containing ferric sulfate and organic aliphatic anions.

12. The method of pickling copper or its alloys which comprises immersing the same in an aqueous bath containing a mineral acid, and then subjecting it to the action of an aqueous acid reacting bath containing water-soluble ferric ions and organic anions.

13. The method of pickling copper or its alloys which comprises immersing the same in an aqueous bath containing a ferric salt and a mineral acid, and then subjecting it to the action of an aqueous acid reacting bath containing water-soluble ferric ions and organic anions.

14. The method of pickling copper or its alloys which comprises immersing the same in an aqueous bath containing not more than about 20% of a ferric salt and not more than about 15% of a mineral acid, and then subjecting it to the action of an aqueous acid reacting bath containing not more than about 20% of a ferric salt and not more than about 3% of organic aliphatic anions.

15. The method of pickling copper or its alloys which comprises immersing the same in an aqueous bath containing ferric sulfate and sulfuric acid, and then subjecting it to the action of an aqueous bath containing ferric sulfate and citric acid.

16. The method of pickling copper or its alloys which comprises immersing the same in an aqueous bath containing ferric sulfate and sulfuric acid, and then subjecting it to the action of an aqueous acid reacting bath containing ferric sulfate and cream of tartar.

17. The method of pickling copper or its alloys which comprises immersing the same in an aqueous bath containing ferric sulfate and sulfuric acid, and then subjecting it to the action of an aqueous bath containing ferric sulfate and acetic acid.

18. An aqueous acid reacting bath for pickling copper or its alloys containing a ferric salt and an ester of an organic aliphatic acid.

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