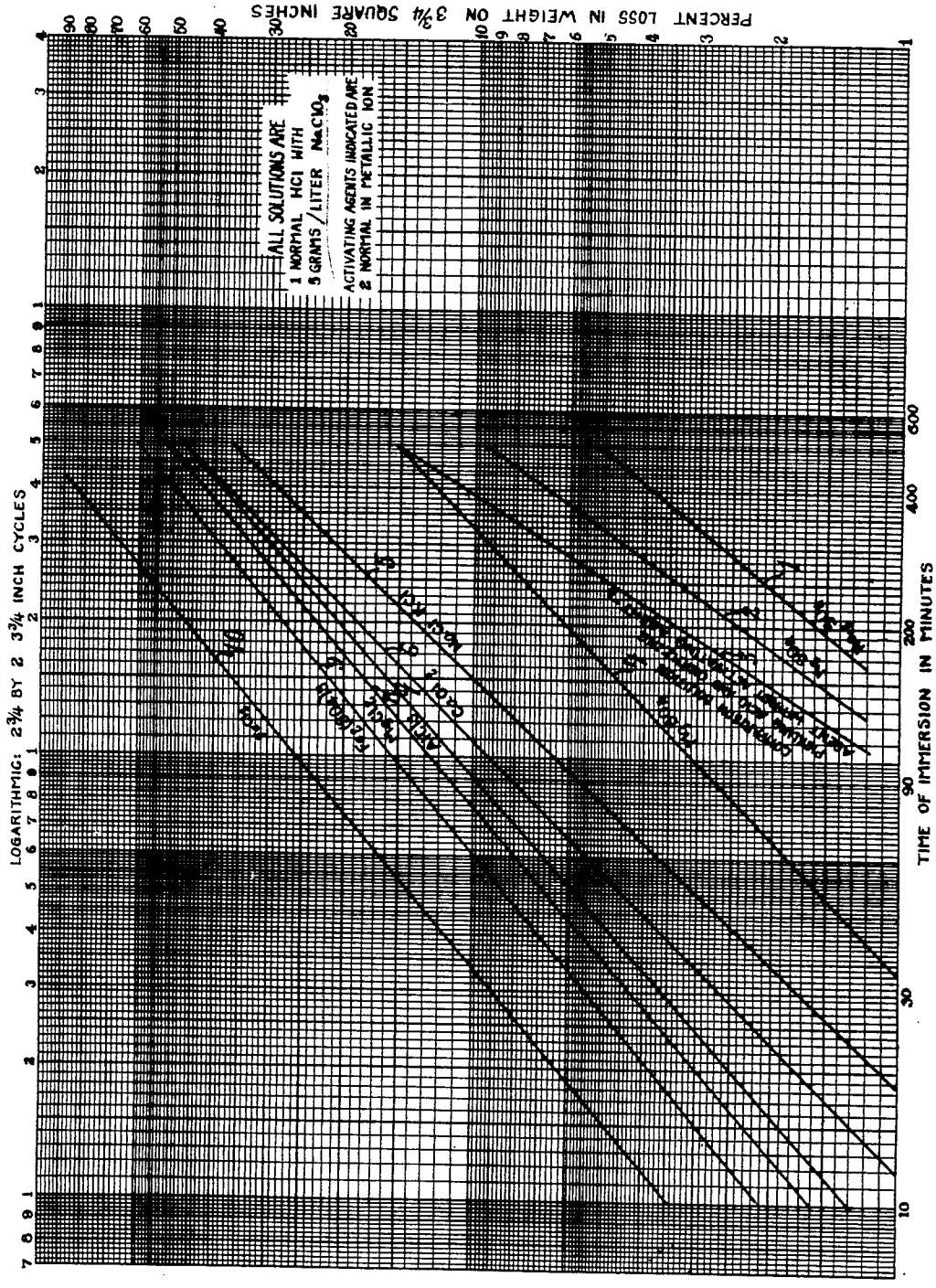
100

Exa

Aug. 13, 1940. M. L. WOOD 2,211,400

PICKLING SOLUTION FOR COPPER-BASE ALLOYS

Filed Aug. 10, 1938



Inventor
By Maurice L. Wood
Seymour Earle Nichols
Attorneys

100 Patented Aug. 13, 1940 2,211,400

UNITED STATES PATENT OFFICE

2,211,400

PICKLING SOLUTION FOR COPPER-BASE ALLOYS

Maurice L. Wood, Thomaston, Conn., assignor to Chase Brass & Copper Co. Incorporated, Waterbury, Conn., a corporation

Application August 10, 1938, Serial No. 224,196

2 Claims. (Cl. 148—8)

This invention relates to an improvement in pickling or scale-removing solutions, and more particularly to pickling or scale-removing solutions for the treatment of copper-base alloys, the surfaces of which have become scaled as a result of annealing or other heat treatments.

When sheets, rods, wires, etc., formed of copper-base alloys, are annealed or subjected to other heat treatments, the surfaces of such articles become coated with a layer of scale composed mainly of oxides but which frequently also includes redeposited metallic films, sulphides, carbonaceous material, etc. Such scale must be removed not only to improve the appearance of the material, but to render the material more workable and render it suitable for welding, tinning, plating, etc. The exact chemical composition of the layer of scale, above referred to, will, of course, vary considerably with the composition of the base metal, and also, to a considerable degree, with the atmosphere surrounding the alloys while they are at an elevated temperature. In copper-zinc alloys, either binary or those of a more complex character, the zinc has a tendency to diffuse to the surface of the alloy when the latter is at elevated temperatures and especially when the zinc is in excess of approximately 20%. The resultant scale is composed predominantly of zinc oxide.

In alloys containing from about 10% to about 20% of zinc, the reaction occurring at elevated temperatures is a very complicated one, and the composition of the scale varies considerably with the temperature maintained and the character of the surrounding atmosphere. In copper-zinc alloys containing less than approximately 10% zinc, the resultant scale occurring as a result of annealing or other heat treatments has substantially the same proportions of metals as existed in the base or body material. Furthermore, when small amounts of certain metals are present in addition to the copper and zinc referred to, such, for instance, as silicon or aluminum, etc., a relatively-larger proportion of these latter metals is usually found to be present in the scale than in the base or body alloy, thus indicating the diffusion of these metals to the surface of the article when the same is at an elevated temperature.

In the case of certain of the more complex copper-base alloys, and especially those containing silicon, great difficulty is usually encountered in completely removing the scale in a manner which will produce a uniform smooth-textured surface, by means of ordinary pickling or scale-removing solutions. A somewhat similar difficulty, though not as extensive, is met in connection with the pickling of high-nickel-content copper-base alloys, since here the scale is softened and somewhat loosened by ordinary pickling solutions, but is not effectively removed.

By way of example, it may be stated that heretofore when attempting to remove particularly tenacious or recalcitrant scales containing silicon, it has been customary to employ in succession two, three, or even four solutions in addition to mechanical scrubbing.

In addition to the above, further difficulties in the treatment of copper-base alloys usually result from the particular form, thickness, tenacity and composition of the scale referred to, depending largely upon conditions of contact between contiguous convolutions or layers of a coil of wire or rod or of flat bars, strips, or the like, while under treatment. For instance, where two adjacent layers are annealed in relatively-tight contact at one point and are relatively well separated at some other point, a marked difference in the scale formation at these two positions usually results. Under such conditions, the employment of ordinary pickling or bright dipping solutions usually results in the metal being preferentially attacked at one zone as compared to the other zone, and the differences initially apparent in the character of the scale become exaggerated rather than decreased. In particular, it has been found that the difficulties such as those just referred to are most troublesome in connection with the scale appearing upon silicon-bearing copper-base alloys.

Another difficulty frequently encountered in the pickling of copper-base alloys to remove the scale therefrom is the difficulty due to the redeposition of a film of metallic copper on the base or body metal of the article being treated. This redeposition of copper may, for instance, be due to the presence of a more electropositive metal in the pickling solution, such, for instance, as iron. This redeposited film of copper is not readily attacked by the ordinary non-oxidizing pickling solution, and, therefore, is not removed to a satisfactory degree. Furthermore, the said redeposited film of copper acts as a shield or stop-off which prevents the complete and satisfactory removal of oxide, etc, which may be located beneath the said film, or which may be admixed with it.

One of the objects of the present invention is to provide a superior pickling solution for the

treatment of copper-base alloys, which will produce upon such alloys a uniform fine-textured surface substantially independently of variations in the type and amount of scale initially present on such alloys.

Another object of the present invention is to provide a superior pickling solution for the treatment of copper-base alloys which will guard against the harmful effects of redeposited film of metallic copper.

A further object of the present invention is to provide, in combination with the primary pickling acid or acids, an oxidizing agent which will effectively oxidize redeposited surface films of copper.

A still further object of the present invention is to provide a superior pickling solution for the treatment of copper-base alloys which will include, in addition to the primary pickling acid or acids, an activator or accelerator which will act to increase the activity of the primary pickling acid.

Still another object of the present invention is to provide a superior pickling solution of the character referred to, which will effectively perform the scale-removing function of complex scales without requiring the multiplicity of steps and solutions common in the art for this purpose.

Another object of the present invention is to provide a superior pickling solution for the removal of scale from copper-base alloys, which is capable of forming complex ions tending to increase the solubility of the solution product and, therefore, increase the life of the pickling solution.

A further object of the present invention is to provide a pickling solution of the character referred to, which will effectively remove tenacious scale containing such metals as silicon, nickel, etc., by an action which is both chemical and mechanical in its nature.

A still further object of the present invention is to provide a superior pickling solution for copper-base alloys which will economically provide upon such alloys a surface of such character as will facilitate resistance-welding of parts made from the said alloys.

With the above and other objects in view, as will appear to those skilled in the art from the present disclosure, this invention includes all features in the said disclosure which are novel over the prior art.

The accompanying drawing is a logarithmic curve-sheet or graph illustrating in particular the effects achieved by the addition of accelerating or activating agents as compared to pickling solutions without such agents.,

As will appear more fully from the following, the present invention contemplates a pickling solution embodying three main features, namely (*a*) a primary pickling acid or a combination of such acids (preferably inorganic), (*b*) an oxidizing agent or a combination of such agents, and (*c*) an activating or accelerating agent or a combination of such agents. The designation "activating" agent or "accelerating" agent has been adopted for the purpose of clarity of description, since no pretense is here made that the actual modus operandi of such agents are fully understood, save that their beneficial effects have been clearly determined.

The principal function of the pickling acid constituent of the present improved pickling solution is as an agent for effecting the dissolution and hence the removal of the scale (mainly oxides or the like) originally on the surface of the base-metal and/or the dissolution and hence the removal of the products of the reaction of the oxidizing agent on the base-metal itself or on metallic constituents (such as redeposited metallic films) of the scale.

One of the principal functions of the oxidizing agent of the present invention is to oxidize metals to form compounds capable of being dissolved by the acid. It might be mentioned that the metals involved when in the metallic state are practically insoluble in simple non-oxidizing acid solutions.

Another of the principal functions of the oxidizing agent is to maintain the metallic ion of the activating agent in its state of highest valency (where it has more than one valence), that is, in the state of highest oxidation.

One of the principal functions of the activating or accelerating agent is to increase the activity and therefore the rate of reaction of the pickling acid itself. In certain cases, but not necessarily in all, the activating agent may also perform the function of an oxidizing agent, but in all such cases its principal function is nevertheless that of activating the pickling acid constituent rather than oxidizing metal.

Preferably, the three features of the pickling solution of the present invention should embody all of the following characteristics, though it is to be understood that all of the characteristics listed are not essential.

Pickling acids

(*a*) From the standpoint of maximum activity and minimum cost, the acid or combination of acids (sometimes singularly and collectively referred to herein as "pickling acid") preferably should be inorganic, though organic acids may be employed.

(*b*) The acid or combination of acids should be such that the cupric salts and the cuprous salts (if formed), and the salts of the other metals in the alloys, are readily soluble in the solution.

(*c*) The acid constituent or constituents should have high chemical activity.

(*d*) The acid constituent (whether formed of a single acid or a combination of such acids) should be highly ionized in solutions.

(*e*) The said acid or acids should preferably, though not necessarily, have a monovalent acid radical.

By way of example, it has been found that hydrochloric acid and sulphuric acid possess to the proper degree the preferred properties above referrred to.

Oxidizing agents

(*a*) The oxidizing agent or agents (sometimes singularly and collectively referred to herein as "oxidizing agent") should have a high oxidation potential, that is to say, higher than that necessary to oxidize copper to the cuprous or cupric states, or to oxidize cuprous oxide to cupric oxide. The oxidation-reduction potential should preferably be in excess of about 0.51 volt referred to the hydrogen-hydrogen ion couple as zero. When other metals are present in the scale in any considerable amount, the oxidizing agent or agents should have the capacity for similarly oxidizing such other metals.

(*b*) The oxidizing agent or combination of oxidizing agents should be readily soluble in the acid component.

(*c*) The oxidizing agent or agents should be

such that all the reaction products thereof will be readily soluble in the pickling solution.

(*d*) The oxidizing agent or combinations thereof should be chemically stable prior to their addition and use in the pickling solution.

Among the materials suitable for use as oxidizing agents in accordance with the present invention, the following may be mentioned for purpose of illustration: chlorates or perchlorates of alkali or alkaline earth metals, peroxides, such, for instance, as hydrogen peroxide, and persulphates, such, for instance, as sodium persulphate.

Halogens when used as oxidizing agents may be added in the gaseous form or generated by the passage of an electric current between suitable electrodes when the solution contains hydrochloric acid or chlorides or bromides from other sources.

Similarly, in solutions containing iron or cobalt salts as activators, an electric current can serve as an oxidizing means by reoxidizing the ferrous ions to ferric ions and cobaltous ions to cobaltic ions, as some of these higher valence ions are reduced during the dissolution of metal. Although the ferric and cobaltic ions are themselves oxidizing, their chief function is nevertheless definitely that of an activating agent.

It should also be noted that under certain conditions the pickling acid as above described might also perform the function of an oxidizing agent; that is, the acid itself might be oxidizing. Examples of such would be nitric acid or hot strong sulphuric acid.

Activating or Accelerating Agents

(*a*) The activator or accelerator or combinations of the same (sometimes singularly and collectively herein referred to as "activating agent") should preferably, though not necessarily, have the same acid radical as the pickling acid constituent itself.

(*b*) This agent or combination of agents should preferably, though not necessarily, have a high valence, i. e., a salt of a bivalent metal would have a greater activity and, therefore, be preferable to a monovalent salt. For the same reason, a salt of a trivalent metal is preferable to one of a bivalent metal.

(*c*) The activating or accelerating agent or agents should have a high degree of solubility in the pickling solution used in combination therewith.

(*d*) The reaction products of the activators or accelerators should have a high degree of solubility in the solution.

(*e*) Preferably, but not necessarily, the activating or accelerating agent or agents employed should in itself or in themselves be capable of discharging an oxidizing action on the scale formation and, therefore, be capable of aiding the direct action of the oxidizing agent or agents as such.

(*f*) Either neutral or acid salts are suitable activators.

(*g*) The oxidation-reduction potential, if any, should be less than the oxidation-reduction potential of the oxidizing agent.

By way of example of suitable activating or accelerating agents, the following may be mentioned:

Salts of univalent metals:

Lithium chloride
Potassium chloride
Sodium chloride
Sodium sulphate
Ammonium chloride
Ammonium sulphate

Salts of bivalent metals:

Calcium chloride
Magnesium chloride
Magnesium sulphate
Barium chloride
Zinc chloride
Strontium chloride

Salts of trivalent metals:

Ferric chloride (oxidizing as well as activating)
Aluminum chloride
Aluminum sulphate
Ferric sulphate (oxidizing as well as activating)
Cobaltic sulphate (oxidizing as well as activating)

Salts of quadrivalent metals:

Ceric sulphate (oxidizing, as well as activating)

The constituents herein referred to may be combined in almost innumerable ways and proportions. Generally speaking, the pickling acid (or combinations of the same, also included in the term "pickling acid") may fall within the range from about 2% to more than 20% by volume; the oxidizing agent (or combinations of the same, also included in the term "pickling acid") from about 0.1% to about 25% by weight; and the activating agent (connoting also combinations of the same) from about 0.25% to about 20%.

The following examples of complete pickling solutions embodying the present invention, are illustrative only and not restrictive:

No.	Acid (commercial purity by volume in water)	Oxidizing agent (by weight)	Activator (by weight)
1	3% hydrochloric	0.1% sodium chlorate	3% ferric chloride.
2	3% hydrochloric	0.5% sodium chlorate	10% ammonium chloride.
3	10% hydrochloric	0.25% sodium chlorate	5% ferric chloride.
4	10% hydrochloric	0.15% calcium chlorate	7% ferric chloride.
5	7% hydrochloric	0.35% ammonium persulphate	8% ferric chloride and 4% magnesium sulphate.
6	6% sulphuric	0.15% potassium chlorate	9% ammonium sulphate.
7	15% sulphuric	0.2% hydrogen peroxide	6% ferric sulphate and 6% aluminum chloride.
8	20% sulphuric	0.35% sodium chlorate	7% ferric chloride and 10% sodium chloride.
9	10% sulphuric	0.2% ammonium persulphate	10% ferric sulphate and 5% ferric chloride.
10	5% hydrochloric	0.25% hydrogen peroxide	4% ammonium chloride and 6% calcium chloride.
11	8% hydrochloric	0.4% calcium chlorate	10% ferric chloride and 5% aluminum chloride.
12	7% hydrochloric	0.25 sodium hypochlorite	8% ferric sulphate and 6% ammonium sulphate.
13	6% hydrochloric + 4% sulphuric	Chlorine (added in gaseous state to continuously form appreciable amounts of hypochlorus acid).	7% ferric chloride.
14	10% hydrochloric	0.1% sodium chlorate and 0.35% ammonium persulphate.	10% ferric sulphate and 5% ferric chloride.

When ferric salts are used as activating agents, such salts also act in part as oxidizing agents and may be repeatedly added as such to the pickling solution when necessary, or such salts may be continuously regenerated either by electrolytic oxidation or by the addition of other oxidizing agents as, for instance, sodium chlorate, in which latter case, the ferric salt would really act as an oxygen carrier. In either such event, the cost of maintaining such oxidizing agent may be materially less than were the ferric salt alone to be relied upon as an oxidizing agent.

By way of example, let it be considered that the copper-base alloy being pickled is one containing approximately 77% copper, 22% zinc and 1% silicon.

Under these conditions, when the improved pickling solution of the present invention is employed for the removal of scale from such an alloy as that above referred to, the scale will include under ordinary conditions cuprous oxide, cupric oxide, zinc oxide, and silicon dioxide.

As the scale removing takes place, the oxidizing agent acts to convert certain of the cuprous oxide to the cupric oxide state and further acts upon the base metal itself to a measurable degree to convert the same into oxide forms. The primary pickling acid is thus enabled to more readily dissolve the scale when the same is oxidized to the cupric stage and also to dissolve portions of the surface of the base metal itself to minimize pittings, scale marks, etc., when such base metal is, as described, oxidized by the oxidizing agent or agents. The zinc oxide present in the scale will be quite readily soluble in the primary pickling acid and the zinc of the base metal will be oxidized by the oxidizing agent so as to become readily soluble in the primary pickling acid.

In such cases as a redeposition of copper should occur upon the scale, such redeposited copper will be oxidized and dissolved in the solution.

By the actions above described, the remaining silicon dioxide becomes so loosened as to be readily removable by agitating the copper-base articles in the bath, or by mechanical scrubbing where necessary, but in any event, the normally-tenacious film of silicon dioxide is rendered quite tractable.

With respect to the action of the activating agent or agents, no pretense is here made that the actual modus operandi of such agent or agents is fully understood, save that their beneficial effects have been clearly determined. It may here be acknowledged that according to some accepted chemical theories, the addition of the activating agent or agents to the solution containing the primary pickling acid or acids and the oxidizing agent or agents should deleteriously affect the result, but contrary to such chemical theories, the effect actually is directly the reverse, as may be readily seen by reference to the accompanying drawing, which clearly indicates the beneficial effects of the activating agents.

The graph shown in the accompanying drawing indicates the relative rate at which the metal of the copper-base alloy is taken into solution and, hence, is similarly indicative of the efficiency of pickling solutions of the present invention in cleaning scale, etc., from copper-base alloys.

The graph or curve sheet further shows quantitatively the effect of added salts or activators on the rate of attack on a silicon brass (77% Cu—22% Zn—1% Si) in an acid solution with an oxidizing agent. The individual solutions have the same equivalent or reacting weights of the various salts used. It should be noted that salts of mono-, bi- and trivalent metals are used, and that they range from those of the alkaline metals (sodium and potassium) through the alkaline earths (magnesium and calcium) to the heavy metals (iron and aluminum).

The following general conclusions may be drawn from a study of the curves shown in the diagram:

(*a*) The chloride of any metal whether it be alkali, alkaline earth or heavy metal, is invariably more effective when used as an activator in hydrochloric acid solution than is the sulphate of the same metal. This effect is illustrated by the relative position of curve **5** and the positions of curves **1** and **2**; by the position of curve **8** and that of curve **4**; and by the position of curve **10** and that of curve **9**.

(*b*) The higher the valence of the metallic ion used for a given negative ion, the greater the effect (with the exception of aluminum chloride). This effect is illustrated by the successively higher positions occupied by curve **5**, curves **6** and **8**, and curve **10**. The relative positions of curve **7** and curve **8** illustrate a slight exception to this general conclusion.

(*c*) All of the added activating agents used, markedly accelerate the action of the base solution except the sulphates of potassium and sodium. As explained in more detail below, the apparently anomalous behavior of these salts may possibly be due to differences in hydration of the silica. This effect is illustrated by the relatively-higher positions occupied by curves **4** to **10** inclusive as compared to the position of curve **3** and the exception to this general rule is illustrated by the relatively-lower positions of curves **1** and **2** compared to that of curve **3**.

The tests represented in the accompanying drawing were made on identical specimens suspended in the various solutions indicated. The composition of the base-metal was substantially 77% copper, 1% silicon, remainder zinc. By a cam arrangement, the specimens were alternately raised and lowered to give the same amount of stirring to all the specimens. Exact control of stirring is important in such tests on silicon-copper alloys because of the largely mechanical removal of the siliceous film. Loss of weight of the specimens was selected as the basis of comparison.

By way of example, a generally used commercial practice requires twenty minutes for the removal of the black scale which is largely cupric oxide. With some of the activated solutions of the present invention, the same result is obtained in one to two minutes and the whole pickling process takes only about eight minutes. After the removal of the black scale, the process is largely the formation of a gelatinous film with the silica in the scale and slight dissolution of the base-metal. By the combined action of mechanical agitation and slight dissolution of the base-metal, the gelatinous film of hydrated silica is removed.

In these solutions of the same equivalent concentrations, salts with higher valence are more effective. Additions of sulphates to HCl solutions are not as effective as the same concentration of the same positive ion added as a chloride. This point is very important in its relationship to the common ion effect which, according to classical physical chemistry, might be expected to give exactly the opposite result.

The fact that so many salts of widely differing character give an increased rate of dissolution shows that the general principle of adding a salt as an activator is experimentally demonstrated. In fact, this same effect has been amply demonstrated by large-scale commercial practice wherein marked improvements in the quality, lowering of pickling time and cost in the treatment of copper-base alloys have been attained by the use of pickling solutions of the present invention. Not only has a marked improvement in the appearance and uniformity of the surface of the metal resulted, but the cost of the operation has been found to be but a fraction of the cost incident to the use of the best pickling solutions of the prior art.

The effect of variations of valence of the activating agents is in general clearly shown. The fact that aluminum chloride is somewhat less effective than magnesium chloride may be due to differences in hydration of the silica or some specific effect of the ion; but the solution rate is greater than for calcium, sodium or potassium chlorides. Ferric salts are more energetic in their action, apparently because the ferric ion is an oxidizing agent as well as an activator. The lower rate of dissolution effected by solutions containing sulphates as activating agents, as compared to solutions containing chlorides as activating agents, may also be due to differences in hydration of the silica. This may be inferred from the appearance of the gelatinous film developed during the pickling treatment, which appearance has been found to vary in different solutions.

The invention may be carried out in other specific ways than those herein set forth without departing from the spirit and essential characteristics of the invention, and the present embodiments are, therefore, ot be considered in all respects as illustrative and not restrictive, and all changes coming within the meaning and equivalency range of the appended claims are intended to be embraced therein.

I claim:

1. The method of removing scale from copper-base alloys comprising subjecting a copper-base alloy to the simultaneous action in water of: a pickling acid dominantly of hydrochloric acid; an oxidizing agent having the power to oxidize copper to the cuprous state and selected from the group consisting of chlorates, persulphates, peroxides and hypochlorites; and an activating agent selected from the group consisting of chlorides of the metals calcium, iron, magnesium and aluminum.

2. The method of removing scale from copper-base alloys comprising subjecting a copper-base alloy to the simultaneous action in water of: approximately 0.5% to 12% by weight of hydrochloric acid; an oxidizing agent comprising a substantial amount of sodium-chlorate not materially in excess of about 1% by weight; and an activating agent comprising approximately 0.25% to 20% by weight of ferric-chloride.

MAURICE L. WOOD.