COPPER AND ALUMINUM PICKLING
Leslie E. Lancy, Ellwood City, Pa., assignor to Lancy Laboratories, Inc., Zelienople, Pa., a corporation of Pennsylvania
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8 Claims

ABSTRACT OF THE DISCLOSURE
A cleaning or pickling solution and method for brightening copper or aluminum surface workpieces by removing metal oxides in the nature of copper oxides. In the aqueous pickling or cleaning composition, uses is made of an inorganic sulfuric or sulfamic acid or equivalent acid salt (sodium acid sulfate), of hydrogen peroxide, and of an organic stabilizer compound containing at least two functional groups that are sterically unhindered by themselves and by other groups and that carry polar hydrogen atoms, that is, an organic compound employed to restrain breakdown of the peroxide. For maximum brightness and for cleaning aluminum surface workpieces, a chelating compound or agent may also be used in the solution.

CROSS REFERENCE
This is a continuation-in-part of my co-pending application No. 451,278, entitled "Copper Pickling," filed Apr. 27, 1965, now abandoned.

BACKGROUND OF THE INVENTION
This invention relates to the cleaning or pickling of aluminum, copper, copper alloy and copper plated metals and particularly, to the cleaning of surface portions of metal which have been altered by or subjected to the action of a copper or copper alloy member. A phase of the invention relates to the removal of copper oxides and the brightening of metal as in the form of a plate or strip workpiece which has been processed, for example, by being subjected to a hot treatment, such as a hot rolling operation. The purpose is to remove scale and oxides, such that the strip or plate, after being hot rolled, may be suitably conditioned for further forming, such as by cold drawing or cold rolling.

There are two types of copper oxides which are recognized as being formed in hot processed copper containing or surfaced members. They are so-called black or cupric oxide (CuO) or red or cuprous oxide (Cu₂O). It has been found that the cuprous oxide forms mainly at lower temperatures and represents an intermediate stage in oxide formation. Basically, the dense black scale produced, for example at hot rolling temperatures, is cupric oxide.

Heretofore, it has been customary to remove the black cupric oxide scale before further processing the metal sheet or strip by introducing it into a pickling solution containing about 10 to 30% by volume of sulfuric acid and having a temperature in the neighborhood of about 120° to 180° F. The black oxide is completely soluble in such a pickling solution, but I have found that the red copper or cuprous oxide is nearly insoluble. When it is necessary to provide a clean product, it has been customary to add an oxidizing agent, such as chromic acid, to the sulfuric acid pickling solution. The chromic acid has a solvent action on the cuprous oxide, but when reacting, is reduced to the trivalent chromium salt and thereafter loses its effectiveness. Although the solution may be rejuvenated for a while by the addition of chromic acid, I have found that the life of the pickling acid solution is limited. The acid solution has to be dumped and a new sulfuric acid solution with chromic acid additions made up.

Another disadvantage of a solution of the above type, is that it is impossible to remove dissolved copper from the solution through electrolysis, since the chromic salts inhibit cathode deposition of the copper. Thus, the acid is not only wasted and neutralized, as required in waste treating the acid before it can be discharged into a sewage system, but the dissolved copper content is lost from the standpoint of simple reclamation or recovery. Since chromic acid is highly toxic, it contaminates the rinse waters after pickling and the waters also require meticulous waste treatment which further adds to the cost of the operation.

Summarized, the invention relates to the provision and use of cleaning or pickling solutions that will enable the obtaining of bright surfaces on copper, copper containing alloy, and aluminum workpieces which are effectively devoid of metal oxides in the nature of copper oxides. It involves the discovery that there is a tendency, even during an acid pickling or cleaning operation, for cuprous copper oxide to form and adhere to the surface of the workpieces. The invention not only eliminates such a normal tendency, but also makes practical and economical utilization of hydrogen peroxide in a copper cleaning solution by limiting or restricting its breakdown to that which is essential to the cleaning operation and by making it more effective in its use. In this connection, the cleaning or pickling is accomplished by a new solution composition and utilization of dissolved ingredients that assures a bright metal surface through the agency of simple procedure in an economical manner to assure a bright surface, irrespective of whether copper predominates or is present in minor amounts.

It has thus been an object of the invention to devise a new approach to the cleaning or pickling of copper metals or copper or copper alloy-surfaced metals to eliminate the problem which has heretofore been presented in accordance with conventional processing.

Another object of the invention has been to provide a pickling or cleaning solution which will effectively and efficiently remove all the copper oxides from a metal surface containing copper or copper alloy metal and meet the problem which has been economically recovered.

Another object of the invention has been to discover the factors which enter into the presence of copper oxides on a copper or copper alloy metal surface and to develop an improved, simplified and economical process for removing them;

A further object of the invention has been to devise a process for removing copper oxides from a copper or copper alloy metal surface in accordance with which the dissolved copper content of the pickling or cleaning solution may be economically recovered.

A still further object of the invention has been to develop a new and improved solution for removing copper oxides and new and improved procedure employing such solution, in accordance with which the solution may be rejuvenated and will have a substantially continuous useful life.

These and other objects of the invention will be apparent to those skilled in the art from the disclosure including the claims.

In the drawing, the figure is a somewhat diagrammatic fragmentary section illustrating a workpiece with copper oxides thereon. This, but a typical metal workpiece 10 that is to be processed in accordance with the invention to remove typical adherent cupric oxide platelets 11 and cuprous oxide powder 12. It will be noted that the
cupric oxide 11 tends to enclose, entrap or hold the cuprous oxide 12 along the immediate surface area of the workpiece 10.

In studying the problem involved, it has been determined that the red copper (cuprous) oxide, not only appears on the surface of the metal after its hot treatment, but there is a tendency for it to increase by progressive formation thereafter. It has been found that while a small quantity of cuprous oxide may be present in the scale film, when the black or cupric oxide scale is dissolved, an additional electrochemical reduction reaction appears to take place which greatly increases the quantity of cuprous oxide dust that remains on the pickled surface. The cupric oxide dust in the form of a film remains on the pickled copper surface after a sulfuric acid pickle. Normally, at least some of the cuprous oxide that is entrapped by the black scale would be lifted off the surface as the black scale is dissolved, and would flow as a sludge to the bottom of the pickling tank, if it were not for the above-mentioned electrochemical reduction reaction. However, it has been found that, as a result of the reaction, the quantity of red oxide greatly increases and that this is the reason why there is more on the surface after the acid cleaning reaction.

It has been further determined that the heavier the black scale layer, the heavier the red copper oxide dust that remains on the surface after pickling, using a conventional sulfuric acid solution. The phenomenon involved can be explained as a reduction by the metallic copper, involving an electrochemical reduction reaction by the metallic copper, and the cupric oxide under the acid influence corresponding to an electrochemical cell. That is, the cupric ions react with metallic copper to form the cuprous ions, and the cupric oxide is, itself, reduced in the process to cuprous oxide. This reaction is as follows: 

$$\text{Cu}^{++} + \text{Cu}^+ = 2 \text{Cu}^+$$

The equation of Table I indicates that the cupric ion (Cu^{++}) in contact with metallic copper (Cu^+) will be reduced to a cuprous ion and that the copper metal is oxidized to the cuprous ion. The one electron lost by the metallic copper is received by the cupric ion. The lower part of the equation (plus and minus electrons) indicates that the cupric electron (Cu^{++}) has received an electron and that the metallic copper (Cu^+) has lost an electron.

Although it would appear to be detrimental if the cuprous oxide remaining on the pickled metal surface was originally there, was formed during the hot rolling operation, was partially formed during the hot rolling, or was fully or partially formed or created during the pickling operation, itself, a solution to the problem involved has been provided in view of the startling discovery of the fact that most of the cuprous oxide is formed during the acid cleaning process. Research into the mechanism of the cuprous oxide formation and as to reasons for the formation of the cupric oxide has enabled the development of a radically different solution which will meet the problem.

Having thus recognized that the metal surface contributes to the formation of the red copper oxide dust, even during the pickling operation, it has been found that it is unnecessary and undesirable to use an oxidizing agent in sufficient concentration to provide measured oxidizing potential on the other hand, a small quantity of range of content of oxidizer has been found in the reduction by the metal surface and to brake or control the formation by the sulfuric acid of red copper oxide dust.

A completely clean and bright copper surface has been obtained by either directly pickling or cleaning in an acid solution in accordance with the invention, or by using the solution as a second step after a sulfuric acid pickle has been employed to remove major quantities of cupric oxide scale. The aqueous pickling solution (also containing sulfuric acid) provides a maximum economy in a two-step operation.

In preparing a combined two-step treating solution in accordance with the invention, for the first step of the operation, the workpiece is subjected to a sulfuric acid, sulfamic acid or equivalent dissolved acid salt (such as NaH2SO4) aqueous pickling solution or bath in one tank. The solution contains about 1% to 40% by volume or 1.84% to 55% or 18 to 550 g./l. by weight of the acid (e.g. 1.84 specific gravity concentrated H2SO4) and, as an optimum, about 10% to 20% by volume or 17% to 31.6% by weight of the acid in water, and is maintained at an operating temperature of about 180°F. For the second step, an aqueous solution is prepared containing nitric acid, and sulfuric acid in accordance with the invention, and then the workpiece is subjected to the solution in a second tank or bath. In other words, a solution is prepared of the same sulfuric acid, sulfamic acid or acid salt content as the first solution, but in a maximum amount of about 55% or 530 g./l. and in a minimum amount of about 1.84% by weight or 18 g./l., hydrogen peroxide (H2O2) is added thereto within a low range of concentration of about 0.1 g./l. up to about 50 g./l. by weight and the solution is maintained at about 80° to 150° F. Using air (oxygen-containing gas) circulated through or in the peroxide containing bath or baths during treatment in both the single and two-step operations, enables the solution to be operated within the lower range of hydrogen peroxide; the lower limit without air bubbling is about 1 g./l. or 1% by weight.

In the peroxide concentration range of the invention, the quantity is so low in the pickling solution that its oxidizing potential does not appreciably raise the electrode potential of the sulfuric acid pickling solution containing, for example 2 to 3 ounces per gallon of copper as dissolved copper sulfate. At the same time, the solution is capable of providing a clean copper surface, irrespective of the dissolution of the copper during the pickling operation, and without forming new copper oxide on the metal surface. It will be noted that the pickling solution, after it is used, will also contain cupric sulfate. It may contain at least about 1 ounce per gallon of copper as sulfate, and the concentration may go up to the solubility limit of about 9 oz./gal. of copper as sulfate.

For example, a sulfuric pickling solution has been employed containing 5% by volume or 8.8% by weight of sulfuric acid and 17.4 g./l. of copper as cupric sulfate. This solution has an electrode potential measured with gold and glass electrodes at 120°F. Of -240 millivolts. By adding hydrogen peroxide to the solution so that it contains 0.34%, measured at the same temperature, the electrode potential was found to be -116 mv. which is not in the oxidizing range. The addition of 0.64% hydrogen peroxide (6.4 g./l. of H2O2), gave an electrode potential under similar conditions of -60 mv. An addition of 1% hydrogen peroxide (10 g./l. of H2O2), under similar conditions gave an electrode potential of -4 mv. It was found that the electrode potential went through the positive side at a concentration of about 12 g./l. of H2O2 and that with a concentration of 13.2 g./l. of H2O2, the potential was +12 mv. Thus, although successful employment of up to about 1.5% by weight of H2O2 has been made, as an optimum, it is preferable to use a maximum average working content of about 1.2%. In any event, an electrode potential is avoided that is appreciably on the positive side. When aluminum is being cleaned or faster reaction rates are desired, hydrogen peroxide may be used in amounts of up to about 5 g./l.

Summarized, it has been determined that within a range of about 0.01% (1.0 g./l. of H2O2) to 5% (50 g./l. H2O2) by weight, the hydrogen peroxide assists in the pickling reaction by the sulfuric acid in two ways. In the first place, it counteracts the stiplacing tendencies of the copper metal and will not allow or restrict the cupric oxide that may be on the surface from being reduced to cuprous oxide.
In the second place, since cuprous oxide is present in the scale, or because the workpiece has been previously pickled in a sulfuric acid pickling solution such that there is some copper oxide dust on its surface, the hydrogen peroxide will assist or enable the sulfuric acid to act as a solvent on the cuprous oxide. The reaction for the oxidation of the cuprous oxide by the hydrogen peroxide and dissolution by the sulfuric acid is as follows:

\[
\text{Cu}_2\text{O} + \text{H}_2\text{O}_2 \rightarrow 2 \text{Cu}^+ + \text{H}_2\text{O}
\]

Table II

(A) \(\text{Cu}_2\text{O} + 2\text{H}_2\text{O}_2 \rightarrow 2\text{Cu}^+ + 2\text{H}_2\text{O}\)

(B) \(\text{CuO} + \text{H}_2\text{O}_2 + \text{CuSO}_4 + \text{H}_2\text{O}\)

The invention essentially differs from previous practices where a general oxidizing condition was desired and was effected by the utilization of chromic acid, hypochlorous acid, perborates, persulfates or hydrogen peroxide, with the range of such agents being relatively high, from about 50% to 80% by weight. The relatively minor concentration that has been found effective for the present process depends on the time available for pickling and the temperature used. As an example, a concentration of 10 g./L. of H\(_2\)O\(_2\) represents an optimum, if the pickling is conducted at 120° F, and the available time for reaction is only 30 seconds; then 50 g./L. of H\(_2\)O\(_2\) can be used, if the pickling temperature is about 90° F. and the total time available is only 30 seconds. On the other hand, about 1% or 1 g./L. of H\(_2\)O\(_2\) is sufficient for a bright, smut-free pickling at 120° F. with 4 to 5 minutes time. Such conditions will prevail with a pickling solution of 8 to 10% by volume or 13.6 to 17% by weight of sulfuric acid having a concentration of about 15 to 40 g./L. by weight as copper sulfate, within a temperature range of about 90° to 120° F.

In carrying out the process, it has been found that the stability of hydrogen peroxide has not been satisfactory. For example, in making up a pickling solution using chemically pure chemicals, as above indicated, it has been found that in the solution to which 10 g./L. of H\(_2\)O\(_2\) is added and employed at a temperature of 120° F., the loss of the hydrogen peroxide from a standing solution, without its being used for pickling, is about 1 g./L. per hour. This condition is even worse if some iron contaminates the pickling solution. This is the usual condition, because many of the pickling tanks are made of stainless steel, as are the chains, hooks and racks. Also, the piping, heating coils, etc., tend to lead to iron contamination of the pickles. With iron concentration in the pickle of about 1 g./L. the peroxide loss at 120° F. solution temperature was found to be 10 g./L. per hour.

It has been discovered that fatty acids or simple salts of these acids when added to the pickling solution will inhibit control, restrict or greatly reduce the breakdown of peroxide. As an example, to the above pickling solution containing 10 g./L. of H\(_2\)O\(_2\) and 1 g./L. of iron, the following compounds were added, and with a solution at a temperature of about 120° F., the peroxide loss in grams per liter was:

**Table III**

<table>
<thead>
<tr>
<th>H(_2)O(_2) loss, g./L/hr.</th>
<th>1% by vol. of formic acid</th>
<th>1% by vol. of acetic acid</th>
<th>1% by vol. of propionic acid</th>
<th>1% by vol. of butyric acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.9</td>
<td>1.9–2.9</td>
<td>0.2–0.5</td>
<td>1.1</td>
<td></td>
</tr>
</tbody>
</table>

Although all these fatty acids and their sodium or potassium salts and other simple compounds that will again form the fatty acid when dissolved in sulfuric acid, will reduce the breakdown of hydrogen peroxide and counteract the effects of iron contamination, from the above Table III, it will be evident that propionic acid is the most effective of the chemical compound materials. It will be noted that up to about 10% by volume of acetic acid is required to bring the loss of H\(_2\)O\(_2\) down to the same amount as accomplished by 1% by volume of propionic acid. Thus, up to about 10% by volume of the organic fatty acid or acid salts is required. While a concentration has been used of this acid of from about 0.1% to 15% by volume, the optimum range is about 1 to 2% by volume, using the acid or equivalent weights if dry salts are dissolved. The following table illustrates the hydrogen peroxide breakdown rates for various concentrations of propionic acid in a solution containing about 5 g./L. of H\(_2\)O\(_2\) and 1 g./L. of iron, with a solution temperature of about 120° F.:

**Table IV**

<table>
<thead>
<tr>
<th>H(_2)O(_2) loss, g./L/hr.</th>
<th>0.0%</th>
<th>0.5%</th>
<th>1.0%</th>
<th>2.0%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0%</td>
<td>0.11</td>
<td>0.08</td>
<td>0.04</td>
<td>0.08</td>
</tr>
<tr>
<td>0.5%</td>
<td>1.50</td>
<td>1.00</td>
<td>0.60</td>
<td>0.40</td>
</tr>
</tbody>
</table>

It will be noted in comparing Tables III and IV that the breakdown rate is less with a lesser content of peroxide in the solution, for the same propionic acid inhibitor content.

In addition to fatty acids, other organic stabilizer compounds containing carboxyl or hydroxyl functional groups that carry polar hydrogen atoms and are not sterically hindered either by themselves or other groups, are glycols such as ethylene glycol. An ethylene glycol type of stabilizer has been found to have an even better stabilizing effect than propionic acid for idle or non-operating solutions containing hydrogen peroxide and, especially with a dissolved iron content. Such an iron content normally has a tendency to drive the peroxide out of the solution by catalyzing breakdown of the peroxide. Propionic and other volatile organic acids have an increased vapor pressure as the temperature of the pickling solution is increased or if increased heat of the pickling action is not quantitatively removed. As distinguished from a continuous loss of volatile acid, a stabilizing agent such as glycol which is only lost by dry-out, is advantageous. Further, glycol, in addition to having the ability of operating at an elevated temperature (such as 120° to 140° F.) and without an unpleasant odor, permits a faster pickling rate with lower peroxide concentrations or a faster pickling rate in the 1 to 2 second range with 2 to 5% hydrogen peroxide concentrations, if a fast pickling rate is desirable. Elevated temperatures tend to increase spontaneous breakdown of the peroxide and increase vapor pressure of the volatile acids, thus leading to loss; this is substantially eliminated by the use of a glycol.

As an example, ethylene glycol which has good characteristics and which falls within the classification of an organic compound having two or more functional groups that carry polar hydrogen atoms and are not sterically hindered either by themselves or other groups, is represented by the formula \(\text{CH}_2\text{OH}—\text{OH}\). On the other hand, chloral hydrate which has poor characteristics, does not fall within the classification because of its sterically hindered groups; its formula is:

\[
\text{CH}_2\text{O} + \text{H}_2\text{O}\]

It has been determined that a stabilizing agent or compound of the invention may be used in the solution within a range of 1 to 150 g./L or 1 to 15% by volume, with an optimum range being within 10 to 20 g./L. or 1 to 2% by volume. The following table illustrates the loss or breakdown of hydrogen peroxide under various conditions including those in which the solution contains no dissolved iron and contains dissolved iron and where the solution is heated up to a temperature of about 150° F. For best results, the temperature of treatment should be within the range of about 120° to below 150° F., since
at 150° and above, the loss tends to increase greatly (see item 10 of Table V).

**TABLE V**

<table>
<thead>
<tr>
<th>Stabilizing compounds</th>
<th>Temp.</th>
<th>H₂O₂ loss, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) None</td>
<td>120</td>
<td>1.02</td>
</tr>
<tr>
<td>(2) None</td>
<td>110</td>
<td>0.8</td>
</tr>
<tr>
<td>(3) Phosphoric acid (1% by vol.)</td>
<td>120</td>
<td>0.19</td>
</tr>
<tr>
<td>(4) Glyoxylic acid (1% by vol.)</td>
<td>120</td>
<td>0.13</td>
</tr>
<tr>
<td>(5) Glycine (1% by vol.)</td>
<td>120</td>
<td>0.25</td>
</tr>
<tr>
<td>(6) Benzoic acid (1% by vol.)</td>
<td>120</td>
<td>0.28</td>
</tr>
<tr>
<td>(7) Propanoic acid (1% by vol.)</td>
<td>120</td>
<td>0.28</td>
</tr>
<tr>
<td>(8) Salicylic acid (1% by vol.)</td>
<td>120</td>
<td>0.90</td>
</tr>
<tr>
<td>(9) Ethylene glycol (1% by vol.)</td>
<td>Non</td>
<td>0.04</td>
</tr>
<tr>
<td>(10) Ethylbenzoic acid (1% by vol.)</td>
<td>120</td>
<td>1.19</td>
</tr>
</tbody>
</table>

Using an acid pickle in accordance with the invention, wherein the pickling acid is made up at 1% to 40% by volume or 1.84% to 55% by weight or 18 to 550 g/l. of sulfuric acid added to water to form an aqueous solution, and containing up to 9 oz./gal. by weight of copper as cupric sulfate, and operated at a temperature between about room temperature (80° F.) and 150° F., with hydrogen peroxide added in concentrations within a range of about 1 g/l. to 15 g/l. and a pickling time of a few seconds to 5 to 10 minutes and up to about 50 minutes (or up to 30 minutes by employing the sulfuric acid pickling solution separately and then passing the workpiece into a second inorganic acid solution made up of the specified concentration of hydrogen peroxide and holding for the specified time), a great improvement is provided in the resultant copper surface. That is, a copper surface as provided in accordance with the invention, will not be covered with the usual red copper oxide smut and will be clean and bright, such that it is highly suitable for subsequent cold working operations. The dust smut is highly disadvantageous in a workpiece that has to be cold drawn, such as by wire or tube drawing, in that the dust is drawn many times into the metal, where it acts as a foreign inclusion to reduce its tensile strength and conductivity and to, in other ways, impair the quality of the finished product. Also considerable tool wear will result from the loose dust in the lubricant.

A further advantage of the invention is that the process lends itself easily to a subsequent or continuous electrolytic recovery of copper dissolved during the pickling operation. With the usual oxidizing agents, such as chromic acid, etc., this cannot be done economically. However, with low concentrations of peroxide used in accordance with the invention, electrolytic refining of the copper can be carried out at nearly 100% efficiency. Assuming a hydrogen peroxide concentration of 0.4% (4 grams per liter), with the pickling process operated at about 100° F., the plating out of the copper can be carried out at approximately 50% efficiency. If the plating is conducted continuously, and only a small stream is removed continuously from the pickling process to allow the plating out of the same quantity of copper as is dissolved in the acid, the small stream continuously going through the electrolytic recovery cell can be cooled down to 90° F. At this temperature, with 0.4% of H₂O₂ in the sulfate pickling solution, the plating efficiency will be about 86%.

Another feature of the invention is that it allows the continuous use of the bright pickling solution, without the necessity for discarding the used pickle, and without incurring the neutralization costs for waste treatment; at the same time, it enables the recovery of dissolved copper metal in an economical manner, as by ordinary electrolysis.

In carrying out the invention, it has been found that the range of concentration of peroxide serves to prevent or inhibit the transformation of cupric oxide to cuprous oxide, and the formation of cuprous oxide from the copper surface of the workpiece. The concentration of hydrogen peroxide is critical from the standpoint of assuring the full dissolving of the cuprous oxide carried by the cupric scale, without being sufficient to give an active oxidizing action and to prevent the inorganic acid from reacting to form additional cuprous oxide. The use of a stabilizer or inhibitor of the invention restrains the natural breakdown of the peroxide and tends to slow it down in the reaction to assure a most effective and economical employment of the peroxide in the solution.

The bubbling of air (or moving oxygen-containing gas) through a bath or solution of the invention, reduces the consumption of the peroxide. Although it has been found that air alone will not do the job, air has a cumulative effect on the peroxide. For example, the lower limit of 0.1 g/l. of peroxide is made practical with the use of air. It has been found that about 1 g/l. of peroxide is a good working content irrespective of whether oxygen gas is or is not employed.

Summarizing, in carrying out the invention, an aqueous pickling or cleaning solution containing inorganic sulfuric or sulfamic acid or equivalent sodium acid sulfate salt is employed at a suitable temperature in an effective amount to react with, dissolve and remove the cupric oxide from the surface of the workpiece. Hydrogen peroxide is employed in the solution in a minor but effective amount to enable the inorganic acid to also remove the cuprous oxide and dissolve it in the aqueous solution and to do so without forming additional cuprous oxide and to remove both the cupric and cuprous oxides from the surface of the metal workpiece without forming additional cuprous oxide on the surface. An effective but minor amount of a chemical compound, in the nature of an organic stabilizer or compound containing functional groups that carry polar hydrogen atoms is dissolved in the aqueous solution and utilized to limit or restrain the breakdown of the hydrogen peroxide, which may be termed its natural breakdown, as distinguished from its breakdown under the reactions or its active operation in effecting the cleaning of the workpiece with one solution. In this connection, of fatty acids and salts thereof found effective for the purpose, propionic acid and its salts are particularly effective and represent the optimum, and of glycols, ethylene glycol represents the optimum.

When utilizing a two-step procedure in accordance with the invention, the first treatment of the workpiece is employed to remove the substantial portion of the cupric oxide from the surface of the workpiece and the second step is employed to remove any remaining cupric oxide and all of the cuprous oxide so as to provide a bright and clean copper-bearing surface on the workpiece. Although one such a one-step procedure has been found to be fully effective, the two-step procedure is preferred where the cupric oxide is in the form of a heavy layer or encrustation. That is, it shortens the time required for the final cleaning step and, in effect, limits the application of the final treating or pickling solution as to time and temperature and the work load which it has to carry, and thus, is more economical of the amount of hydrogen peroxide and inhibiting chemicals which are employed. However, in both processes, the copper which is dissolved in the solution of the final step in the form of copper sulfate can be readily removed by a conventional electrolysis procedure and is removed to keep the sulfate content within practical working limits.

Briefly, the bright pickling or cleaning solution of the invention, whether it is used in a two-step or single step operation, will contain at least 18 g/l. and up to 18 g/l. and a maximum of about 55% by weight or 550 g/l. of inorganic concentrated acid in the nature of sulfuric acid, sulfamic acid or the equivalent acid salt (sodium acid sulfate solution); a good working range is about 1.8% to 20% by weight. The hydrogen peroxide is provided in the solution within a range of about .1 to 50 g/l. or up to 5% by weight, with the solution maintained at an operating temperature of about 80° to 150° F.; a good working range of H₂O₂
3,537,895

is 1 to 15 g./L for higher copper bearing workpieces and up to 50 g./L for lower copper bearing workpieces and for the removal of copper or aluminum where the copper content of the solution is lower; a good working range of temperature is about 90° F. to 120° F.

The solution may, as previously pointed out, have an oxygen containing gas, circulating, bubbling or moving therethrough to enhance the utilization of the hydrogen peroxide, and will have minimum of about 1% by volume of the copper stabilizer compound dissolved therein. For an organic fatty acid, such as formic, acetic, butyric, propionic or equivalent salts thereof, a good working range for the fatty acid content is about .5 to 15% by volume and for the stabilizer compounds in general is about .1 to 10% by volume. The stabilizer content is critical for controlling or restraining the breakdown of the hydrogen peroxide in the solution and thus, in conserving it and in enhancing its use.

For improved or maximum brightness and for cleaning aluminum or copper containing aluminum workpieces, a chelating agent is used in the solution in the minimum amount of .1 oz./gal. with about .1 to 6 oz./gal. or 0.75 to 45 g./L representing a good working range, and with an optimum of about 1 oz./gal. The chelating agent or compound may be of a common type, such as ethylenediaminetetraacetic acid (EDTA), nitritrietric acid N(CH₂COOH)₂, and ethyleneglycolic acid (beta-aminoethy1.1-2, N-tertracetic acid (HOOCCH₂)₂

N-CH₂CH₂OCH₂CH₂OCH₂CH₂N(CHCOOH)

the trademarked line of agents CHELON have been found suitable. Chelating agents which are particularly suitable for a copper containing solution are amines, such as monoamines, diamines, or polyamines as, for example, EDTA or its salts as well as mono, di, tri and teta sodium salts or modified acids, such as for example N-hydroxymethylenenime triacetates. A particularly useful agent is disodium ethylenediamine tetraacetate.

One phase of the invention rests in the discovery that hydrogen peroxide acts in the presence of copper in an aqueous inorganic acid picking or cleaning solution to prevent the formation of additional cuprous oxide during the dissolution of cupric oxide. Another phase rests in the discovery that hydrogen peroxide can be conserved, stabilized and enhanced in use in an aqueous inorganic acid containing, metal surface treating solution by providing and employing an organic stabilizing compound in the solution within a minimum content of about 0.1% by volume or 1 g./L. A further phase relates to the determination that the flow of oxygen through a hydrogen peroxide containing aqueous cleaning solution is beneficial. A final phase deals with the discovery that the use of a minimum amount of about 0.1 oz./gal. or 0.75 g./L. of a chelating agent in an aqueous hydrogen peroxide solution used for cleaning copper, copper alloy surfaces would enhance brightness of the surfaces and would assure a bright and clean cleaning or surface conditioning of aluminum and copper containing aluminum alloys.

As to salts of the fatty acids, reference is made to equivalent quantities of simple water soluble salts of the fatty acids which after dissolution in the sulfuric acid of the pickling or cleaning solution, will form the fatty acids of which they are derivatives. As to the organic stabilizer compounds such as fatty acids, it has been found that .1 to 15% by volume or 1 to 150 g./L concentrations are of beneficial value in other solutions (such as etching or pickling solutions) employing sulfuric acid and where a hydrogen peroxide concentration of 15% or any alloy weight is to be used. By way of example, a pickling solution has been employed for removing cuprous and cupric oxides, copper metal or alloys thereof from a workpiece which, in addition to the inorganic sulfuric or sulfamic acid or equivalent sodium acid sulfate salt content in a concentration of about 1% to 40% by volume or 1.8% to 55% by weight 18 to 550 g./L, contains copper in the form of cupric sulfate when cuprous oxides are to be removed, sulfates of any alkali metal that may be removed, and an effective amount of hydrogen peroxide as an oxidizing agent. In such a solution, an organic stabilizer compound concentration of about .1 to 15% by volume is important from the standpoint of the hydrogen peroxide, independently of the copper oxide control features encountered in the employment of the copper oxide cleaning solution of my invention.

Although for the purpose of illustrating the invention, details of its operation and specific examples of the solutions involved have been set forth, including the ingredients thereof and their utilization, it will be apparent to those skilled in the art that various modifications and adaptations of the invention may be made without departing from the spirit and scope thereof and as represented by the claims.

I claim:

1. A final stage method of fully removing copper oxides from a copper-containing workpiece which comprises: introducing the workpiece in an aqueous cleaning solution containing an inorganic acid of the class consisting of sulfuric acid, sulfamic acid and equivalent acid salt thereof in the nature of sodium sulfate within a concentration range of about 18 to 550 g./L. and utilizing it to dissolve cupric oxide from the surface of the workpiece, providing about 1 g./L. to 50 g./L. of hydrogen peroxide within the solution and employing it to prevent the formation of additional cuprous oxide during dissolution of the cupric oxide by the inorganic acid and to oxidize cuprous oxide into cupric oxide and make the inorganic acid effective to thus remove all copper oxide from the surface of the workpiece, providing a dissolved organic stabilizing compound in the aqueous cleaning solution of the class consisting of benzoic, glycolic and propionic acids; glycine, ethylene and propylene glycols within a range of about 1 to 150 g./L., employing the stabilizing compound to effectively limit the tendency of hydrogen peroxide to break down in the aqueous solution where the solution may attain an operating level at which it has a dissolved iron content of at least 1 g./L. and a copper content of up to its solubility limit as a sulfate therein, maintaining the aqueous solution at a temperature within a range of about 80° to 150° F. during the treatment of the workpiece, and retaining the workpiece in the solution until its surface has a cleanliness and brightness representing a condition suitable for cold working.

2. A method as defined in claim 1 wherein the dissolved organic stabilizing compound is limited to the class consisting of glycine, ethylene and propylene glycols.

3. In a method as defined in claim 1, electrolyzing the aqueous solution after a period of use, and recovering the dissolved copper content therein to reconstitute the solution.

4. A method as defined in claim 1 wherein a chelating agent is employed in the aqueous solution within a range of about 0.75 to 45 g./L. for enhancing the brightness of the surface of the workpiece.

5. In a method as defined in claim 4, employing the hydrogen peroxide in the solution in a minimum amount of about 1 g./L., and bubbling an oxygen-containing gas in the aqueous solution during the treating of the workpiece.

6. A final stage cleaning-pickling solution for fully removing copper oxides from copper containing workpieces that comprises an aqueous solution containing: an inorganic acid of the class consisting of sulfuric acid and equivalent acid salt thereof in a concentration within a range of about 18 to 550 g./L. for dissolved cupric oxide from the surface of the workpiece, containing hydrogen peroxide within a range of 18 to 550 g./L. for preventing the formation of additional cuprous oxide during dissolution of the cupric oxide by
the inorganic acid and for making the inorganic acid effective in fully removing cuprous oxide as cupric oxide from the surface of the workpiece, and also containing a dissolved organic stabilizing compound of the class consisting of benzoic, glycolic and propionic acids; glycerine, ethylene and propylene glycols within a range of about 1 to 150 g./l., and the solution having an operating temperature of about 80° to 150° F.

7. A cleaning-pickling solution as defined in claim 6 wherein the stabilizing compound content is limited to the class consisting of glycerine, ethylene and propylene glycols.

8. A cleaning-pickling solution as defined in claim 6 which additionally contains in solution a chelating agent within a range of about .75 to 45 g./l.
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,537,895 Date: November 3, 1970

Inventor(s) Leslie E. Lancy

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

Column 3, line 47, after "cupric" change "electron" to --ion--.

Column 7, last line of Table V, change H2O2 loss from "1.99" to --1.09--.

Column 8, line 67, before "18 g./l." delete "and".

Column 9, line 26, change "nitrotriacetic" to --nitrilotriacetic--.

Column 10, line 6, after "volume" insert --or 1 to 150 g/l--.

SIGNED AND SEALED
JAN 5 1971

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents