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3,544,389

PROCESS FOR SURFACE TREATMENT OF COPPER AND ITS ALLOYS

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9 Claims

ABSTRACT OF THE DISCLOSURE

This is a method for surface treatment of copper and its alloys which results in an improved adhesive joint between the metal and organic adhesive materials and comprises treatment in an alkaline permanganate solution.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to the surface treatment of copper and its alloys by use of an alkaline permanganate solution, in order to improve adhesive joints between such surfaces and organic adhesive materials, and also relates to the joined product.

Description of the prior art

Adhesive joining of copper and its alloys to both metals and nonmetals is common practice. Corrosion products ordinarily present on the surface of the metal interfere with such joining and have in the past been removed and replaced by a chemically produced oxide layer which prevents further corrosion and provides a surface suitable for joining.

This layer has been achieved generally by oxidizing the surface of the metal with various solutions containing chlorite ions. See, for example, U.S. Pat. 3,198,672.

There are several disadvantages involved in the use of chlorite as an oxidizing agent, the most serious of which is that the solution tends to etch the surface of the metal, thus interfering with the formation of a tenacious oxide layer which is suitable for adhesive joining. This etching action is more severe towards metals which are commonly alloyed with copper such as zinc and tin, to the extent that when such alloying agents are present in the metal in total amounts greater than about 10 percent, the use of such a solution is no longer practical. A further disadvantage is that it is not economical to treat substantial amounts of metal surfaces due to the relatively high cost of this oxidizing agent.

SUMMARY OF THE INVENTION

This invention is essentially a joining technique in which the surface of copper and its alloys is treated with an alkaline permanganate solution prior to joining, and results in joints which are significantly improved over those obtained previously. In addition, this solution is more economical to use than previously used solutions.

Since the surface to be treated ordinarily contains contaminants such as dirt, grease and corrosion products, it is usually necessary to remove these prior to the permanganate treatment, and to aid the practitioner exemplary procedures are briefly described.

Furthermore, since the treatment is essentially one to prepare the surface of copper and its alloys for joining to an organic adhesive material, bonds to dissimilar metals as well as to similar metals and also bonds to nonmetals are contemplated.

DETAILED DESCRIPTION

This process applies to copper and any of its alloys containing at least 50 percent copper.

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Preliminary cleaning is by methods well known in the art. Thus, the following description of preliminary cleaning is intended to be exemplary and not limiting.

Preliminary cleaning is generally divided into degreasing and descaling. For example, degreasing is generally effective in removing only oils and grease and is ineffective in removing corrosion products such as naturally formed oxide scale. Descaling, which may be either mechanical or chemical, will, however, generally remove substantially all of the surface contamination. However, descaling chemically without first degreasing may result in rapid contamination of the solution, replacement of which may be both costly and time consuming.

Removal of oils and grease may be accomplished by the use of organic solvents such as alcohols, ketones and chlorinated solvents such as trichloroethylene and perchloroethylene. Such removal may also be accomplished by use of alkaline cleaners. Commonly used components of such cleaning mixtures are: sodium hydroxide, used for its saponifying power; phosphates and silicates, used for their emulsifying and wetting abilities; surface active agents such as alkyl aryl polyether alcohols, used for their wetting ability; and detergents, used for their wetting and saponifying ability.

An example of an effective alkaline cleaning solution is one which contains from 1 to 10 percent by weight sodium metasilicate, from 1 to 10 percent trisodium phosphate and from 1 to 10 percent of an alkyl aryl polyether alcohol, remainder water. Cleaning in this solution may be carried out for from 1 to 30 minutes at a temperature of from 70 to 180° F.

Descaling is usually accomplished by the use of acid solutions or by mechanical abrasion. The particular method chosen for descaling will depend on the thickness, composition and character of the scale, which depends upon the composition of the metal and upon its history, particularly its thermal history.

The usual practice is to use an aqueous solution containing from 1 to 10 percent by weight of nitric acid, immersing the metal therein at a temperature of from 70° F. to 150° F. for from 1 to 30 minutes. However, such a treatment is often ineffective in removal of the scale. It is thus preferred to add phosphoric acid to this solution, to increase the acidity of the solution. Such a solution contains from 1 to 80 percent by weight phosphoric acid, from 1 to 40 percent by weight nitric acid, remainder at least 20 percent water, and is used within the same temperature range as is the nitric acid solution.

Too high a concentration of nitric acid attacks the surface too rapidly, taking away substantial amounts of pure metal. Too high a concentration of phosphoric acid or too low a concentration of nitric acid results in the solution becoming less effective against severe contamination and requires excessively long cleaning times for moderate surface contamination.

Phosphoric acid may also be used to contribute to the formation of a smooth and bright surface, if it is present in amounts above about 40 percent by weight of the solution, within the ranges already specified.

Examples of mechanical abrasion methods for descaling are abrasive blasting, wire brushing, and grinding. In general, these methods are more wasteful of metal and produce surfaces somewhat rougher textured than do solution methods. However, rough surfaces are particularly advantageous for increased peel strength of subsequently formed joints. Sandblasting is often used for this reason. In operation, grit or sand which passes a standard screen from No. 150 to 500 is introduced into an air stream at pressures of 25 to about 100 pounds per square inch and the blast directed over the surface of the metal until the scale is removed.

A rough surface may also be achieved chemically of

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course, as for example, by adjusting the concentration of an acid pickling bath to a high concentration of nitric acid within the ranges described or by using a chemical etching solution containing for example hydrochloric acid and either ferric chloride or cupric chloride each in the amounts of from 1 to 10 percent by weight.

A more complete description of degreasing and descaling methods may be found in *Protective Coatings for Metals*, Third Edition, American Chemical Society, Monograph 163 by R. M. Burns and W. W. Bradley, pp. 27 to 54, Reinhold (1967).

Once the removal of surface contamination has been effected, the clean metal surface should be either treated with permanganate solution promptly or stored under non-corrosive conditions until treatment, since exposure of the clean surface to a nonprotective atmosphere will soon result in reformation of corrosion products and exposure for longer than about two days will render the subsequent permanganate treatment substantially ineffective.

The concentration of permanganate ions in the solution is not critical and may range from 0.001 percent by weight to saturation. The ions may be introduced in combination with the Group I alkali metals; lithium, sodium, potassium, rubidium and cesium or the Group II alkaline earth metals; beryllium, magnesium, calcium, strontium and barium. It is essential that the solution have a pH of at least 6 in order to insure against dissolution of the oxide layer which is formed.

Alkalinity may be achieved by using any compound which will yield hydroxyl ions in solution as, for example, the Group I and Group II metal phosphates, hydroxides and carbonates. Treatment may range from 1/2 to 60 minutes at a solution temperature of from room temperature to its boiling point, and results in an oxide layer of from about 150 to 1200 angstroms in thickness, below which the layer is thin enough to significantly reduce joint strength and above which the layer is mechanically weak, resulting in weak joints. Optimum results however are achieved by a closer control of the parameters so that a layer of from about 400 to 500 angstroms in thickness results.

The rate of formation of the layer generally increases as the concentration and temperature of the solution and the duration of the contact increase. Layers having thicknesses substantially within the preferred range may be obtained by treating the surface with a solution containing permanganate ions in the amount of from 1 to 10 percent by weight and having a pH of at least 11, at a temperature of from 180 to 200° F. for from 3 to 5 minutes, the lower concentrations corresponding to the higher solution temperatures and longer immersion times.

Example 1

This example illustrates the control which may be had over the thickness of the layer formed by varying the parameters involved. Preliminary treatment of the samples comprises vapor degreasing followed by acid etching in a solution containing phosphoric acid, nitric acid and water in the amounts of 75 percent, 10 percent and 15 percent by column, respectively, for one-half minute at a temperature of approximately 75° F., followed by rinsing with distilled water. Results are shown in Table 1.

TABLE 1

	Sample No.				
	1	2	3	4	5
Potassium permanganate present in solution (wt. percent).....	1	1	10	10	1
Sodium hydroxide present in solution (wt. percent).....	1	1	10	10	1
Temperature of solution (° F.).....	180	180	180	180	200
Time of immersion of sample (mins.).....	5	10	3	6	5
Thickness of resulting layer (A.).....	250	295	485	950	430

After the permanganate treatment a rinsing step is preferred for optimum results. Air drying is satisfactory.

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In this condition, the material is ready for subsequent joining.

Since the method described is essentially directed toward improving adhesive joining by improving the surface of the metal, it is not limited for use with certain adhesives, but is useful in preparing surfaces for application of any organic materials such as the usual adhesives; epoxy and modified epoxy resins; nitrile rubber phenolics; polyvinyl butyrals; and polyvinyl formals.

Example 2

Three sets of six each samples of copper, .063 inch thick, were vapor degreased with trichloroethylene. The samples in Sets 1 and 2 were then acid etched in a 20 percent by volume nitric acid solution for 1 minute. Set 3 was acid etched in a solution containing nitric acid and phosphoric acid in the amounts of 75 percent and 10 percent by volume, respectively, for 1 minute. All of the samples were then rinsed with distilled water. Set 1 was then treated in a solution containing chlorite ions for 3 minutes at 200° F. Sets 2 and 3 were treated in a solution containing 1 percent by weight each of potassium permanganate and sodium hydroxide for five minutes at 180° F. All the samples in each set were then rinsed with distilled water and air dried at room temperature. The samples were then joined with other identically treated samples by means of a modified epoxy resin using a standard one-half inch lap joint and a bond thickness of 3 mils and measured for tensile shear strength according to ASTM Procedure D-10002. Rupture was also measured by observing the time to failure when a static load of 3,000 pounds per square inch was applied in an ambient atmosphere of 95° F. at 90 percent relative humidity. Results are shown in Table 2.

TABLE 2

	Set No. 1	No. 2	No. 3
Average tensile shear (p.s.i.).....	4,840	5,280	5,360
Days to failure.....	* >41	>45	>45

* 1 of the 6 joints failed after 23 days.

These results indicate that Sets 2 and 3, treated with permanganate solution, were superior to Set 1, treated with chlorite solution, both in terms of tensile shear values and in days to failure under static load. Further, Set 3, treated with a nitric-phosphoric acid solution prior to permanganate treatment, showed a noticeable improvement in tensile shear values over Set 2, which was treated with a nitric acid solution.

Example 3

Two sets of six each samples of Muntz metal (60 percent copper, 40 percent zinc), .063 inch thick were vapor degreased with trichloroethylene. They were then acid-etched in the same manner as Set 3 in Example 2, and then rinsed with distilled water. Set 1 was then treated with a solution containing chlorite ions for two minutes at 200° F. Set 2 was treated with a solution containing 1 percent by weight each of potassium permanganate and sodium hydroxide for five minutes at 195° F. All of the samples were then rinsed with distilled water, air dried at room temperature, and tested as in Example 2, except that rupture was measured for a static load of 800 p.s.i. Results are shown in Table 3.

TABLE 3

	Set No. 1	No. 2
Average tensile shear (p.s.i.).....	1,900	2,330
Days to failure.....	* >31	** >75

* 4 out of 6 failed.

** None failed.

These results show that improvement is obtained in tensile shear value which is comparable to that obtained for the copper samples of Example 2. They also indicate, however, a significantly greater improvement in days to failure under a static load than was obtained for copper,

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and accordingly illustrate the advantage of the substantially noncorrosive nature of a permanganate solution towards the zinc alloying agent.

Example 4

Three sets of six each samples of beryllium copper (1.9 percent beryllium) .063 inch thick were vapor degreased with trichloroethylene. They were then acid-etched as was Set 3 in Example 2, and rinsed with distilled water. Set 1 was then treated in a solution containing chlorite ions for three minutes at 200° F. Set 2 was treated in a solution containing 1 percent by weight each of potassium permanganate and sodium hydroxide for five minutes at 180° F. Set 3 was treated in the same permanganate solution for five minutes at about 200° F. All of the samples were then rinsed with distilled water and air dried at room temperature. They were then tested as in the previous examples for an average tensile shear value. The results are shown in Table 4.

TABLE 4

	Average tensile shear (p.s.i.)
Set No. 1-----	5700
Set No. 2-----	5880
Set No. 3-----	6140

The permanganate treatments for Sets 2 and 3 correspond to treatments for Sets 1 and 5, respectively, in Example 1. It is therefore apparent that the permanganate treatment resulting in an oxide layer having a thickness of about 400 angstroms gives results which are significantly improved over those obtained for a sample having a layer whose thickness is less.

Example 5

One of two sets of six each samples of an alloy containing 65 percent copper, 18 percent nickel and 17 percent zinc, .063 inch thick, was vapor degreased with perchloroethylene. The second set was subjected to alkaline cleaning at 130° F. for five minutes, followed by treatment in a solution containing 1 percent by weight each of potassium permanganate and sodium hydroxide for five minutes at 195° F. All of the samples were then rinsed with distilled water and air dried at room temperature. They were then tested as in the previous examples. The results are shown in Table 5.

TABLE 5

	Set No. 1	No.2
Average tensile shear (p.s.i.)-----	3,580	5,570
Days to failure (under a static load of 3,500 p.s.i.)--	(1)	>60
Days to failure (under a static load of 4,000 p.s.i.)-----		>42

¹ Less than 1 hour.

The results indicate that permanent joints under static loading are obtainable by use of the permanganate treat-

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ment for alloys containing substantial amounts of alloying agents.

The invention has been described with reference to particular embodiments thereof, but it is intended that variations therefrom which basically rely on the teachings of the invention are to be considered as within the scope of the invention and the appended claims.

What is claimed is:

1. A method for joining a surface containing at least 50 percent by weight copper to an organic material, characterized in that said joining is preceded by the step of contacting said surface with an aqueous solution containing permanganate ions and positive ions, said positive ions consisting essentially of one or more ions selected from the group consisting of sodium and potassium ions, said solution having a pH of at least 6.

2. The method of claim 1 in which said solution contains permanganate ions in the amount of from 0.001 percent by weight to saturation.

3. The method of claim 2 in which said solution contains permanganate ions in the amount of from 1 to 10 percent by weight.

4. The method of claim 1 in which the step of contacting said surface with said solution is carried out at a temperature of from 25° F. to the boiling point of said solution for from one-half to sixty minutes, the lower temperatures corresponding to longer immersion times.

5. The method of claim 4 in which said step of contacting said surface with said solution is carried out at a temperature of from 180° F. to 200° F. for from three to five minutes, the lower temperatures corresponding to longer immersion times.

6. The method of claim 1 in which the pH of said solution is at least 11.

7. The method of claim 1 in which the pH of said solution is achieved by use of a compound of a member selected from the group consisting of phosphates, hydroxides and carbonates.

8. The method of claim 1 in which the step of contacting said surface with said solution is preceded by descaling.

9. Product produced by the method of claim 1.

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