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[54] METHOD FOR PROTECTING COPPER SURFACES AGAINST CORROSION

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[58] **Field of Search**.... 148/6.24, 6.21, 6.17, 6.14 R; 106/14; 252/390

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[57] **ABSTRACT**

This invention relates to the corrosion protection of cupriferous surfaces. According to the invention, effective corrosion protection is obtained by treating the copper surfaces with a solution of elementary sulfur in certain organic solvents viz. in organic amines of the group comprising alkyl amines, aryl amines, hydroxyalkyl amines, and hydroxyaryl amines. Before use, these solutions are diluted with water, preferably in a ratio of approximately 1:500. It is believed that by this treatment a copper sulfide layer is formed on the treated surfaces, with simultaneous inclusion of sulfur into the copper lattice near the surface. While the surface layer of copper sulfide has but poor mechanical resistance, the layer containing included sulfur is firmly adherent and gives an effective protection of the copper articles.

3 Claims, No Drawings

METHOD FOR PROTECTING COPPER SURFACES AGAINST CORROSION

SUMMARY OF THE INVENTION

Method for protecting copper surfaces against corrosion, comprising the treatment of the surfaces to be protected with a solution of elementary sulfur in organic amines of the group comprising alkyl amines, aryl amines, hydroxyalkyl amines, and hydroxyaryl amines, said solution being diluted with H_2O in the ratio 1:100 to 1:1000 before application.

It is known to use sulfur-containing cleaning agents to prevent a tarnishing of the surfaces of copper, bronze and brass. These cleaning agents serve only to restore a bright metallic surface but the latter can corrode again. It has also been attempted to provide lubricating layers on metal surfaces by a treatment with sulfur-containing gases. Pure copper has been coated with a prefabricated solution of cuprous thiocyanate. This solution may be incorporated in resin, barnish etc. but will not change the metallic copper itself.

It has now been found that the resistance of copper surfaces to corrosion can be much improved by a transformation of the surface copper into copper-sulfur compounds.

Such transformation is accomplished according to the invention in that the surfaces are treated with solutions of elementary sulfur in organic amines, namely, in alkyl amines, aryl amines, hydroxyalkyl amines or hydroxyaryl amines, which solutions are preferably diluted with water for use. This treatment results in the formation of a relatively loosely deposited copper sulfide layer and a layer, which has been formed by chemical interdiffusion and can be detected by a microscopic examination revealing an exchange of copper by sulfur in the crystal lattice of the copper. The first-mentioned layer has only a small resistance to mechanical and thermal stresses. The layer formed by chemical interdiffusion is the result of the incorporation of a foreign substance and resists all stresses which may occur.

EXAMPLES

A monoethanolamine (colamine)-sulfur solution containing 20% sulfur was diluted 1:500 with water and used to treat specimens of highly polished soft copper tubes at 20° C. for about 30 minutes. These experimental conditions resulted in a highly satisfactory formation of the sulfide layers described above. A substantial shielding against an access of air or atmospheric carbon dioxide is recommended because such shielding considerably improves the durability of the sulfur solutions. The deposited outer sulfide layer was then almost completely removed by an ultrasonic treatment or by a treatment with other suitable solvents. The specimens were subsequently exposed together with untreated specimens for 4–40 weeks to an aqueous testing fluid which contained particularly aggressive substances.

Investigations have been made how useful incorporated sulfide layers can form under different experimental conditions, such as higher dilutions, higher temperatures or prolonged times of the action of the sulfidic aqueous sulfur solutions. It was found that a treatment for about 60 minutes was required, e.g., in case of a dilution of 1:1000 and a temperature of 20° C., and a treatment of only about 30 minutes was required at a temperature of 30° C.

The quantities of copper dissolved in the testing fluid were colorimetrically determined in an AF 201 Lovibond Comparator by the sodium-diethyldithiocarbamate method. The quantities of dissolved copper were higher by about one power of ten for the untreated tubes than for the treated tubes, as follows:

Untreated Copper Tube mg Cu/l		Sulfide-coated Copper mg Cu/l	
First specimen:	2.00	Third specimen:	0.25
Second specimen:	3.00	Fourth specimen:	0.25–0.30

In testing specimens 5 and 6, freshly precipitated ferric hydroxide was flushed into the testing fluid and the specimens were also left in the testing fluid for 4–40 weeks. The specimens were then removed from the testing fluid and the ferric hydroxide still contained in the fluid was flushed out with distilled water. Distinct bulges due to corrosion were observed on the uncoated tube where it had been supported. Only rough areas were observed on the coated tube.

Additional experiments conducted with isopropanolamine sulfur containing 15% sulfur and diluted 1:500 with water had similar results. It was also found that the sulfide layer formed by chemical interdiffusion just as all substances incorporated into the lattice structure resists a dissolution much more than amorphus substances and that the mechanical properties of this layer are so good that the layer resists all stresses to which it may be subjected as it is processed, e.g., by bending on a very small radius, heating during soldering (unless the temperature exceeds the value required for soldering).

The following experiments have been conducted for a further explanation of the process according to the invention and its results:

Corrosive agents:

1. Tap water + Cl_2 in amounts of 0.3, 0.1, and 5.0 milligrams per liter;
2. Tap water + $CaCl_2$ in amounts of 30 and 100 milligrams per liter;
3. Tap water + NO_3 (as $Ca(NO_3)_2$ or $Mg(NO_3)_2$) in amounts of 20 and 100 milligrams per liter;
4. Tap water + 2 and 10 milligrams P_2O_5 (as tripolyphosphate containing 56% P_2O_5 or as Austrophosphat containing 69% P_2O_5) per liter;
5. Tap water + 10 grams silicates per liter.

To enable an accurate evaluation, a sulfide-covered specimen and an untreated specimen were subjected to each corrosion test.

For this reason, 13 sulfide-covered specimens and 13 untreated specimens are required for a comparative test run.

The following test results were obtained with specimens that had been treated with solutions of monoethanolamine sulfur and isopropanolamine sulfur in different concentrations and at different temperatures and for different times.

The specimens treated with aqueous solutions of monoethanolamine containing 20% sulfur and with isopropanolamine containing 15% sulfur in a dilution of 1:500 at room temperature (20° C.) for a time of 5 minutes or 10 minutes showed in uncovered surface portions as a result of an insufficient degreasing. Besides, the covering was very thin so that the copper still shines through. After a treatment under the above-mentioned conditions for a time of 30 or 60 minutes, the covering formed by the treatment with monoethanolamine-sulfur was satisfactory and had a mat finish and the covering formed by the treatment with isopropanolamine-sulfur was uniform (surface without defects) but thinner.

Specimens treated for 30 or 60 minutes with an aqueous solution of monoethanolamine-sulfur in a dilution of 1:500 at 50° C. were not improved in surface finish over the specimens treated at 20° C.

To form an even thicker sulfide layer on the copper, the previously degreased copper tubes were additionally degreased with carbon tetrachloride and acetone. The treatment with an aqueous solution of monoethanolamine-sulfur at 20° C. for 30 or 60 minutes resulted in a much thicker copper-sulfur layer.

Individual black surface portions having a high gloss were formed on polished plates of strip copper after a treatment for 120 minutes with a solution diluted 1:500 at 20°.

A treatment with solutions of monoethanolamine-sulfur in a dilution of 1:250 always gave less satisfactory results, also in a dilution of 1:1000, so that a dilution of 1:500 appears to be most desirable for the formation of a sulfide surface layer.

A treatment of brass tubes and bronze rods under the above mentioned conditions did not result in a visible sulfide surface layer.

Experiments were also conducted with aluminum bronze coins. Some sulfide surface layer was formed on a coin of 95% Cu and 5% Al. The surface of coins containing 10% Al was not changed at all.

Whereas chromates are used to treat silver surfaces so as to form a transparent surface layer of silver chromate in order to prevent a darkening due to a formation of silver sulfide, the use of such chromates instead of alkylolamine-sulfur solutions in the treatment of copper has not been successful. The experiments were conducted with aqueous solutions of potassium bichromate in different concentrations and at temperatures increased in steps.

Copper tubes 40 centimeters long and 14 millimeters in diameter were provided. Part of these tubes were in the as-drawn condition and another part had been blown through with superheated steam. When these copper tubes were treated with a monoethanolamine-sulfur solution at a dilution of 1:500 at 20° C. for about 30 minutes, a glossy sulfide surface layer was formed in both cases on the inside surface of the tube. No bare copper areas were found in the tubes that had been blown through with superheated steam.

The following test was conducted to examine the sulfide surface layer:

The tube having a length of 40 centimeters and 14 millimeters in diameter, which had been provided with sulfide surface layers on the outside and inside, was bent through 180° on a mean diameter of 10 centimeters and was cut open in the longitudinal direction of the bend. The following was found: Some matter could be rubbed off the thick sulfide layer on the inside surface of the tube, but a uniform, firmly adhering layer remained.

One-half of the cut-open bend was now heated to red heat by means of a blower. In a dotlike area at the center of the heated surface, the surface layer crumbled off because the CuS was roasted to CuO. On both sides of that dotlike area, an unaffected homogeneous copper sulfide layer was found in spite of the very high temperature. Even naturally occurring copper sulfide would be roasted to copper oxide at the temperature reached at the center of the heated surface.

A plurality of copper tubes having a length of 40 centimeters and 14 millimeters in diameter were treated once as described hereinbefore for 30 minutes with a solution of monoethanolamine-sulfur in a dilution of 1:500 at 20° C. for 30 minutes and once for 60 minutes with a similar solution but in a dilution of 1:1000 at 20° C. The resulting specimens were investigated.

Tap water with the above-mentioned additions was used for a chemical test of the sulfide surface layer for resistance to corrosion.

The quantities of copper dissolved from treated and untreated specimens selected at random were ascertained and compared to ascertain the protection afforded by the sulfide surface layer against corrosion.

The results of these tests confirm the above-mentioned numerical data showing that the corrosive action of said fluids, as determined by the quantities of copper which have been dissolved, is lower by about one power of 10 for copper surfaces protected by the surface layers according to the invention than for unprotected surfaces.

What is claimed is:

1. A method for protecting copper surfaces against corrosion, comprising treating the surfaces to be protected with a solution of elementary sulfur in the proportion of 15 to 20% by weight in a hydroxyalkyl amine, said solution being diluted with H_2O in the ratio of 1:100 to 1:1000 before application.

2. A method for protecting copper surfaces against corrosion, comprising treating the copper surfaces with a 20% by weight solution of elementary sulfur in monoethanolamine which is diluted with water in the ratio of 1:500.

3. A method for protecting copper surfaces against corrosion, comprising treating the copper surfaces with a 15% by weight solution of elementary sulfur in isopropanolamine which is diluted with water in the ratio of 1:500.

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