
Candidate's answer**PATINATING SOLUTIONS AND PROCESSES**

The present invention relates to aqueous solutions for patinating a surface of copper or a copper alloy. Patinating is the process of providing a copper or copper alloy surface with a patina.

Copper surfaces, when exposed to atmospheric conditions in an urban environment, are slowly chemically altered and develop a green surface layer. This green layer is known as a patina and typically takes at least 10 years to fully develop. A green patina will not only develop on copper surfaces, but also on the surface of brass and bronze (brass and bronze are copper alloys).

More specifically, the invention relates to aqueous solutions as defined in claim 1.

The invention also relates to a process for patinating a copper or copper alloy surface of claim 6.

Solutions and processes for patinating a copper or copper alloy surface are known in the art.

D1 discloses *patinating solution for copper, bronze or brass surfaces having a pH of 8-10 and containing water, ammonium sulphate, ammonium chloride and copper sulphate, where the concentration of sulphate ions is at least 40 g/l and the concentration of chloride ions is at least 1 g/l.*

However the solutions disclosed in D1 produce a patina which have a low adherence to the surface. It is therefore an object of the invention to provide solutions which can provide a copper or copper alloy surface with a patina with high adherence to the surface.

D2 discloses an aqueous solution having a pH of 5 containing 100 g/l sulphate ions, 15 g/l chloride ions, 5 g/l copper ions, 5 g/l zinc ions and 10 g/l arsenic trioxide. These solutions are, however, unsuitable for commercial use because of the safety and disposal costs involved with them.

Processes for patinating copper or copper alloy surfaces are known from D1 and D2. D1 discloses a natural weathering process, and D2 discloses a process comprising drying and curing a treated copper surface in an oven at 50°C for 48 hours.

The applicant has surprisingly found that the new and inventive process disclosed herein produces a patinated copper surface wherein the patina adheres to the surface with a sufficiently high adhesion to enable the preparation of patinated panels, such as roofing panels, prior to installation. Panels prepared by the method of the invention can be assembled after the patina is applied without causing damage to the patina.

Description

In one aspect the invention provides a solution according to claim 1. The presence of copper and zinc ions improves the adhesion of patinas prepared using the claimed solution.

In a preferred embodiment, the solution comprises a wetting agent, which improves the contact of the solution to the metal surface.

In a further preferred embodiment, the solution comprises ammonia. In yet further preferred embodiments, the solution comprises the components of claim 4 and claim 5.

Also provided is the process of claim 6. The artificial aging step d) enables the patina to form on a copper or copper alloy surface with high adhesion. Any solution of claims 1-5 may be used in the process of claim 6.

Preferably, the artificial aging step d) is performed at 60°C-100°C, more preferably 80°C. Results shown in the examples demonstrate that a temperature of 80°C provides patinas with very high adhesion.

Preferably, the solution is applied to the surface by spraying the surface with the aqueous solution. The aqueous solution preferably has a temp. of 10-30°C. In a preferred embodiment, the cleaning step a) is performed by spraying the surface with a phosphate-based liquid.

The defined features of the preferred embodiments can be combined with one another to provide a process with any combination of the preferred embodiments. This also applies to the preferred embodiments of the aqueous solutions, and the use of any preferred embodiments or combination of embodiments of the aqueous solutions in any embodiments or combination of embodiments of the process.

In a further embodiment of the invention, patinated panels are provided prepared by any process disclosed herein using any aqueous solution disclosed herein. Also provided are methods of constructing a structure by pre-patinating a panel comprising a copper or copper alloy surface and then installing the panel. In a preferred embodiment, the panels are roofing panels.

The invention is further disclosed and supported in the following examples:

Examples

Example 1

Ten litres of the following aqueous patinating solutions were prepared:

Solution 1

Sulphate ions 100 g/l

Chloride ions 20 g/l

Copper ions 5 g/l

Zinc ions 5 g/l

1 g/l of Greenwet (a commercial wetting agent)

The pH of the solution was adjusted to 9 using ammonia.

Solution 2

Sulphate ions 100 g/l

Chloride ions 15 g/l

Copper ions 5 g/l

Zinc ions 5 g/l

Arsenic trioxide 10g/l

The pH of this solution was adjusted to 5 with sulphuric acid.

Solution 3

Sulphate ions 100 g/l

Chloride ions 20 g/l

Copper ions 5 g/l

1 g/l of Greenwet (a commercial wetting agent)

The pH of the solution was adjusted to 9 using ammonia.

Example 2

Samples of copper roofing panels with an area of 10cm² were prepared by spray washing with a phosphate-based cleaning solution (Cuplimp) and carefully rinsed with water. The panels were then sprayed with solution 1, solution 2 or solution 3 and aged using the conditions shown in the table. The panels were evaluated for colour and rated on a scale of 1-5, where the higher the number the better the rating, with a rating of at least 4 being essential.

The adherence of the patina was evaluated by treating a 10cm² panel, bending the panel by 90°, applying adhesive tape over the surface, removing the tape and evaluating the area of the surface still covered by patina. The adherence was rated 1-10. An adherence rating of at least 7 is essential for a useful process.

Sample number	Solution	Aging Time (Hours)	Relative Humidity (%)	Temperature (°C)	Colour Rating	Adherence Rating
1	1	12	80	60	4	3
2	1	12	80	70	4	8
3	1	12	80	80	4	9
4	1	12	80	90	4	8
5	1	12	80	100	4	5
6	1	12	70	80	4	4
7	1	6	80	80	4	2
8	2	12	80	80	5	7
9	2	12	80	80	5	3
10	3	12	80	80	4	7
11	3	12	80	80	4	2

These results we have obtained show that very high quality patinas can be obtained on copper panels using any one of the solutions 1-3.

Example 3

The use of the process for making patinated full size roofing panels in our factory was investigated. It was decided to use solution 1 as the patinating solution. The quality of the patina obtained with solution 3 is lower. Solution 2, since it contains arsenic, is highly toxic. The safety and waste disposal costs involved with using an arsenic-containing solution are at present so high that the use of such a solution is of no commercial interest.

Claims

1. An aqueous patinating solution comprising
 - at least 40 g/l sulphate ions;
 - at least 1 g/l chloride ions;
 - copper ions;
 - zinc ions; and
 - having a pH between 8 and 10.
2. The solution of claim 1 further comprising a wetting agent.
3. The solution of claim 1 or 2 further comprising ammonia.
4. The solution of any of claims 1 to 3 comprising
 - 60-120 g/l sulphate ions;
 - 10-30 g/l chloride ions;
 - 2-10 g/l zinc ions;
 - 2-10 g/l copper ions; and
 - optionally 1-2 g/l wetting agent.

5. The solution of claim 1 comprising
 - 100 g/l sulphate ions;
 - 20 g/l chloride ions;
 - 5 g/l copper ions;
 - 5 g/l zinc ions;
 - 1 g/l of a wetting agent;
 - sufficient ammonia to adjust the pH to between 8 and 10;
 - and water.
6. A process for patinating a copper or copper alloy surface comprising the steps of:
 - a) cleaning the surface so that the surface is free of grease and dirt;
 - b) rinsing the surface with water so that all traces of cleaner are removed;
 - c) treating the surface with an aqueous solution comprising
 - (i) at least 40 g/l sulphate ions;
 - (ii) at least 1 g/l chloride ions; and having a pH of 3-6 or 8-10, wherein if the pH is 3-6 the solution comprises arsenic trioxide; and
 - d) artificially aging the surface by heating the treated surface for 8-24 hours in an atmosphere of at least 80% humidity, so that the patina adheres to the surface.
7. The process of claim 6 wherein the aqueous solution further comprises copper ions and zinc ions.
8. The process of claim 6 or 7 wherein step d) is performed at a temperature of between 60°C and 100°C.
9. The process of claim 8 wherein step d) is performed at a temperature of 80°C.
10. The process of claim 6 to 9 wherein the aqueous solution is the aqueous solution of any of claims 1 to 5.
11. The process of claims 6 to 10 wherein step c) is performed by spraying the surface with the aqueous solution.
12. The process of claims 6 to 11 wherein the aqueous solution has a temperature of 10°C – 30°C.
13. The process of claims 6 to 12 wherein step a) is performed by spraying the surface with a phosphate-based cleaning liquid.
14. A copper or copper alloy surface prepared by the process of claims 6 to 13.
15. A panel comprising a patinated copper or copper alloy surface, wherein the surface is patinated by the process of any of claims 6 to 13.
16. The panel of claim 15 wherein the panel is a roofing panel.

17. A method for assembling a structure comprising the steps of;
 - a) preparing a panel of claim 15
 - b) installing the panel of claim 15.
18. The method of claim 17 wherein the structure is a roof and the panel is a roofing panel of claim 16.