EUROPEAN QUALIFYING EXAMINATION 2009

PAPER A
CHEMISTRY

This paper comprises:

LETTER FROM THE APPLICANT

Ruftiler AB
12 Verdigrisgatan
Uppsala, Sweden

To Mr P. Agent
132 Strandsgatan
Stockholm, Sweden

Dear Mr Agent,

I am the technical director for Ruftiler AB, a small company specialising in high value roofing materials. We were recently approached by the Gamla cathedral administration and were invited to submit an offer for the replacement of some of the cathedral's copper roofing panels. The existing roofing panels have been in place for over a hundred years and a number had recently been damaged in a storm.

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).

The green roof of Gamla cathedral is a distinctive feature of this historic building. The cathedral administration was not prepared to wait for the patina to develop naturally. The cathedral administration insisted that the replacement panels must have an artificial patina that matches the green coloration of the existing panels. We investigated the standard published process (see document D1) for forming artificial patinas and found it to be unsatisfactory. We have improved on the known processes and intend to commercialise the new process we have developed. We wish to obtain a European Patent for this invention. Please file an application urgently since we need to present the new process in our offer document to Gamla cathedral administration next Tuesday.

The process involves cleaning a copper panel, contacting it with a patinating solution and then aging the treated surface under controlled conditions. The solution we intend to use commercially is an aqueous solution containing 100 g/l sulphate ions, 20 g/l chloride ions, 5 g/l copper ions, 5 g/l zinc ions, sufficient ammonia to adjust the pH to between 8 and 10, water and 1 g/l of a wetting agent.

Whilst developing the new process we first considered the nature of the natural patina. A group from the University of Stockholm has recently published a paper (document D2) detailing their investigation of the patina on a sample taken from a roof panel removed from Gamla cathedral. This paper shows that a natural patina is a mixture of a basic copper sulphate and a basic copper chloride. Since we were attempting to recreate the natural patina as closely as possible it was clear that we would need a solution containing sulphate and chloride ions. The solution must also be able to dissolve out copper ions from the metal surface. These ions are needed to react with the sulphate and chloride ions. The solution must not however attack the metal too vigorously. These conditions will be fulfilled when using an acidic solution of a pH of 3-6 or a basic solution having a pH of 8-10.

The process involves first cleaning the metal surface to ensure that the metal surface is free of grease and dirt before it is contacted with the patinating solution. The patina formed will otherwise tend to locally peel off the surface. The cleaning is preferably performed by spraying the surface with a phosphate-based commercial cleaning liquid. The surface must then be carefully rinsed with water to remove all traces of the cleaner.

The cleaned and rinsed surface is then treated with the patinating solution. This step is preferably performed by spraying the metal surface with the solution. The solution preferably has a temperature of 10-30°C.

It is subsequently necessary to age the treated metal surface. This is typically achieved by heating the treated metal for 8-24 hours in an atmosphere with a high relative humidity. If a more intense colour is desired the process can be repeated up to three times. If the process is properly performed a copper, brass or bronze surface can be provided with a patina of a colour which matches that of the natural patina and which adheres well to the metal surface. These attributes are essential for commercial success. The adhesion of the patina produced by our new process is so good that we can form the patina on roofing panels before they are installed on the roof.

The patinating solution is aqueous and must contain at least 40 g/l sulphate ions and at least 1 g/l chloride ions. Optional components include copper ions to accelerate the process or both copper and zinc ions to improve the adhesion. The solution, as is obvious to anyone working in the field, may also contain a wetting agent to improve the contact of the solution with the metal surface. If the solution is acidic arsenic trioxide must be added. This ensures that the required colour is developed. The pH of the solution is preferably adjusted with ammonia for basic solutions and hydrochloric or sulphuric acid for acidic solutions.

The patinating solutions preferably contain 60-120 g/l sulphate ions, 10-30 g/l chloride ions, 2-10 g/l copper ions and 2-10 g/l zinc ions. Arsenic trioxide is used at 5-15 g/l. The wetting agent if used is any commercially-available wetting agent. The concentration of the wetting agent is typically 1-2 g/l.

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 10 g/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 10 cm^2 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 10 cm^2 panel, bending the panel by 90°, applying adhesive tape over the surface, removing the tape and evaluating the area of the surface still covered with 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	60	5	3
10	3	12	80	80	4	7
11	3	12	80	60	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.

The patinas on the panels of samples 3, 8 and 10 were studied by X-ray diffraction to determine the composition of the patina. The basic copper sulphate and basic copper chloride known to be present in natural patinas were detected in samples 3 and 10. The patina of sample 8 contained copper chloride, copper sulphate and copper arsenate. A further crystalline phase, which we have not yet been able to identify, was also present in the patinas of all of the samples.

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.

We have successfully patinated roofing panels of a wide range of sizes. The panels could be assembled to make a copper roof without any damage to the patina.
Please confirm that you have filed the patent application as soon as possible. Any fees falling due can be deducted from our account. I have enclosed documents D1 and D2.

Yours Sincerely

C.U. Shingle

DOCUMENT D1

Copper, brass and bronze articles such as copper roofs or bronze statues that have been exposed to the weather for a number of years, develop a green patina. This is a very attractive finish and one that would be very desirable to recreate.

Previous attempts to create this finish artificially have resulted in a colour that does not match the natural colour of the patina very well.

The invention seeks to provide a solution able to form a patina with a colour that closely matches that of a natural patina.

The patinating solution of the invention has a pH of 8-10 and is an aqueous solution containing ammonium sulphate and ammonium chloride. The solution must contain at least 40 g/l sulphate ions and at least 1 g/l chloride ions. The solution also contains copper sulphate and sufficient ammonia to adjust the pH to the desired value.

The concentrations of the sulphate, chloride and copper ions in the solution are preferably as follows:

Sulphate ions:	50-120 g/l
Chloride ions:	2-21 g/l
Copper ions:	2-15 g/l

The concentration of ammonium ions will depend on the pH used and is not important. Preferably no metal ions except for copper are present at a concentration above 1 g/l.

The metal surface has to be clean before it is treated and is typically washed by spraying it with a phosphate-based cleaning solution. The surface is then carefully rinsed with water. The surface must be well wetted by the rinsing water otherwise the cleaning should be repeated.

The cleaned surface is then sprayed with the patinating solution. The spraying must be performed after the copper, bronze or brass article has been installed in its final location, at a site exposed to the weather since the patina only adheres very weakly to the metal surface during the first six months after the treatment. Initially no colour is visible, but it usually develops within 24 hours under the influence of the weather. The desired coloured patina is only obtained under suitable weather conditions. The precise weather conditions required to form a patina are not well established. It is however known that it should not rain within six hours of the treatment and that a relative humidity of above 80% is beneficial. If a patina initially fails to develop, the surface may be sprayed further times with the patinating solution.

Example

A newly installed copper roof was spray-cleaned, rinsed and then treated with the following aqueous solution:

Sulphate ions: 95 g/l
Chloride ions: 14 g/l
Copper ions: 4.5 g/l

The pH was adjusted to 9.1 with ammonia.

After 8 hours the roof had developed a green patina having a colour indistinguishable from that of a natural patina.

Claim

1. 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.

DOCUMENT D2

Copper Patinas: Formation and Structure

Introduction:

Copper surfaces when exposed to the atmosphere for long periods of time form a green patina. The composition and the mechanism of formation of this layer are poorly understood. This study seeks to identify the components present in such a natural patina and to compare them with the phases formed in an artificial patina.

Experimental:

Samples of copper roofing panels with a natural patina were obtained from Gamla cathedral in Sweden. The panels had been in place for 122 years.
A copper panel with an artificial patina was prepared by first spraying a cleaned and rinsed copper surface with an aqueous solution having a pH of 5 containing sulphate ions (100 g/l), chloride ions (15 g/l), copper ions (5 g/l), zinc ions (5 g/l) and arsenic trioxide (10 g/l). The treated panel was dried and cured in an oven at 50°C, for 48 hours. A cross-section was cut through the coating on each panel and X-ray diffraction was used to identify the phases present.

Results and discussion:

1. Natural Patina
In the cross-section the natural patina is observed to consist of two distinct layers, an inner layer of copper oxide and an outer layer consisting mainly of basic copper sulphate with some basic copper chloride. The outer layer is responsible for the green colour of the patina.

The structure identified provides support for the theory proposed by Allen et al that the formation of a patina initially involves the formation of copper (I) oxide which is oxidised to basic copper sulphate and basic copper chloride by rainwater.

The chemistry of rainwater in Gamla was also studied. The composition of the rainwater (average of ten samples) was 0.015 g/l sulphate ions, 0.002 g/l chloride ions, 0.007 g/l ammonium ions, 0.003 g/l nitrate ions, 0.002 g/l sodium ions, 0.001 g/l calcium ions and 0.002 g/l magnesium ions. Sulphate ions are thus present at a significantly higher concentration than chloride ions. This is believed to be why the basic copper sulphate as opposed to the basic copper chloride is the predominant phase in the patina at Gamla.

2. Artificial Patina

The artificial patina has a different structure. It consists of a single green layer. X-ray diffraction revealed that the layer contained copper chloride, copper sulphate and copper arsenate. The copper arsenate is believed to contribute significantly to the colour of the layer, since it is a known green pigment. The artificial patina is thus formed differently to the natural patina.