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(54) **Method for the fabrication of a multi-layered patina and said multi-layered patina**

(57) The invention relates to a method for forming a patina surface on a substrate, which is preferably made of copper or copper alloy. According to the method, the patina surface is formed on top of the surface of the substrate material in at least two different layers of corrosive

patination material, of which the colour and/or composition differ from each other. The invention also relates to the patina, which is formed as at least two layers.

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Description

FIELD OF THE INVENTION

[0001] The invention relates to a method for the formation of a patina on a substrate, which is preferably manufactured from copper or copper alloy. A patina formed of several layers is fabricated using the method. The invention also relates to the corresponding multi-layered patina.

BACKGROUND OF THE INVENTION

[0002] Copper and copper alloys are coated with an oxide layer in normal atmospheric conditions. Outdoors a brown oxide forms on the surface of the copper and later a patina is formed at a varying rate, depending on where and how the surface is exposed. The colour of the patina in urban and rural environments is green and in marine environments mainly blue-green. Copper is recognised as a long-lasting and maintenance-free material for roofs and facades. A natural patina is a consequence of the corrosion of metal in the atmosphere. A patina layer has a certain protective effect. The formation of a patina on the surface of a copper substrate takes many years. It takes an especially long time in a clean rural environment, where a patina may not be formed at all.

[0003] Several methods of artificial patination have been presented earlier. When forming an artificial patina the copper surface to be patinated is first treated oxidatively, so that a dark copper oxide layer forms on the surface.

[0004] US patent 3,152,927 refers to a method and paste, in which method a patina gel is formed from basic copper nitrate and ferric sulphate. Basic copper nitrate is not thermodynamically stable in rainwater, and instead changes gradually into a stable basic copper sulphate. The colour of basic copper sulphate and copper nitrate is blue-green, but iron sulphate is added to the patina and the yellow colour compounds formed from iron during precipitation give the product its green colour.

[0005] WO application 03085169 describes a method for the fabrication of patina pastes of different colours using stable metal compounds as colour pigments in order to obtain the desired shade.

[0006] In addition to roofs and rainwater systems, patinated copper is used nowadays more and more as a cladding material. As a facing material, a patinated surface, either of the traditional green or of a different colour obtained by means of metal compounds, is on the other hand quite uniform in colour. Surface designers, however, have requested the possibility to get a more vibrant surface, in other words to treat it with several different shades.

[0007] An attempt has been made to form a vibrant patina surface by spraying patination material in droplets directly on top of a dark copper oxide surface, so that the patina does not cover the entire surface. In this case there

is the danger that the amount of patina per square metre is too little, so that over time it may dissolve away in rainwater, particularly on sloping surfaces.

5 PURPOSE OF THE INVENTION

[0008] The purpose of the method according to the invention is to fabricate a multi-layered patina on top of a substrate material of copper or copper alloy, covering the entire substrate.

SUMMARY OF THE INVENTION

[0009] The invention relates to a method for forming a multi-layered patina on a substrate material, which is preferably made of copper or copper alloy. The patina of the method is formed on the surface of the substrate material in at least two different layers of corrosive copper-based patination material, where the colour and/or composition of the layers vary from each other. According to the method, the transfer of different patination materials onto the substrate is performed on one processing line. It is preferable that at least the first patination layer is made to cover the surface and the others are sprayed as droplets.

[0010] The invention also relates to a patina, which is formed in at least two layers on top of a substrate material of copper or copper alloy and so that the colour and/or composition of the copper-based patina layers differ from each other.

[0011] The essential features of the invention will be made apparent in the attached claims.

DETAILED DESCRIPTION OF THE INVENTION

[0012] When a patina surface is formed on top of a substrate material of copper or copper alloy, the first layer on the substrate is usually a black- or brown-toned copper oxide layer. In conventional patination, the patina of the desired colour is sprayed as a uniform layer on top of the copper oxide layer. Now in the method according to this invention, a patina is formed on top of the copper oxide layer of at least two copper-based patination materials, which either differ in colour from each other and/or they differ in composition. When patinating the substrate, the spraying of the different patination materials is preferably done on a single processing line, which consists of a separate spray and tank for each patination material, from which each patination material is fed in turn.

[0013] One method to manufacture a vibrant patina is to form two layers of patina of different colours on top of the copper oxide layer. The first is a covering layer and the second is droplet sprayed on top of the first layer. The first layer is for example black-toned and the second the traditional green. The first layer may also be traditional green and the second layer for instance grey-toned.

[0014] Firstly, the first patination material is sprayed

onto the copper oxide surface of the substrate, in a quantity that is around 70 - 90% of the total amount of patina. After this, a surface layer of the desired shade is drop-let-sprayed on top of the first layer. In this way a vibrant surface is obtained and at the same time the thickness of the patina layer is still sufficient to withstand the effect of rainwater.

[0015] A black-toned patina can be obtained for instance by oxidising the patination material in the fabrication stage more than usual, so that the patination material is at least partially oxidized into an oxide and turns black. It is sufficient to form a black-toned patina when about 10-20% of the patination material is oxidized into an oxide with the rest remaining normal patination material. Another method to produce a black-toned patination material is to add a black pigment such as graphite to an ordinary green-toned patination material. Grey patination material may also be made by adding graphite to a green-toned patination material. As described in the prior art, patination materials are produced from copper salts.

[0016] A method according to the invention has been described above, in which the patina is formed of two layers and certain shades of colour. However, it is clear that within the framework of the invention, other desired shades may be chosen. As the need arises, a patina may also be formed by using several patination materials of different shades. In the alternative described above, both the first and second layers and any subsequent layers are stable, in other words they will not change substantially over time. For example, brochantite or basic copper sulphate, which is a preferred patination material for the surface layer, is very stable. Brochantite is blue-green in colour, but usually iron is added to it to achieve the traditional green colour.

[0017] Another method according to the invention to produce a multi-layered vibrant patina is to form a patina on the surface of the substrate (on top of the copper oxide layer), which is a reactive base layer and a stable surface layer. A reactive base layer patination material is for example basic copper nitrate, which over time turns into brochantite. A reactive base layer may also be an unstable basic copper sulphate with various crystalline forms, which is essentially blue in colour. The unstable crystalline forms of basic copper sulphate include ramsbeckite $[\text{Cu}, \text{Zn}_{15}(\text{SO}_4)_4(\text{OH})_{22} \cdot 6\text{H}_2\text{O}]$, wroewolfeite $[\text{Cu}_4(\text{SO}_4)(\text{OH})_6 \cdot 2\text{H}_2\text{O}]$, copper sulphate hydroxide hydrate $[\text{Cu}_4(\text{SO}_4)(\text{OH})_6 \cdot \text{H}_2\text{O}]$ and posnjakite $[\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot 2\text{H}_2\text{O}]$.

[0018] As a stable surface layer patination material, for example brochantite may be used, which is very weather-resistant. Since the amount of sulphur and sulphates in rainwater is so small nowadays, brochantite also acts partially as a source of sulphate for the reactive layer patination material. When brochantite acts as a source of sulphate small amounts of copper and sulphate are dissolved from it into the rainwater, and are precipitated back as brochantite according to the chemical balance. Pure brochantite is blue-green in colour, but iron is usually added to it to give the patina its traditional green

colour.

[0019] When some reactive patination material is used as the patina base layer, one advantage of the reactive crystals formed using this method is that the gradual change of the patination material into brochantite results in better adhesion to the substrate than the direct manufacture of patination material as brochantite. The base layer is sprayed on as a covering layer and the coverage of the brochantite surface layer is around 80-100%, preferably between 80 - 95%.

[0020] The invention also relates to a patina that is fabricated in at least two separate layers on top of a substrate made of copper or copper alloy and so that the colour and/or composition of the copper-based patination materials differ from each other.

[0021] The first layer of the patina according to the invention is made a covering layer and the second and any further layers as droplike layers.

[0022] According to one embodiment of the invention, the patina is formed from at least two layers, which are stable and different in shade. When the first layer is formed to be black in tone, it may be done in at least two ways. A black tone has been made by using a green-toned patination material, of which some has oxidised into copper oxide. A black tone has also been made by adding a black pigment such as graphite to the green-toned patination material. The patination material of the second layer in this embodiment is preferably green in tone. When the first layer is formed to be the traditional green shade, the second and any subsequent layers have been made a different colour. When a grey shade is required graphite has been added to a green-toned patination material.

[0023] According to another embodiment of the invention, the first layer of patina is made reactive so that over time it becomes stable. The patination material of the reactive layer is preferably basic copper nitrate or unstable basic copper sulphate, which is at least one of the following: ramsbeckite $[\text{Cu}, \text{Zn}_{15}(\text{SO}_4)_4(\text{OH})_{22} \cdot 6\text{H}_2\text{O}]$, wroewolfeite $[\text{Cu}_4(\text{SO}_4)(\text{OH})_6 \cdot 2\text{H}_2\text{O}]$, copper sulphate hydroxide hydrate $[\text{Cu}_4(\text{SO}_4)(\text{OH})_6 \cdot \text{H}_2\text{O}]$ or posnjakite $[\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot 2\text{H}_2\text{O}]$. Unstable basic copper sulphate is blue. The patination material of the second layer of patina is preferably stable brochantite, of which the coverage is around 80-100%, preferably 80-95%.

EXAMPLES

Example 1

[0024] Changes to copper sheets caused by weathering were studied where the sheets had either a totally covering patina surface or where the patination material had been sprayed as droplets on the copper oxide surface. The test was carried out as a climate chamber test, which has been found to correlate well with atmospheric testing. The length of the test was 250 h. It was found that the totally covering patina surface withstood changes

is the air well. On the other hand, in the sheets where the copper oxide was partially exposed, the copper oxide reacted and became reddish in parts.

Claims

1. A method for the formation of a patina on a substrate made essentially of copper or copper alloy, onto which a copper oxide surface is first formed, **characterised in that** the patina is formed on the substrate as at least two different layers of corrosive copper-based patination material, of which the colour and/or composition differ from each other.
2. A method according to claim 1, **characterised in that** the feed of patination materials onto the substrate is made on a single process line.
3. A method according to claim 1 or 2, **characterised in that** the first patination layer is a covering one and the other layers are droplet-sprayed on top of it.
4. A method according to any of claims 1-3, **characterised in that** the amount of the first patination layer is 70 - 90% of the total amount of patina.
5. A method according to any of claims 1-4, **characterised in that** the first patination layer is black-toned and the second the traditional green.
6. A method according to any of claims 1-3, **characterised in that** the first patination layer is reactive and the others stable.
7. A method according to claim 6, **characterised in that** the first patination layer is of basic copper nitrate.
8. A method according to claim 6, **characterised in that** the first patination layer is of unstable basic copper sulphate, which is at least one of the following group: ramsbeckite $[\text{Cu}, \text{Zn}_{15}(\text{SO}_4)_4(\text{OH})_{22} \cdot 6\text{H}_2\text{O}]$, wroewolfeite $[\text{Cu}_4(\text{SO}_4)(\text{OH})_6 \cdot 2\text{H}_2\text{O}]$, copper sulphate hydroxide hydrate $[\text{Cu}_4(\text{SO}_4)(\text{OH})_6 \cdot \text{H}_2\text{O}]$ and posnjakite $[\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot 2\text{H}_2\text{O}]$.
9. A method according to any of claims 6-8, **characterised in that** the patina is formed of two patination materials, so that the second layer is brochantite.
10. A patina formed on top of a copper oxide layer of a substrate made of copper or copper alloy, **characterised in that** the patina is formed as at least two layers, in which the colour and/or composition of the copper-based patination materials differ from each other.
11. A patina according to claim 10, **characterised in that** the first layer of the patina is made to be covering and the others droplike.
12. A patina according to claim 10 or 11, **characterised in that** the first layer is made black in tone.
13. A patina according to claim 12, **characterised in that** a black tone is formed by oxidising a part of the patination material into copper oxide.
14. A patina according to claim 12, **characterised in that** the shade is formed by adding black pigment to a green patination material.
15. A patina according to claim 10 or 11, **characterised in that** the first layer is a green-toned patination material and the second is of a different colour.
16. A patina according to claim 10 or 11, **characterised in that** the patination material of the first layer is made reactive and the subsequent layers stable.
17. A patina according to claim 16, **characterised in that** the first patination material is made of basic copper nitrate.
18. A patina according to claim 16, **characterised in that** the first patination material is formed of unstable basic copper sulphate, which is one at least of the following group: ramsbeckite $[\text{Cu}, \text{Zn}_{15}(\text{SO}_4)_4(\text{OH})_{22} \cdot 6\text{H}_2\text{O}]$, wroewolfeite $[\text{Cu}_4(\text{SO}_4)(\text{OH})_6 \cdot 2\text{H}_2\text{O}]$, copper sulphate hydroxide hydrate $[\text{Cu}_4(\text{SO}_4)(\text{OH})_6 \cdot \text{H}_2\text{O}]$ and posnjakite $[\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot 2\text{H}_2\text{O}]$.
19. A patina according to any of claims 16-18, **characterised in that** the patina is formed of two layers, of which the second is brochantite, with a coverage of 80 -100%, preferably 80 - 95%.