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(72) Inventeur/Inventor:
LEUCHTE, JUERGEN, DE
(73) Propriétaire/Owner:
KM EUROPA METAL AKTIENGESELLSCHAFT, DE
(74) Agent: NORTON ROSE CANADA
S.E.N.C.R.L.,S.R.L./LLP

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(54) Title: METHOD FOR COVERING COPPER WITH PATINA

(57) **Abrégé/Abstract:**

A process for patinating articles comprising copper or a copper alloy is described. The articles to be patinated are treated with a preferably aqueous patination solution which preferably contains copper ions and zinc ions and are subsequently subjected to a maturing process. This is, in particular, carried out in a temperature- and humidity-controlled chamber.

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Abstract

A process for patinating articles comprising copper or a copper alloy is described. The articles to be patinated are treated with a preferably aqueous patination solution which preferably contains copper ions and zinc ions and are subsequently subjected to a maturing process. This is, in particular, carried out in a temperature- and humidity-controlled chamber.

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DescriptionMethod for covering copper with patina

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[0001] The invention relates to a process for producing a patina on articles comprising copper or copper alloys and a patination solution used in this process.

- 10 [0002] It is generally known that a greenish layer having, inter alia, a protective function is formed on the surface of copper parts when they are exposed to weathering for a long time. This layer is referred to as copper patina. At our latitudes, it normally takes from ten to fifteen years for a copper surface to be coated completely with the green layer.
- 15 Various methods of shortening this long period of time have been developed in the past with the objective of imitating or readily producing a natural patina on copper surfaces.

- [0003] Thus, for example, US-3,497,401-A discloses a process and a
- 20 reaction solution for producing a patina. Here, a copper part is dipped into an acidic, aqueous solution comprising potassium chlorate and copper sulfate at room temperature. US-5,160,381-A, too, describes the production of a patina on a copper article. In the multistage process described there, the copper part to be patinated is, after cleaning,
- 25 treated with an aqueous solution containing copper, sodium, acetate, chloride, sulfate, H^+ and OH^- ions. After careful cleaning and drying, the copper piece is treated in a second process step with an aqueous solution of copper carbonate, ammonium chloride, copper acetate, arsenic trioxide, copper nitrate and hydrochloric acid. EP 0 943 701 A1
- 30 also concerns the production of a patina, once again by treatment of a

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copper article with an aqueous copper salt solution. This process is particularly suitable for preoxidized copper surfaces.

[0004] However, the known processes have a number of disadvantages.
5 Thus, components which are toxic and harmful to health, e.g. the abovementioned arsenic trioxide, are used in the preparation of some known patination solutions. For reasons of environmental protection and for health reasons, it is desirable to avoid the use of such constituents. Other processes have limited applicability. Thus, some processes are
10 generally less well suited to the patination of untreated copper surfaces, since they require preoxidation of the copper parts to be patinated.

[0005] In terms of the quality properties, too, both with regard to optical aspects and with regard to mechanical aspects, many synthetically
15 produced patina layers display deficiencies. They often have unsatisfactory adhesion properties, i.e. the artificial protective layer flakes off even under light mechanical stress.

[0006] It is therefore an object of the invention to provide a process
20 which avoids the disadvantages of the prior art and solves as many as possible of the problems indicated.

[0007] It is another object of the invention to provide a process for patinating articles comprising copper or a copper alloy by means of an
25 aqueous patination solution containing copper ions, wherein the article is treated with the patination solution, characterized in that the article which has been treated in this way is subjected to a maturing process in a temperature- and humidity-controlled chamber, the maturing process encompassing the maturing steps

30 - allowing the treated article to rest at a first rest temperature in the range from 20°C to 70°C and a first rest atmospheric humidity in the range from 30% to 90% for a first rest time up to one week

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- irrigating the treated article at least once at an irrigation temperature in the range from 20°C to 70°C and an irrigation atmospheric humidity in the range from 30% to 95% for an irrigation time up to one day, and
- 5 - allowing the treated article to rest at a second rest temperature in the range from 20°C to 70°C and a second rest atmospheric humidity in the range from 30% to 90% for a second rest time up to one week, wherein the patination solution contains at least one zinc salt.
- 10 It is another object of the invention to provide a patinated article comprising copper or a copper alloy produced by a process as defined herein.
- [0008] In the process of the invention, articles comprising copper or a
15 copper alloy are treated with a preferably aqueous patination solution

containing copper ions and subsequently subjected to a maturing process.

[0009] The maturing process is made up of individual maturing steps
5 which encompass a choice of atmospheric humidities and temperatures. The setting and control of the two parameters temperature and atmospheric humidity can, in particular, readily be carried out in a temperature- and humidity-controlled chamber provided for this purpose.

10 [0010] A preferred sequence of maturing steps can be summarized as follows: the treatment of the article with the patination solution, in particular the application of the patination solution to the article to be patinated, is followed by the article being allowed to rest at a first rest
15 temperature and a first rest atmospheric humidity for a first rest time. The article is then irrigated at least once at an irrigation temperature and an irrigation atmospheric humidity for an irrigation time, again followed by the article being allowed to rest at a second rest temperature and a second rest atmospheric humidity for a second rest time.

20 [0011] During the first resting step, the temperature in, in particular, the temperature- and humidity-controlled chamber is preferably in the range from 20°C to 70°C, in particular from 25°C to 55°C (first rest temperature). The atmospheric humidity is preferably in the range from 30% to 90%, in particular from 40% to 50% (first rest atmospheric
25 humidity). These preferred ranges for temperature and atmospheric humidity indicated for the first resting phase correspond essentially to the preferred ranges for the second rest temperature and the second rest atmospheric humidity.

30 [0012] During the irrigation step, the temperature in the temperature- and humidity-controlled chamber is preferably in the range from 20°C to 70°C, in particular from 25°C to 55°C. The atmospheric humidity during

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the irrigation step is preferably maintained in the range from 30% to 95%, in particular in the range from 65% to 80%. Irrigation is usually effected by spraying the treated article with water. This step is preferably repeated from four to five times at intervals of from 90 minutes to
5 2 hours.

[0013] The first rest time can be up to one week, but preference is given to a period of from two to three days. The same applies to the second rest time. The irrigation time is usually not more than one day, but can
10 be as short as from 5 to 10 hours.

[0014] As mentioned above, the patination solution used is a solution containing copper ions whose preferred composition will be described in more detail below. Furthermore, it should be emphasized that it is
15 particularly preferred that the article to be patinated is cleaned and/or has its surface roughened before application of the patination solution. Any grease or oil residues and other contaminants present on the surface can have an adverse effect on the adhesion of the patina formed. This is countered, in particular, by chemical degreasing and/or
20 blasting of the surface to be patinated with broken glass spheres. As an alternative, it is also possible to use, for example, an eccentric grinder or a belt grinder.

[0015] The article to be patinated is, if appropriate after an optional
25 pretreatment of the type indicated, subjected to the maturing process, preferably by transferring it to the previously mentioned temperature- and humidity-controlled chamber. It is not absolutely necessary, but preferred, for the application of the patination solution to be carried out in the chamber.

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[0016] The patination solution is preferably applied in finely divided form, particularly preferably sprayed on. The temperature (preferably in the

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temperaturé- and humidity-controlled chamber) is preferably in the range from 30°C to 70°C, in particular from 40°C to 55°C, during this application. The patination solution is usually applied in at least two, preferably in four or five, treatment steps, in particular at intervals of
5 about 1 hour.

[0017] It has surprisingly been found that, in contrast to classical processes for the patination of copper parts which consist essentially of a single or multiple treatment with an aqueous copper salt solution and a
10 subsequent air drying step, the use of a maturing process, in particular in a temperature- and humidity-controlled chamber, offers great advantages, in particular in respect of the optics and the quality of the patina produced. The artificial patina formed gives a uniform and intensive color impression.

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[0018] An after-treatment of the freshly patinated surface can optionally be carried out. It is possible either to lighten or darken the surface. If appropriate, the surface can also be sealed since the unsealed patina can sometimes react further under natural weathering influences.

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[0019] The process indicated is preferably provided for the patination of copper plates, strips or shingles. However, it can in principle also be applied to all shaped parts or articles comprising copper or copper alloys. Partial patinations of shaped parts such as roof guttering are also
25 possible. Thus, for example, in the case of roof guttering the bead region can be strongly patinated while the outside of the water channel is only oxidized. This results in the visual impression that the copper piece has been exposed to atmospheric influences for years and decades. Such effects are frequently used in the optical structuring of new buildings, but
30 in particular in the restoration or repair of relatively old listed buildings in order to obtain the overall historic impression.

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[0020] Further features possessed by the patina produced by the process of the invention are a good resistance to mechanical stress and excellent adhesion properties.

5 [0021] These positive properties can also be attributed to the patination solution which is preferably used and is likewise subject matter of the present invention. It consists of an aqueous solution in which a copper salt, preferably copper nitrate, is present in a proportion of up to 20% by weight, in particular in a proportion of from 3% by weight to 5% by
10 weight. It is preferred that a zinc salt, in particular zinc chloride, is additionally present in the solution, preferably in a proportion of from 0.1% by weight to 5% by weight, in particular in a proportion of from 0.2% by weight to 1% by weight. Furthermore, the solution can contain various chloride and carbonate additives, in particular sodium chloride,
15 ammonium chloride, calcium chloride and ammonium carbonate. The pH of the patination solution is preferably in the basic range, in particular in the slightly basic range of pH 7 - 10.

[0022] Among the components present in the patination solution of the
20 invention, the zinc salt deserves particular emphasis. It has surprisingly been found that the addition of zinc salts has a positive effect on the adhesion properties of the patina formed. In addition, such an addition results in a lighter greenish appearance.

25 [0023] Finally, the invention encompasses the patinated article comprising copper or a copper alloy itself. After conclusion of the maturing process, the article is coated with a green-turquoise patina containing copper ions and preferably also zinc ions. The patina usually has a thickness of from 0.02 mm to 0.06 mm, in particular from 0.03 mm to 0.05 mm.

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[0024] Further features of the invention can be derived from the following examples. Here, the features and properties presented can in each case either be realized alone or in a combination of a plurality thereof.

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Example

[0025] To produce the patination solution, the following components are dissolved in one liter of water:

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- 40 g of copper(II) nitrate
- 3 g of zinc chloride
- 8 g of calcium chloride
- 2 g of sodium chloride
- 15 - 20 g of ammonium chloride

[0026] The temperature- and humidity-controlled chamber has a base area of about 3 x 2.5 m. A copper sheet whose surface has been thoroughly ground by means of an eccentric grinder and is free of grease and other contaminants is placed in the temperature- and humidity-controlled chamber. The temperature in the temperature- and humidity-controlled chamber is set to 50°C. At this temperature, the patination solution is sprayed four times at intervals of in each case one hour onto the surface of the copper piece. During the subsequent first rest time, the temperature is maintained at about 45°C. The atmospheric humidity is regulated to about 45%. After allowing the copper sheet to rest for three days, the treated copper part is irrigated a number of times. It is sprayed with water a total of five times at intervals of in each case 90 minutes. The atmospheric humidity in the temperature- and humidity-controlled chamber during this time is about 75%, and the temperature is, as in the case of the treatment with patination solution, about 50°C. The parameters atmospheric humidity and temperature are subsequently reduced again to 45% and 45°C,

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respectively, and the copper sheet is allowed to rest for a further 3 days. The patination is then concluded. The copper sheet is coated absolutely uniformly by the artificial protective layer.

Claims

1. A process for patinating articles comprising copper or a copper alloy by means of an aqueous patination solution containing copper ions, wherein the article is treated with the patination solution, characterized in that the article which has been treated in this way is subjected to a maturing process in a temperature- and humidity-controlled chamber, the maturing process encompassing the maturing steps
 - allowing the treated article to rest at a first rest temperature in the range from 20°C to 70°C and a first rest atmospheric humidity in the range from 30% to 90% for a first rest time of between two days and one week,
 - irrigating the treated article at least once at an irrigation temperature in the range from 20°C to 70°C and an irrigation atmospheric humidity in the range from 30% to 95% for an irrigation time of between 5 hours and one day, and
 - allowing the treated article to rest at a second rest temperature in the range from 20°C to 70°C and a second rest atmospheric humidity in the range from 30% to 90% for a second rest time of between two days and one week,wherein the patination solution contains at least one zinc salt in a proportion of from 0.1% by weight to 5% by weight.
2. The process as claimed in claim 1, characterized in that the rest temperatures are in the range from 25°C to 55°C, and the rest atmospheric humidities are in the range from 40% to 50%.
3. The process as claimed in claim 1 or 2, characterized in that the second rest temperature corresponds essentially to the first rest temperature and the second rest atmospheric humidity corresponds essentially to the first rest atmospheric humidity.

4. The process as claimed in any one of claims 1 to 3, characterized in that the irrigation temperature is in the range from 25°C to 55°C, and the irrigation atmospheric humidity is in the range from 65% to 80%.
5. The process as claimed in any one of claims 1 to 4, characterized in that the first rest time and the second rest time are each from 2 to 3 days.
6. The process as claimed in any one of claims 1 to 5, characterized in that the irrigation time is from 5 to 10 hours.
7. The process as claimed in any one of claims 1 to 6, characterized in that the patination solution contains at least one copper salt in a proportion of from 1.5% to 20% by weight.
8. The process as claimed in claim 7, characterized in that the copper salt is copper nitrate.
9. The process as claimed in claim 7 or 8, characterized in that the proportion of copper salt is from 3% to 5% by weight.
10. The process as claimed in any one of claims 1 to 9, characterized in that the zinc salt is zinc chloride.
11. The process as claimed in any one of claims 1 to 10, characterized in that the patination solution contains the zinc salt in a proportion of from 0.2% by weight to 1% by weight.
12. The process as claimed in any one of claims 1 to 11, characterized in that chloride and carbonate additives are present in the patination solution.

13. The process as claimed in claim 12, characterized in that the chloride and carbonate additives are sodium chloride, ammonium chloride, calcium chloride, ammonium carbonate or combination thereof.
14. The process as claimed in any one of claims 1 to 13, characterized in that at least one surface treatment selected from the group consisting of cleaning and roughening of the surface is carried out prior to the treatment of the article.
15. The process as claimed in claim 14, characterized in that the cleaning procedure is degreasing.
16. The process as claimed in claim 15, characterized in that the degreasing is a chemical degreasing.
17. The process as claimed in any one of claims 14 to 16, characterized in that the roughening procedure is grinding or a blasting treatment.
18. The process as claimed in claim 17, characterized in that the blasting treatment is glass sandblasting.
19. The process as claimed in any one of claims 1 to 18, characterized in that the patination solution is applied in finely divided form.
20. The process as claimed in claim 19, characterized in that the patination solution is sprayed on.
21. The process as claimed in any one of claims 1 to 20, characterized in that a treatment temperature in the range from 30°C to 70°C is selected in the treatment of the article with the patination solution.

22. The process as claimed in claim 21, characterized in that the treatment temperature is in the range from 40°C to 55°C.
23. The process as claimed in any one of claims 1 to 22, characterized in that the patination solution is applied in at least two treatment steps.
24. The process as claimed in claim 23, characterized in that the patination solution is applied in 4 - 5 treatment steps.
25. The process as claimed in any one of claims 1 to 24, characterized in that at least one surface after-treatment selected from the group consisting of sealing, lightening and darkening of the surface is carried out after the maturing process.
26. The process as claimed in any one of claims 1 to 25, characterized in that the article to be patinated is selected from the group consisting of plate material, strip material, shaped part and ornament.