

PROCESS AND REAGENT SOLUTION FOR PRODUCING PATINA

TECHNICAL FIELD

The invention relates to a process and a reagent solution for producing patina on the surface of articles made of copper or a copper alloy.

BACKGROUND OF THE INVENTION

A thin green, protective layer of basic copper compounds develops in air on copper surfaces. This is called patina. Depending upon the environmental influences, the development of natural patina sometimes takes several decades. Induced patination, e.g., by applying soluble copper salts or ammonia salts, serves to imitate this natural patina which often develops only within long time intervals. In the case of imitated patina, basic copper compounds are applied as color pigments together with organic or inorganic film-forming media onto a copper surface.

The known reagent solutions, however, do not always render the desired success as far as quality and color of the film are concerned. The handling and storage of some of them is expensive. They are therefore suitable only to a limited extent for use in industry to produce patina in the factory or on a building site. Further, when some of these reagent solutions are used on pre-oxidised or partly patinated copper surfaces, e.g., for repairing damaged patina, there is the risk of nonuniform development of the film and the coloring.

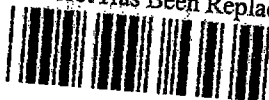
SUMMARY OF THE INVENTION

Therefore, the problem underlying the invention is to create a process for producing mechanically stable patina preferably on previously weather-exposed copper surfaces, with the patina produced having reduced copper solubility and allowing interaction with the atmosphere, like a natural patina. A further goal of the invention is to provide an improved reagent solution for producing patina on copper surfaces, which is, in addition, simple to handle and store.

The solution of the process-related aspects of this problem is based on the measures recited in Claim 1.

Accordingly, a reagent solution consisting of an aqueous solution of copper salts and salts of inorganic acids is applied onto the surface of a copper article after cleaning the same. The copper article which was treated in this way is then exposed for drying with protection against the effects of the weather.

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Drying usually takes place in air until the patina has completely hardened. The patina produced with the process is mechanically stable and has only a slight copper solubility. The time required for producing the patina is comparatively short.

According to the measure recited in Claim 2, the patina produced is provided with a transparent protective coating of varnish.

For this purpose a water-based two-component varnish containing caoutchouc is preferably used. The varnish is clear.

Prior to its application, the varnish is prepared with a hardening agent. The ratio of hardening agent to varnish is usually 1:4. The standing time is at most 20 min. The ready, mixed varnish is applied to the patina preferably with a spraying unit.

After drying, the varnish is cured and can be exposed to the weather. Depending upon the prevailing environmental conditions (temperature, atmospheric moisture, etc.), the drying period may last 15 to 24 hours.

The varnish coating which was applied according to the invention has the following particular properties and advantages:

- the varnish coating is transparent and matt. It does not modify the optical properties of the patina underneath.
- The varnish coating can be treated with cleaning solutions.

Accordingly, it is possible to remove, for example, stains such as sprayed-on graffiti, by means of special cleaning solutions without leaving any residues and without damaging the patina.

- The varnish coating allows the penetration of water vapour by diffusion. In this way, the patina underneath can continue to interact with the atmosphere.
- The varnish coating results in a strengthening of the patina surface underneath. Patinated copper articles therefore can be worked mechanically, e.g., by bending or joining with lock seams, without flaking of the patination.

The solution of the object-related part of the problem according to Claim 3 resides on a reagent solution consisting of an aqueous solution of copper salts and salts of inorganic acids.

Advantageous embodiments of the inventive reagent solution are characterised in dependent Claims 4 to 7.

The inventive reagent solution makes use of the combination of two different principles of patina formation. On the one hand, the reagent solution contains reactive components in the form of salts of inorganic

acids which react with the copper oxides of the patinated surface to form basic copper compounds. The rate of this reaction depends upon the conditions of weather exposure. Furthermore, the solution already contains the copper compounds formed in these reactions in the form of copper salts as a sort of colour pigments. For this reason, a very good coloured appearance is obtained immediately after the application. The natural patina, which otherwise develops often only after long time periods is reproduced within a short time. The subsequent chemical reaction intensifies the coloured appearance and strengthens the entire patina film.

Optimal success is attained with the inventive reagent solution when it is used on a pre-oxidised or already partially patinated copper surface. For this reason, the copper articles should undergo an appropriate pre-treatment of the surface. The copper surface can be pre-oxidised or pre-patinated in the factory. But the copper surface may also have a patina film developed by natural exposure to the weather. A copper surface which was not pre-treated should be exposed for about two months or more to natural weather conditions.

The treatment with the inventive reagent solution can be carried out after such a pre-treatment of the surface.

By applying the reagent solution to a pre-oxidised or already partly patinated copper surface, a patina film can be produced in situ or in the factory. Also copper surfaces which are not fully patinated in green or damaged patina films acquire a uniform patina film upon application of the inventive reagent solution. Depending upon the composition of the reagent solution, the colour tone of the patina to be produced can be varied and adapted to the respective surroundings.

Application and handling of the inventive reagent solution is simple. Application to the copper surface can be done by means of brushes, rollers or a spraying unit.

The reagent solution can be stored over extended time periods of several months at room temperature without impairment due to aging.

Copper(I) carbonate, copper(II) carbonate, copper(I) chloride, copper(II) chloride, copper(II) sulfate, copper acetate, copper nitrate or mixtures thereof are well suitable as copper salts used in the aqueous reagent solution. The advantageous concentration range is between 5 and 500 g/L.

Sodium carbonate, potassium carbonate, ammonium carbonate, sodium bicarbonate, potassium bicarbonate, sodium chloride, potassium chloride,

ammonium chloride, sodium sulfate, sodium bisulfate, potassium sulfate, potassium bisulfate, or mixtures thereof are preferably used as reactive component. Also the concentration range of these salts of inorganic acids is preferably in the range between 5 and 500 g/L.

The consistency of the inventive reagent solution can be modified by the addition of wetting agents or thickeners and adjusted to the respective conditions of use. Known wetting agents, e.g., tensides, and/or thickeners are used. They are added to the reagent solution as a fraction of 5%.

The inventive reagent solution produces a high-quality patina of basic copper compounds and is particularly well suitable for pre-oxidised or already partly patinated copper surfaces. The treatment can be carried out in situ on the building site or in the factory. The reagent solution is well suitable for repairing existing patina or for the colour adaptation of a patina.

The reagent solution can be prepared and applied at room temperature. It proved to be convenient to protect a patinated area for at least 48 hours from rain after treatment with the reagent solution.

After that, it is especially advantageous to coat the patina film which was produced in this way with a transparent protective layer in order to avoid damage and to reduce the solubility of copper. As mentioned above, for this purpose one uses varnishes permeable for water vapour, which render a protective layer with open pores and facilitate in this way the natural interaction of the patina surface with the atmosphere.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

An embodiment of the reagent solution and its preparation are described below.

An aqueous solution containing 200 g/L copper sulfate is mixed with 200 g/L sodium carbonate and stirred for one hour at room temperature. After that, 200 g/L sodium chloride are added and stirring is continued for another hour at room temperature. After that, the solution can be directly applied to the surface to be patinated.

A wetting agent, for example a tenside, in a concentration of 50 g/L is added for application with the aid of a spraying unit.

In order to obtain a solution which can be applied with a brush, the solution is thickened with a commercial thickener in a concentration of 50 g/L.

The storage time of a reagent solution prepared in this way is unlimited at room temperature.

The operation for producing patina on the surface of a copper article is explained below by way of an example.

The copper surface to be patinated usually bears a dark brown copper oxide layer which at some points is already covered with copper salts (patina). Prior to patination, the surface is freed from grease and tightly adhering dirt. The removal of lightly adhering dirt particles can be effected with water and manual or mechanical aids.

The copper oxides remaining on the surface and the patina already present are not removed. The copper articles are advantageously treated in dry weather; if necessary, the surface to be patinated must be protected from precipitation by appropriate coverings.

After drying of the cleaned surface, the areas which are not to be patinated are covered with sticky coverings. After that, the previously prepared reagent solution is shaken or stirred and applied. A spraying unit proved to be particularly suitable for this purpose. Depending upon the power of the spraying unit, nozzles with diameters between 0.2 mm and 0.6 mm are used. For uniform coating of the surface, spraying angles of 60° to 90° are considered advantageous. During the treatment, care must be taken to avoid the development of droplets on the surface.

If necessary, a number of patination processes can be carried out. Prior to each additional patination process, care must be taken to have the surface completely dry.

Once the desired appearance of the copper surface has been obtained, the same is exposed to drying. The drying process should be as slow and uniform as possible. In this way, the quality of the patina is improved. Depending upon the weather conditions, but conveniently after 48 hours at the earliest, the protective layer of varnish can be applied. Also for this purpose the use of a spraying unit is recommended, preferably with nozzles having a diameter between 0.2 mm and 0.3 mm and a spraying angle of 90°.

A single application of the protective layer suffices. During the protective layer's drying, which, depending upon the weather conditions, may last from 20 minutes to 24 hours, the copper article should be protected from precipitation.

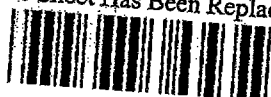
Tests conforming to DIN 50 017/KFW or DIN 50 917, part 1, in which samples treated with the reagent solution according to the invention were exposed or subjected to the natural weather conditions for six months, have shown that no significant changes of the patina can be noted. The patina

produced with the reagent solution therefore has an excellent stability to weather exposure.

**Claims:**

1. A process for producing patina on the surface of an article made from copper or a copper alloy, wherein the surface is first cleaned and, after that, a reagent solution consisting of an aqueous solution of copper salts and salts of inorganic acids is applied onto the surface and then exposed to drying under protection from weather effects.
2. The process according to Claim 1, characterised in that a transparent varnish layer is applied onto the patina.
3. A reagent solution for producing patina on the surface of articles made from copper or a copper alloy, consisting of an aqueous solution of copper salts and salts of inorganic acids.
4. The reaction solution according to Claim 3, characterised in that copper salt is present in the form of copper(I) carbonate, copper(II) carbonate, copper(I) chloride, copper(II) chloride, copper(II) sulfate, copper acetate, copper nitrate or mixtures thereof in a concentration between 5 and 500 g/L.
5. The reagent solution according to Claim 3 or 4, characterised in that salts of inorganic acids in the form of sodium carbonate, potassium carbonate, ammonium carbonate, sodium bicarbonate, potassium bicarbonate, sodium chloride, potassium chloride, ammonium chloride, sodium sulfate, sodium bisulfate, potassium sulfate, potassium bisulfate, or mixtures thereof are contained in a concentration between 5 and 500 g/L.
6. The reagent solution according to any one of Claims 3 to 5, characterised in that a wetting agent is added as a fraction of up to 5%.
7. The reagent solution according to any one of Claims 3 to 6, characterised in that a thickener is added as a fraction of up to 5%.

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