

The invention concerns a process for the production of brown covering layers on semi-product in strip form made of copper, in particular on rolled strips and sheets for roof covering and façade cladding.

In normal atmospheric conditions, a firmly adhering and durable covering layer of copper oxide forms on the surface of bright copper. The initially very thin oxide film already stabilises the surface of the copper material appreciably in the face of the effects of the atmosphere. In the ideal case, the slow continued formation of the oxide layer due to the reaction of the copper with moisture and oxygen in the air gradually produces an even brown colouration (brown patina), and the surface of the copper increasingly loses the metallic shine. In the course of time, the brown covering layer becomes darker and darker and then goes an anthracite brown. This is the final state usually occurring on vertical surfaces of buildings, such as external wall cladding. On inclined roof surfaces the covering layer continues changing colour reacting with substances contained in the atmosphere such as sulphur dioxide, carbon dioxide and chlorides to form basic copper compounds, until the patina green typical of copper is obtained.

However, in certain atmospheric conditions the formation of the brown covering layer can be greatly slowed or accelerated in places so that as a rule it is necessary to wait a relatively long time before an even colouration of the copper surface is obtained. Departures from a uniform colour tone are observed in particular during the initial stage of weathering. In many cases, uneven dark spots and/or stripes form on the surface of the copper at first. However, as the weathering by atmospheric factors continues, these colour differences disappear.

A process for the production of even layers of copper (I) oxide on the surface of copper wire or strip is mentioned for example in Chemical Abstracts, volume 83, no. 2, July 1975, page 258, abstract no. 32184t. With this known process, the copper oxide layer is formed by an oxidising heat treatment at a temperature lying in the temperature range from 300 to 1000°C.

The underlying object of the invention is to disclose a process with which an even and firmly adhering brown covering layer (brown patina) can be produced on the surface of semi-product in strip form made of copper on a large scale and is not damaged or chipped during the further fabrication involved in the building sector in particular.

According to the invention, this object is achieved by the combination of the following process steps:

- the surface of the copper semi-product is first roughened by a mechanical treatment;
- the copper semi-product is then heat-treated in a controlled oxidising atmosphere at a temperature lying in the temperature range from 150 to 650°C for a period from 0.1 to 30 minutes;
- following the heat treatment, the copper semi-product is treated with an aqueous solution of a metal salt from the group comprising potassium chlorate, potassium permanganate and sodium hypochlorite on its own or in a mixture with copper sulphate.

Advantageous variants of the invention are disclosed in the

sub-claims.

With the aid of the measures of the process according to the invention, it is surprisingly simple to obtain a production pre-weathering (brown patination) of the surface of semi-product in strip form made of copper without having to wait for the dark brown colouration of the copper surface dependent on the long term action of atmospheric factors. In particular, this advantage satisfies the aesthetic feeling for an even colouration of the surface of the copper, for example with a roof covering or façade cladding composed of profiled copper elements. Another essential advantage lies in the fact that if repairs become necessary, corresponding copper strips or sheets with a brown patina can be made available to the metal worker. This pre-patinated material then allows direct insertion in façade cladding which has already been exposed to the atmospheric factors for an extensive period without differences becoming visible in the colouration of the brown covering layers on the individual elements of the façade.

It has also been shown that the pre-patinated strips or sheets of copper manufactured by the process according to the invention exhibit covering layers which both exhibit excellent adhesion and remain resistant to deformation during bending or crimping, i.e. exhibit no delamination. Even finger marks which are often unavoidable when fitting roof coverings and façade cladding remain largely unnoticed on the pre-patinated surface.

Even better adhesion of the covering layer and even more uniform brown colouration of the pre-patinated copper surface can be achieved if, immediately following the heat treatment, a further chemical oxidisation treatment is carried out with an aqueous solution of at least one metal salt from the group comprising potassium chlorate, potassium permanganate and sodium hypochlorite on its own or in a mixture with copper sulphate.

Basically, numerous chemical and electrolytic processes are already known for colouring copper surfaces brown. However, without prior thermal oxidation, these frequently lead to insufficient colour saturation of the covering layers, particularly on a large scale. In addition, it is otherwise unavoidable that spots and streaks are left behind on the surface, in particular with a treatment solution applied by immersion.

In the following the invention is described in greater detail with reference to an embodiment example.

A cold-rolled and possibly degreased strip of SF copper to DIN 1787 with a thickness of 0.6 mm and a breadth of 1000 mm was roughened evenly by means of a sanding device. Sanding belts with nos. 180 and 320 grit abrasives were used for the surface treatment. The copper strip was then passed through a gas-heated continuous oven for the heat treatment. A controlled gas atmosphere containing approximately 25% by volume oxygen was set in the oven for the surface oxidation of the copper strip continuously heat treated in the temperature range from 150 to 350°C, preferably at approximately 275°C. After a short cooling section, the pre-oxidised copper strip was then immersed at a working temperature of approximately 80° in a bath which contained an aqueous solution of a mixture of 50 g/l potassium chlorate and 100 g/l copper sulphate pentahydrate. The

working time of the treatment solution was approximately 2 to 3 minutes. Then the copper strip was rinsed with water and dried with hot air. After these treatment steps the copper strip exhibited a very even covering layer with an intense dark brown colouration. The brown patina proved to be highly resistant to abrasion. After further bending and crimping operations, there was no sign of damage or delamination of the covering layer.



#### PATENT CLAIMS

1. Process for the production of brown covering layers on semi-product in strip form made of copper, in particular on rolled strips and sheets for roof covering and façade cladding, characterised by the combination of the following process steps:
  - the surface of the copper semi-product is first roughened by a mechanical treatment;
  - the copper semi-product is then heat-treated in a controlled oxidising atmosphere at a temperature lying in the temperature range from 150 to 650°C for a period from 0.1 to 30 minutes;
  - following the heat treatment, the copper semi-product is treated with an aqueous solution of a metal salt from the group comprising potassium chlorate, potassium permanganate and sodium hypochlorite on its own or in a mixture with copper sulphate.
2. Process for the production of brown covering layers according to claim 1, characterised in that the mechanical treatment is effected by sanding or brushing.
3. Process for the production of brown covering layers according to claim 1, characterised in that an aqueous solution of 20 to 70 g/l potassium chlorate and 50 to 150 g/l copper sulphate pentahydrate is applied to the surface of the copper semi-product.
4. Process for the production of brown covering layers according to one of claims 1 to 3, characterised in that the copper semi-product is immersed in the aqueous solution at a temperature lying in the temperature range from 20 to 90°C for a period from approximately 1 to 10 minutes.