



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 0 976 845 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention
of the grant of the patent:
16.07.2003 Bulletin 2003/29

(51) Int Cl.7: **C22F 1/08**, C22F 1/02,
B24C 3/32

(21) Application number: **99114365.2**

(22) Date of filing: **21.07.1999**

(54) **Method for producing copper tubes**

Verfahren zur Herstellung von Kupferrohren

Procédé pour la fabrication de tubes en cuivre

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE**

(30) Priority: **30.07.1998 FI 981683**

(43) Date of publication of application:
02.02.2000 Bulletin 2000/05

(73) Proprietor: **Outokumpu Oyj
02200 Espoo (FI)**

(72) Inventor: **Välimäki, Seppo
29600 Noormarkku (FI)**

(74) Representative: **Zipse + Habersack
Wotanstrasse 64
80639 München (DE)**

(56) References cited:
**EP-A- 0 281 641 EP-A- 0 335 999
EP-A- 0 356 732 EP-A- 0 647 723
DE-B- 3 003 228 GB-A- 1 461 961
GB-A- 2 055 061 US-A- 4 351 678
US-A- 4 393 566**

EP 0 976 845 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

5 [0001] This invention focuses on a method for producing copper tube and particularly for hard-drawn temper sanitary tube. According to the method developed, the extruded tube shell is cold formed until almost its final size, after which the tube undergoes inline annealing in oxidizing conditions in order to adjust the tube to its final size in the cold forming step with finally sand blasting to the inner surface of the tube. Through this method, the use of organic solvents is avoided and at the same time a tube with excellent corrosion resistance is achieved.

10 [0002] The conventional method for treating hard tubes has comprised cold forming steps following extrusion, such as bull-block drawing, straightening and cutting and subsequent degreasing, in which drawing lubricant is removed from the inner surface of the tube. Residual lubricant is removed so that it does not form a carbon film during installation, which in turn would promote pitting. In practice, this degreasing step has involved immersing the tubes in an organic solvent such as trichloroethylene.

15 [0003] The washing of tubes in organic solvents is increasingly subject to limits and regulations, since trichloroethylene for example is not considered an environmentally friendly substance. Washing with other solvents however does not always produce a satisfactory result.

[0004] In patent application EP 306 810, there is known a treatment method for hard-drawn sanitary tubes, in which tube is produced from tube shell using normal cold forming steps, after which the tube undergoes degreasing, wherein the tubes are first immersed in organic solvent and subsequently treated with a jet of sand.

20 [0005] In patent publication EP 281 641 a treatment method is described for hard or half hard tubes, where the tubes are formed by cold drawing to their final length, after which they are subjected to inline annealing in an oxygen-enriched atmosphere. During annealing, the traces of drawing grease burn away.

25 [0006] EP patent application 647 723 describes a manufacturing method for half hard or hard tubes, where the intention is for the tube to release as small an amount of copper ions as possible into for example normal drinking water. According to the method, the tube shell is cold formed to an intermediate size, after which the inner surface is roughened. The roughening can be either performed by sand blasting or etching (Beizen). After this, the tube is routed to annealing treatment at a temperature of 350 - 650 °C, wherein a mixture of shielding gas and oxygen (1-7% O₂) is introduced into the tube, in order to form a protective oxide film to the inner surface of the tube. The tube subsequently undergoes cold drawing to a final size, wherein the reduction is about 20%. If required, the tube can be degreased after cold drawing. After the final draw the tube is subjected to further thermal treatment at a temperature of 175 - 275 °C in the presence of oxygenous gas (at least 20% O₂). The result of this treatment is that a very stable malachite layer forms rapidly on the inner surface of the tube, which prevents the dissolution of copper ions into drinking water.

30 [0007] According to the newly developed method, hard copper tubes suitable for sanitary installations can be manufactured in a simple fashion. The extruded tube shell is drawn using conventional cold forming technology until almost its final size. After this, oxygen or oxygen-enriched gas is conducted into the tube coil, and the tube is heated by inline annealing briefly at a temperature of 450 - 650 °C, preferably 500 - 600 °C. In so doing, any residual lubricants on the inner surface are burnt off. After heating, the tube undergoes a final, approx. 5-20% forming step. After this the tube is cut to the specified size and the inner surface of the tube is sand blasted. The essential features of the invention will become apparent in the appended claims.

35 [0008] Even though the method developed still involves annealing the hard tube, it is essential that the drawing of the tube through the annealing furnace is carried out at such a speed, 100 - 200 m/min, preferably 120 - 160 m/min, that the structure has not time to recrystallize or soften. During annealing, there is oxygen or oxygen-enriched gas inside the tube, with oxygen enrichment of at least 20% and preferably at least 50%. There are signs of the onset of recrystallization in the microstructure, but during the final cold drawing after annealing, the tube is formed in such a way that its values are well within the region of hard tube. One advantage of drawing after annealing is that the tube will be formed precisely to the tolerance sets.

40 [0009] Conventionally washing of the inner surface of hard tubes takes place with organic solvents but as stated in the prior art, organic solvents are becoming an environmental hazard. Sand blasting has proven very effective in removing drawing grease residues, thereby preventing carbon film formation and cold water pitting. The newly developed method replaces the previously known one, which used organic solvent to clean the inner surface of tubes.

45 [0010] Another problem has arisen with the use of organic solvents: In the market there is a need to make a colour stamp in addition to the normal punching stamp on tubes and it has been shown that the colour stamp does not withstand washing in organic substances. Adding the colour stamp separately after washing creates a new and therefore expensive additional working step. When sand blasting is used as the cleaning method for the inside of tubes, no additional work step is required to make the colour stamp.

50 [0011] The invention is further described in the following example:
55

Example

[0012] Copper tube was manufactured as normal by extrusion and bull-block drawing, but in the final bull-block drawing the tube was left at a bigger size than the final one. The tube coil was filled with oxygen-containing gas and heated briefly at a temperature of 500-650 °C. The table below lists the properties of the tube after the final drawing (tube size 15 x 1 mm) and a comparison with the requirements set by standard EN1057 for hard tubes. Bending according to the standard means that the bending test is performed in accordance with the conditions laid down in standard EN 10232, so no tear shall be visible to the unaided eye at this stage. The 1st class mentioned in the test results means that the tube meets the stringent requirements of the standard.

Table

	Annealing temperature °C	Hardness HV	Tensile strenght N/mm ²	Inner surf. C-content mg/dm ²	HNO ₃ -test	Bending
EN 1057			min. 290	max. 0,2	no films	bending acc. to standard
Test 1	500	121	438	0,06	-	1 st class
Test 2	600	121	438	0,06	-	1 st class
Test 3	650	121	424	0,06	-	1 st class

Claims

1. A method for manufacturing hard copper tubes for sanitary applications, wherein the tube is manufactured by extrusion and cold forming, **characterized in that** in the cold drawing the tube is drawn until almost its final size, after which oxygen-containing gas is conducted into the tube and the tube undergoes brief inline annealing at a temperature of 450 - 650 °C and at such a speed that the structure has no time to recrystallize or soften, after which the tube undergoes a forming of 5 - 20% and thereafter the inner surface of the tube is sand blasted in order to remove drawing grease residues.
2. A method according to claim 1, **characterized in that** inline annealing is carried out on the tube at a speed of 100 - 200 m/min.
3. A method according to claim 1, **characterized in that** inline annealing is carried out on the tube at a speed of 100 - 160 m/min.
4. A method according to claim 1, **characterized in that** inline annealing is carried out on the tube at a temperature of 500 - 600 °C.
5. A method according to claim 1, **characterized in that** there is oxygen inside the tube during annealing.
6. A method according to claim 1, **characterized in that** there is gas inside the tube during annealing, which gas has oxygen enrichment of at least 50%.
7. A method according to claim 1, **characterized in that** there is gas inside the tube during annealing, which gas has oxygen enrichment of at least 20%.
8. A method according to claim 1, **characterized in that** the final forming step is sinking.

Patentansprüche

1. Verfahren zur Herstellung von harten Kupferrohren für Sanitäranwendungen, wobei das Rohr durch Extrusion und Kaltformen hergestellt wird, **dadurch gekennzeichnet, dass** das Rohr beim Kaltziehen bis fast auf seine endgültige Größe gezogen wird, wonach Sauerstoff enthaltendes Gas in das Rohr geleitet wird und das Rohr kurzer Inline-Glühung bei einer Tem-

EP 0 976 845 B1

peratur von 450 bis 650 ° C und in einer solchen Geschwindigkeit unterzogen wird, dass die Struktur keine Zeit hat, um zu rekristallisieren oder zu erweichen, wonach das Rohr einer Formung von 5 - 20 % unterzogen wird und danach die innere Oberfläche des Rohres gesandstrahlt wird, um Zieh fettüberreste zu entfernen.

- 5 2. Verfahren nach Anspruch 1,
dadurch gekennzeichnet, dass Inline-Glühen an dem Rohr bei einer Geschwindigkeit von 100 - 200 m/min durchgeführt wird.
- 10 3. Verfahren nach Anspruch 1,
dadurch gekennzeichnet, dass Inline-Glühen an dem Rohr bei einer Geschwindigkeit von 100 - 160 m/min durchgeführt wird.
- 15 4. Verfahren nach Anspruch 1,
dadurch gekennzeichnet, dass Inline-Glühen an dem Rohr bei einer Temperatur von 500 - 600° C durchgeführt wird.
- 20 5. Verfahren nach Anspruch 1,
dadurch gekennzeichnet, dass während des Glühens Sauerstoff innerhalb des Rohres ist.
- 25 6. Verfahren nach Anspruch 1,
dadurch gekennzeichnet, dass während des Glühens Gas innerhalb des Rohres ist, welches Gas eine Sauerstoffanreicherung von wenigstens 50 % hat.
- 30 7. Verfahren nach Anspruch 1,
dadurch gekennzeichnet, dass während des Glühens Gas innerhalb des Rohres ist, welches Gas eine Sauerstoffanreicherung von wenigstens 20 % hat.
8. Verfahren nach Anspruch 1,
dadurch gekennzeichnet, dass der letzte Formungsschritt Senkung ist.

Revendications

- 35 1. Procédé pour la fabrication de tubes en cuivre pour des applications sanitaires pour lequel le tube est fabriqué par extrusion et formage à froid, **caractérisé en ce que** dans l'étirage à froid, le tube est étiré jusqu'à presque sa taille finale, le gaz contenant de l'oxygène est ensuite conduit dans le tube, le tube est soumis à un recuit intérieur de courte durée à une température de 450-650°C et à une vitesse pendant laquelle la structure n'a pas le temps de recrystalliser ou de ramollir, le tube est soumis à un taux de formage de 5-20% puis la surface intérieure du tube est sablée afin de retirer les résidus de graisse de l'étirage.
- 40 2. Procédé selon la revendication 1, **caractérisé en ce que** le recuit intérieur est effectué sur le tube à une vitesse de 100-200 m/min.
- 45 3. Procédé selon la revendication 1, **caractérisé en ce que** le recuit intérieur est effectué sur le tube à une vitesse de 100-160 m/min.
- 50 4. Procédé selon la revendication 1, **caractérisé en ce que** le recuit intérieur est effectué sur le tube à une température de 500-600°C.
- 55 5. Procédé selon la revendication 1, **caractérisé en ce qu'il** existe de l'oxygène à l'intérieur du tube pendant le recuit.
6. Procédé selon la revendication 1, **caractérisé en ce que** du gaz est présent à l'intérieur du tube pendant le recuit ; lequel gaz est enrichi en oxygène d'au moins 50%
7. Procédé selon la revendication 1, **caractérisé en ce que** du gaz est présent à l'intérieur du tube pendant le recuit ; lequel gaz est enrichi en oxygène d'au moins 20%
8. Procédé selon la revendication 1, **caractérisé en ce que** le taux de formage diminue pendant le formage final.