(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 2 161 349 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
10.03.2010 Bulletin 2010/10

(51) Int Cl.:
C22C 9/05 *(2006.01)* ***C22F 1/08*** *(2006.01)*

(21) Application number: **09008026.8**

(22) Date of filing: **19.06.2009**

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO SE SI SK TR
Designated Extension States:
AL BA RS

(30) Priority: **01.09.2008 IT TO20080649**

(71) Applicant: **KME Italy S.p.A.**
50127 Firenze (IT)

(72) Inventors:
- **Ammannati, Niccolò**
  55051 Fornaci di Barga (IT)
- **Martellucci, Elena**
  55051 Fornaci di Barga (IT)
- **Giusti, Aldo**
  55028 Piano di Coreglia (IT)
- **Sbrana, Armando**
  50100 Lucca (IT)

(74) Representative: **Pietrzykowski, Anja**
Klosterstrasse 29
49074 Osnabrück (DE)

(54) **use of a copper-based white alloy for producing naturally anticaterial articles and method for producing the same**

(57) Use of a copper-based white alloy for producing articles with antibacterial properties, preferably intended to be employed in the health and/or food field, in which the desired white colour is imparted by adding manganese to the alloy; the latter and possibly other alloying elements, except for impurities, are present in an amount such as to determine machinability, colour and surface properties of the alloy, similar to those of stainless steel, and simultaneously intrinsic antibacterial properties of the articles on respective exposed surfaces thereof.

EP 2 161 349 A1

Description

Field of the art

[0001] The present invention relates to the use of a copper-based white alloy for producing naturally antibacterial articles, which simultaneously have an excellent mechanical resistance, an easy machinability, a high cleaning ease and an appearance similar to that of stainless steel. The invention further relates to a method for producing these articles.

State of the art

[0002] It has been known since ancient times (ancient Egypt) that copper has disinfectant properties. More recently, copper and its alloys (brasses) have been investigated for their bactericidal properties on some pathogen microorganisms [H. T. Michels, ASTM Standardization NEWS, October 2006, pp. 29-31] and compared to stainless steel, on the surface of which the same pathogens that manage to survive on copper and alloys thereof only for a few hours, can instead survive 30 days or more, in the absence of disinfectant treatment. US-EP approved tests have shown the antimicrobial abilities of copper and brasses against Staphylococcus aureus, Enterobacter aerogenes, E. Coli O157:H7, Pseudomonas aeruginosa and MRSA (methicillin resistant Stafilococcus aureus).

[0003] However, copper and brasses have aesthetical and technological features which are generally considered inappropriate to validly replace stainless steel, for instance in the manufacturing of articles such as sanitaryware, sinks, tables, working surfaces for canteens or laboratories, basins for sanitary use, lockers, both because the mechanical features are typically much poorer than those of stainless steel, and because they are not white, but are instead of different colours such as red, pink and yellow. For all of these reasons, the use of copper and alloys thereof in the health field has been for the time being limited to components intended to remain hidden, for instance those of hydraulic or conditioning systems, such as finned heat exchangers.

[0004] There are also known, for producing jewels having an appearance similar to silver and for producing accessories for clothes, such as buttons and zips, white copper alloys, such as copper and nickel alloys, which however are nowadays increasingly less used due to the allergising effects of nickel, and the so-called "white brasses", which are alloys of copper and zinc with the addition of manganese and/or aluminium, which have progressively replaced the previous, such as for instance the alloys disclosed in EP1306453B1 or in US6863746B, in the latter case the disclosed alloy being used to perform weldings on articles made of white gold.

[0005] Although manganese may have a whitening effect on copper similar to that of nickel, the only known white alloys which do not contain nickel and are not brasses, are the so-called "manganins", used for manufacturing electrical resistors due to the low conductivity manganese imparts alloyed copper, already from a few percentage points.

[0006] It is an object of the present invention to therefore allow the replacement of stainless steel for producing articles intended to be employed in the health and/or food field or for which the intrinsic antibacterial properties are in any case important, with a material that has an appearance similar to that of stainless steel, has a low tendency to get dirty, may easily be cleaned with common cleaning products and, especially, has intrinsic antibacterial features, so as not to require frequent disinfection operations which are required instead by stainless steel when used in health and/or food applications.

[0007] It is also an object of the invention to provide a method for producing articles, in particular intended to be employed in the health and/or food field, which are naturally, i.e. intrinsically, provided with antibacterial abilities, so as not to require frequent disinfections of the exposed surfaces.

Summary of the invention

[0008] According to the present invention, the use is therefore provided of a copper-based white alloy for producing articles having antibacterial properties, preferably intended to be employed in the health and/or food field, in which the desired white colour is imparted by the addition of manganese in the alloy, according to claim 1.

[0009] In particular, the manganese, and possible other alloying elements, except for impurities, are present in an amount such as to determine machinability, colour and surface properties of the alloy similar to those of stainless steel and simultaneously intrinsic antibacterial properties of the articles on respective exposed surfaces thereof.

[0010] According to the invention, the employed alloy does not contain aluminium, except as an impurity and preferably, neither zinc nor other alloying elements, but exclusively manganese and copper. Tin, in case it is required, may also be contained as further alloying element, but again in very low percentages, preferably below 2% so as not to produce in use the segregation of precipitates or low-melting phases which impart fragility to the alloy.

[0011] In the preferred embodiment, said alloy exclusively contains, except for impurities, copper and manganese, copper being prevailing.

[0012] The content of manganese ranges, in any case, in varying percentages between 15% and up to 40% by weight and preferably in an amount such as to obtain a crystalline structure of the alloy, exclusively in alpha phase, at ambient

temperature. The optimal nominal composition of the alloy according to the use of the invention is 80% copper and 20% manganese.

[0013] The composition of the alloy according to the use of the invention is in any case such as to display on the surface antibacterial properties directed at least against microorganisms selected from the group consisting of: E.coli, MSRA, Listeria monocytogenes.

[0014] The invention also relates to a method for producing articles, in particular intended to be employed in the health and/or food field, provided with intrinsic antibacterial properties, according to claim 9.

[0015] In particular, the method of the invention comprises the steps of:

- melting a plate or a cylindrical ingot made of a copper-based alloy containing manganese as the main alloying element, in an amount such as to make the alloy white in colour and to impart a crystalline structure in alpha phase at ambient temperature thereto;
- subjecting the plate or ingot to a series of hot plastic deformation machining treatments in sequence (rolling or drawing or extrusion), to obtain a first, predetermined percentage of sectional reduction;
- subjecting the hot semifinished article to a series of cold plastic deformation machining treatments in sequence (rolling or drawing), to obtain a second, predetermined percentage of sectional reduction;
- subjecting the cold semifinished article thus obtained to one or more heat annealing treatments of complete re-crystallization, in a reducing atmosphere;
- subjecting the hot and/or cold semifinished article to at least one step of removing a surface layer thereof with a low manganese contents; and
- obtaining a desired article with the cold annealed semifinished article.

[0016] According to the preferred embodiment, the alloy contains manganese in a varying weight percentage between 15% and 40% and does not contain aluminium, and preferably neither zinc, except as impurities.

[0017] Furthermore, the first and second predetermined percentages of sectional reduction are on the order of 90% and the step of complete re-crystallization annealing of the cold semifinished article is performed at a temperature ranging between 550°C and 750°C and for about 4 hours, if performed in a static furnace or for a total time of about 45 minutes, if performed in a tunnel type furnace.

[0018] A step of abrasive brushing is performed so as to remove a surface layer of the cold annealed semifinished article having a thickness of about 4 microns.

[0019] Thereby, complex articles such as sinks, basins, tanks, working surfaces of tables, furniture tops, plates, bathroom details, as well as tubes, bars or wires, for instance to produce handrails, handles, knobs, sieves, may be obtained according to the invention and substantially without virtually any scraps, the articles having the appearance of stainless steel and being provided at the same time with very good natural or intrinsic antibacterial properties, which substantially make common sterilisation operations with disinfectants useless or at least redundant. Similar stainless steel articles are usually subjected to these disinfection operations, by the way with results which are always less effective as many bacterial strains have developed a considerable resistance to commonly used disinfectants and to antibiotics and have therefore become a continuous danger, in particular in a hospital environment, such as MRSA or E- coli O157:H7.

[0020] Furthermore, according to the results of the experiments performed by the Applicant, the antibacterial properties of copper alloys experimentally tested on many different bacterial strains, are probably due to the surface migration, and therefore on the exposed surfaces of articles made with these alloys, of copper atoms, a migration that is interrupted by the presence of aluminium in the alloy.

[0021] Therefore, according to the invention, the presence of aluminium in the alloy, unless the latter is present only as an impurity (the presence of impurities is in any case inevitable) must be avoided.

Brief description of the figures

[0022] A preferred embodiment of the invention will now be disclosed by way of mere non-limitative example with reference to the figures of the attached drawings, wherein:

- figure 1 shows a diagram that compares the mechanical properties of the alloy according to the invention with another copper alloy and with a stainless steel; and
- figures 2 to 4 comparatively show the biological properties of some copper alloys, among which the alloy of the invention, and of stainless steel, for different types of germs.

Detailed description

[0023] Further features of the invention will be apparent from the following examples for carrying out the invention.

EXAMPLE 1

[0024] Two 900 kg plates were prepared by casting, the plates having dimensions 1800 x 500 x 115 mm (length x width x thickness) and each having the mean composition shown in Table 1.

Table 1

	Mean chemical composition					
Melting N.	Cu %	Mn %	Fe %	Ni %	Sn %	Pb %
P 88500	81.2	18.8	0.015	0.03	<0.01	0.01
P 88501	80.0	20.0	0.02	0.035	<0.01	0.01

Plate P88501 was then used, due to its better quality (chemical composition identical to the nominal composition - 80% copper and 20% manganese).

[0025] The plate was subjected to a hot rolling process bringing it to 740°C for 3.5 hours and was subsequently rolled thus obtaining in subsequent steps a reduction in the section of about 90%; the thickness was in particular reduced from 115 mm to 10 mm in 8 steps, thus reaching a final temperature of about 660-670°; the hot-rolled product was cooled down to about 350°C before forcedly cooling down to ambient temperature with water.

[0026] The rolled product was then examined and analysed to detect the depth and nature of the surface layers oxidised and depleted of alloying elements (manganese).

[0027] The results which were obtained are shown in tables 2 and 3, which follow.

Table 2

Thickness of the oxidising layers measured on both sides of the longitudinal section of Cu80Mn20 hot-rolled plate				
Top - edge 1				
	Mean	**MAX. m**	**MIN. m**	**ST.DEV. m**
Side A	**25.48**	**73.71**	**3.98**	**18.65**
Side B	**24.28**	**47.81**	**10.76**	**9.09**
Top - centre				
	Mean	**MAX. m**	**MIN. m**	**ST.DEV. m**
SIDE A	**13.14**	**27.52**	**4.42**	**6.4**
SIDE B	**17.23**	**85.79**	**3.98**	**17.7**
Top - edge 2				
	Mean m	**MAX. m**	**MIN. m**	**ST.DEV. m**
Side A	**13.26**	**28.73**	**6.78**	**6.07**
Side B	**37.75**	**100**	**5.18**	**27.46**
Bottom - edge 1				
	Mean m	**MAX. m**	**MIN. m**	**ST.DEV.m**
Side A	**20.81**	**41.04**	**5.98**	**9.82**
Side B	**17.42**	**35.48**	**6.77**	**7.39**

(continued)

Top - edge 2				
Bottom - centre				
	Mean m	**MAX. m**	**MIN. m**	**ST.DEV.m**
Side A	**17.92**	**39.06**	**9.57**	**6.51**
Side B	**5.45**	**12.9**	**3.59**	**2.26**
Bottom - edge 2				
	Mean m	**MAX. m**	**MIN. m**	**ST.DEV.m**
Side A	**16.91**	**28.68**	**7.17**	**6.58**
Side B	**39.33**	**110.05**	**9.38**	**29.61**

Table 3

Chemical composition along a linear profile (from the outer surface to 17.5 microns deep)								
Position	**Top**				**Bottom**			
	Edge		Centre		Edge		Centre	
	Wt% Mn	wt% Cu	wt% Mn	wt% Cu	wt% Mn	wt% Cu	wt% Mn	wt% Cu
0	30	70	58	42	21.7	78.3	44.3	55.7
1.75	12.1	87.9	10.7	89.3	0.5	99.5	8.6	91.4
3.5	18.8	81.2	19.9	80.1	12.3	87.7	17.1	82.9
5.25	20.5	79.5	20.4	79.6	18.2	81.8	19.6	80.4
7	20.7	79.3	20.5	79.5	19.8	80.2	20.5	79.5
8.75	20.3	79.7	20.1	79.9	20.2	79.8	20.8	79.2
10.5	20.3	79.7	23.6	76.4	20.4	79.6	20.4	79.6
12.25	20	80	20.2	79.8	21	79	20.4	79.6
14	20.1	79.9	19.9	80.1	21	79	20.7	79.3
15.75	19.3	80.7	19.9	80.1	21.2	78.8	19.9	80.1
17.5	19.5	80.5	20.2	79.8	21	79	20	80

[0028] As may be appreciated, the depth of the detected layers of oxidation and depletion of Mn were relatively high and discontinuous, but such that said layers could easily and totally be removed by the normal milling/scalping operations which are generally performed after hot-rolling.

[0029] Subsequently, the hot-rolled product, after the milling/scalping operation and subsequent removal of the oxidised layers and with depletion of manganese, was subjected to a cold-rolling operation, again obtaining a reduction in the section of about 90% (from 10 to 0.7 mm of thickness) in subsequent steps, with the consequent work hardening and increase of hardness. The cold-rolled product was then subjected to a heat annealing treatment in a static furnace in a reducing atmosphere at 600°C for 4 hours for the re-crystallization. This treatment has been selected on the basis of a series of laboratory tests at different temperatures, in order to identify the optimal treatment, as shown in table 4.

Table 4

Structure and size of the grain of Cu80Mn20 samples after one hour of heat treatment at increasing temperatures.		
	Mean size of the grain (mm)	
Heat treatment	1 mm thickness	0.5 mm thickness
400 °C / 1 hour	Fibrous structure	Fibrous structure
450 °C / 1 hour	Fibrous structure	Fibrous structure
500 °C / 1 hour	Re-crystallization start	Re-crystallization start
550 °C / 1 hour	0.005	0.0075
600°C / 1 hour	0.0075	0.0075
650 °C / 1 hour	0.010	0.015

[0030] Test specimens of the rolled material were subjected to the common tests for identifying the mechanical properties, in comparison to reference materials (other copper alloys and stainless steel). The results which were obtained are shown in figure 1, where the hardness curves of the different materials are shown as a function of the strain hardening, and in the following tables.

Table 5

Material	HV	E (GPa)	Rp(0,2) (MPa)	Rm (MPa)	A50mm (%)
CuMn20	119	118	260	470	32
CuZn20	77	110	115	330	47
AISI 304-316	129	193	205	515	40
Tab.2 Comparison between different materials					

Table 6

Material	IE (mm)	IB	R (%)	H (%)	L.D.R.
CuMn20	10,6	70	≃100	4,9	2,12
CuZn20	10,6-12	66-68	≃96-100	-	1,94-2,00
AISI 304-316	11-12	-	≃50-60*	-	2,18-2,25*
Tab.3 Formability propertie					

Table 7

	Cu80Mn20		**Cu80Zn20**		**Aisi 304**	
temper	Rp (Mpa)	Rm (Mpa)	Rp (Mpa)	Rm (Mpa)	Rp (Mpa)	Rm (Mpa)
Annealed	**256**	**493**	**115**	**330**	**205**	**515**
1/4 Hard	**308**	**498**	**300**	**420**	**413**	**690**
1/2 Hard	**564**	**597**	**440**	**510**	**606**	**827**
Hard	**820**	**860**	**480**	**570**	**772**	**1020**

[0031] Finally, whether there was a surface depletion of manganese due to the heat annealing treatment was identified on the different sample specimens. The results which were obtained are shown in table 8.

Table 8

Position μm from the surface	wt%Mn	wt%Cu
0	19.8	80.2
1.75	12.6	87.3
3.5	16.2	83.8
5.25	19.2	80.8
7	19.9	80.1
8.75	19.7	80.3
10.5	20.2	79.8
12.25	20.3	79.7
14	20.5	79.5
15.75	20.4	79.6
17.5	20.5	79.5

[0032] As may be noted, the depletion involves a layer which is no more than 4-5 microns, which may easily be removed with a common operation of abrasive brushing after the heat treatment.

[0033] From the comparison among the various materials, it may also be noted that the tested CuMn20 alloy is suitable to replace the stainless steel in any application, such as the manufacture of furniture, tools, work surfaces, etc., having a considerable hardness and high mechanical resistance, well beyond those of brasses.

EXAMPLE 2

[0034] The antimicrobial properties of three different copper alloys were compared, and specifically the CuMn20 alloy (alloy 3) according to the invention, previously prepared according to the previous examples, a CuSn6Zn6 alloy (alloy 2) and a CuZn10 alloy (alloy 1), with two different reference materials and specifically DHP copper AISI 304 steel (stainless steel).

[0035] Three different pathogen microorganisms were used for the tests, specifically E. coli, MSRA and Listeria monocytogenes.

[0036] Flat sheet sample specimens, made of the tested alloys and of the reference materials, each of a size equivalent to about 5.5 cm^2 were treated with 10 microlitres of microbial cell suspension in water, having a concentration of about 108 cell units per millilitre.

[0037] Subsequently, the sample specimens were incubated at 37°C. The test was repeated 6 times, varying the time of contact in incubation. Each sample specimen was tested for the following times: 0, 5, 10, 20, 40 and 80 minutes.

[0038] After each incubation step was finished, the sample specimen was recovered and treated with an aqueous solution to remove the pathogens; the solution was then diluted and incorporated in agar and a microscopical count was finally carried out on the survived microbial cells.

[0039] The results which were obtained are shown in figures 2, 3 and 4.

[0040] As may be noted, the antimicrobial activity of the previously prepared and machined alloy, CuMn20 is substantially very similar to that of copper DHP against all of the tested pathogenic microorganisms, while stainless steel is substantially devoid thereof. The antimicrobial activity of the CuMn20 alloy is also comparable (or better), with the content of copper being the same, with respect to that of the other tested alloys, which however have a mechanical resistance and hardness that make them unsuitable to replace steel and, especially, do not have a colour comparable to that of steel, while the CuMn20 alloy according to the invention has a white metal colour comparable to that of steel.

EXAMPLE 3

[0041] Four cylindrical ingots were prepared having a diameter of 305 mm using standard copper ingot moulds with an inner graphite insert so as to render less drastic the cooling of the metal in the ingot mould and therefore avoid the formation of contraction cracks. The metal was taken to a temperature of 1140°C in the melting furnace and, after the analytical controls to verify the adherence to the nominal composition, was poured in the holding furnace; the casting started when the metal reached the temperature of 1100 °C.

[0042] The chemical composition resulting from the mean of the two samples of cast withdrawn respectively at the beginning and at the end of each casting is shown in table 9.

Table 9 Mean chemical composition of the cylindrical ingots in Cu80Mn20.

Melting N.	Cu %	Mn %	Fe %	Ni %	Sn %	Pb %
L88277	80.9	19.04	0.025	0.032	<0.01	<0.01
L88278	79.8	20.10	0.012	0.028	<0.01	0.01
L88279	79.5	20.40	0.017	0.039	<0.01	0.01
L88280	79.7	20.20	0.020	0.035	<0.01	<0.01

[0043] Subsequently, the double-hole extrusion of the ingots was performed so as to obtain wires with a diameter of 26 mm, with a 4000 ton press in a range of extrusion temperatures from 770 to 800 °C, spraying the outputted wires with water coming from appropriate sprayers to limit oxidation of the alloy and/or the depletion of Mn. In these conditions the power absorbed by the press, expressed in tons, varies from 2000 to 2300 due to the high mechanical features of the Cu80Mn20 alloy. From the metallographic point of view, the best results both as regards the mean diameter of the grain and as regards the homogeneity thereof, were obtained with an extrusion temperature equivalent to 780°C. Later, the extruded products were rolled to a diameter of 20 mm and an annealing was performed for 3 hours at 650°C in a reducing atmosphere. Different cold plastic deformation (drawing) operations were then performed from a semifinished product having a 20mm-diameter to a wire having a 2.08mm-diameter, performing an intermediate step of milling from 5.70 to 5.30 mm to remove the layers of oxidation and depletion of Mn, the depth of which was less than that identified for the corresponding layers of example 1 for the rolled products. Finally, after a complete re-crystallization annealing performed at 650°C for 3 hours in a reducing atmosphere, the wires were subjected to a final step of cold drawing to a 2mm- or 1.80mm-diameter, so as to obtain a work hardening of 7.4% or, respectively, of 25% and therefore give rise, with the same alloy, to a final wire material in a medium-hard or hard physical state. As a final step, the possible brushing ensured the absence of surface layers of oxide or of layers depleted of Mn.

[0044] The values of the mechanical features which may be obtained by means of the drawing operations, depending on the different possible strain hardening, are shown in table 10.

Table 10 Summary of the mean values of Rm, Rp and HV measured during the cold plastic deformation cycle as a function of the percentage strain hardening the Cu80Mn20 wire undergoes.

Strain hardening	Rm MPa	Rp MPa	HV 500g/15"
0	490	240	150
7.4	540	310	170
25	717	450	195
37	790	580	215
55	827	710	235
85	875	835	250

EXAMPLE 4

[0045] Billets of Cu80Mn20 alloy were extruded under water to tubes having a 100mm-diameter, 11mm-thickness wall, so as to limit the formation of surface oxides and/or layers depleted of Mn.

[0046] The extrusion of the billet in the form of a tube was performed in a range of extrusion temperatures in the range between 790 and 805°C. In these conditions, the power absorbed by the press, expressed in bars, was about 290, which is an acceptable value considering the high mechanical features of the Cu80Mn20 alloy.

[0047] Subsequently, a cold plastic deformation processing was performed using a pilgrim mill set at 70 hits/minute with a feed of 11.11 mm until tubes having a 45mm-diameter by a 2.25-wall thickness were obtained and later the semifinished products obtained thereby were subjected to a single operation of rectilinear cold drawing to a 35mm-diameter by 1.90 mm-thickness and a following annealing at 650°C for 4 hours in a reducing atmosphere. Subsequently, a series of coil drawing operations (to the spinners) were performed up to a 9.52mm-diameter by a 0.45mm-thickness

as well as a final annealing at 650°C for 4 hours in a funnel type furnace with a reducing atmosphere. The possible final brushing ensured the absence of surface layers of oxide and/or of layers depleted of Mn.

Claims

1. Use of a copper-based white alloy for producing articles preferably intended to be employed in the health and/or food field, wherein the desired white colour is imparted by adding manganese to the alloy, and wherein the latter and possibly other alloying elements, except for impurities, are present in an amount such as to determine machinability, colour and surface properties of the alloy, similar to those of stainless steel, and simultaneously intrinsic antibacterial properties of the articles on corresponding exposed surfaces thereof.

2. Use according to claim 1, **characterized in that** said alloy does not contain aluminium, except as an impurity.

3. Use according to claim 1 or 2, **characterized in that** said alloy does not contain zinc, except as an impurity.

4. Use according to anyone of the preceding claims, **characterized in that** said alloy may contain, in a lower percentage, tin in any case in an amount such as not to produce the segregation of precipitates or of low-melting and/or fragile phases in use.

5. Use according to anyone of claims from 1 to 3, **characterized in that** said alloy exclusively contains copper and manganese, except for impurities, copper being prevailing.

6. Use according to anyone of the preceding claims, **characterized in that** the manganese content in the alloy ranges in varying percentages between 15% and up to 40% by weight and in any case in an amount such as to obtain a crystalline structure of the alloy, preferably in alpha phase, at ambient temperature.

7. Use according to claim 6, **characterized in that** the nominal composition of said alloy is 80% copper and 20% manganese, the percentages being expressed by weight.

8. Use according to anyone of the preceding claims, **characterized in that** said alloy displays on the surface antibacterial properties directed at least towards the microorganisms selected from the group consisting in: E.coli, MSRA, Listeria monocytogenes.

9. A method for producing articles, preferably intended to be employed in the health and/or food field, provided with intrinsic antibacterial properties, **characterised in that** it comprises the steps of:

   - melting a plate or a cylindrical ingot made of a copper-based alloy containing manganese as the main alloying element, in an amount such as to make the alloy white in colour and to impart a crystalline structure in alpha phase at ambient temperature thereto;
   - subjecting the plate or ingot to a series of hot plastic deformation machining treatments in sequence (rolling or drawing or extrusion), to obtain a first, predetermined percentage of sectional reduction;
   - subjecting the hot semifinished article to a series of cold plastic deformation machining treatments in sequence (rolling or drawing), to obtain a second, predetermined percentage of sectional reduction;
   - subjecting the cold semifinished article thus obtained to one or more heat annealing treatments of complete re-crystallization, in a reducing atmosphere;
   - subjecting the hot and/or cold semifinished article to at least one step of removing a surface layer thereof with a low manganese contents; and
   - obtaining a desired article with the cold annealed semifinished article.

10. The method according to claim 9, **characterized in that** said alloy contains manganese in a varying weight percentage between 15% and 40% and does not contain aluminium, and preferably neither zinc, except as impurities.

11. The method according to claim 9 or 10,
characterized in that said first and second predetermined percentages of sectional reduction are on the order of 90%.

12. The method according to anyone of claims from 9 to 11, **characterized in that** said step of complete re-crystallization

annealing of the cold semifinished article is performed at a temperature ranging between 550°C and 750°C, in either a static or a tunnel type furnace, and in a reducing atmosphere.

13. The method according to anyone of claims from 9 to 12, **characterized in that** the hot semifinished article is subjected to a step of surface milling for removing the oxidised, low manganese layers.

14. The method according to anyone of claims from 9 to 13, **characterized in that** the cold annealed semifinished article is subjected to a step of abrasive brushing.

15. The method according to claim 14,
characterized in that said step of abrasive brushing is performed so as to remove a surface layer of the cold annealed semifinished article having a thickness equal to 4 microns.

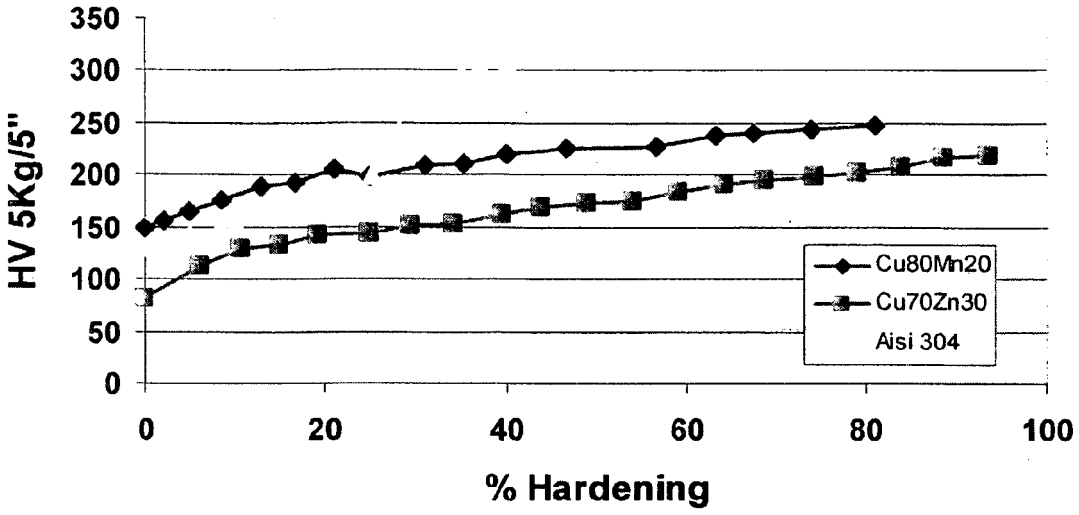


Figure 1

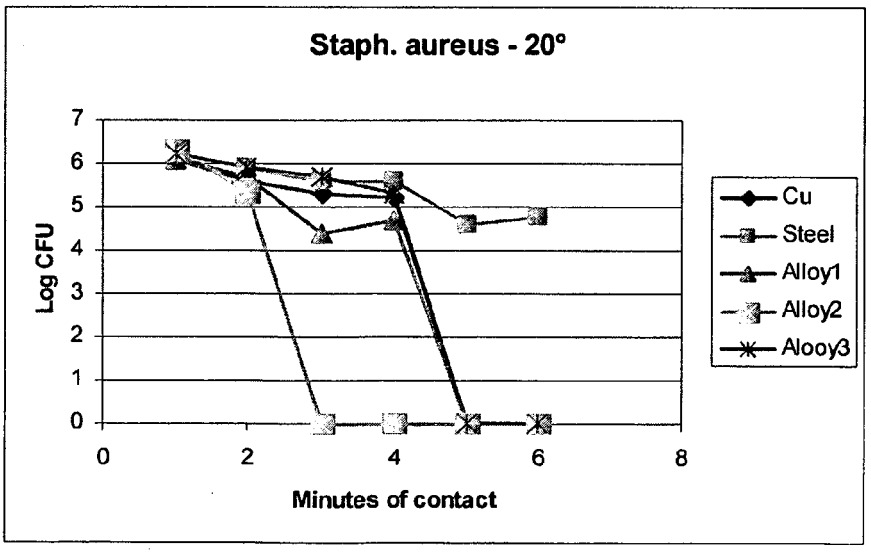


Figure 2

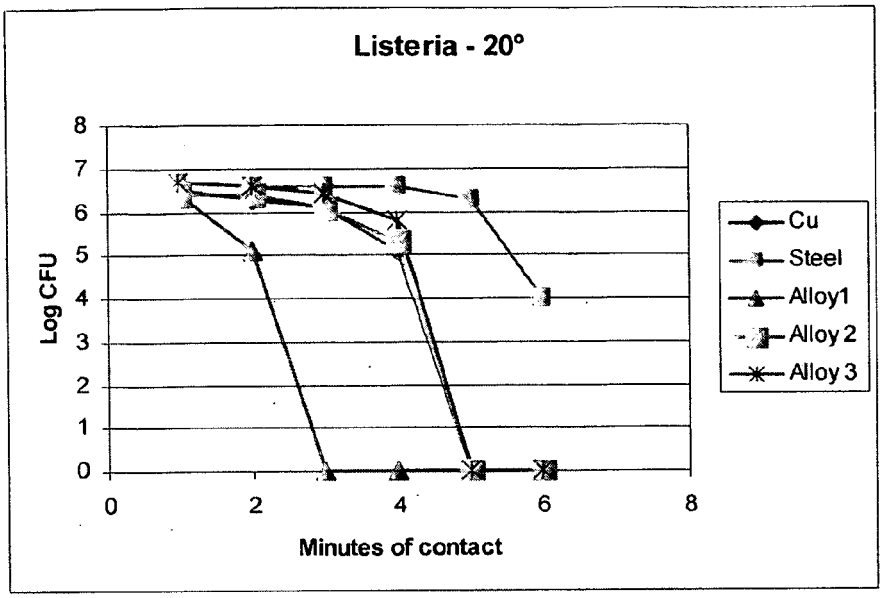


Figure 3

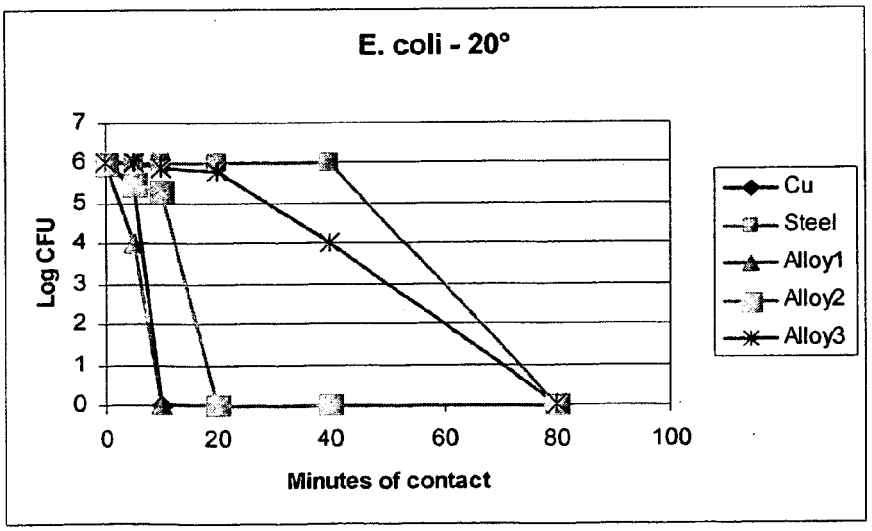


Figure 4

Europäisches Patentamt
European Patent Office
Office européen des brevets

PARTIAL EUROPEAN SEARCH REPORT

which under Rule 63 of the European Patent Convention shall be considered, for the purposes of subsequent proceedings, as the European search report

Application Number EP 09 00 8026

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	MUKHERJEE, D. ET AL: "Antifouling properties of copper-manganese alloys" TOOL & ALLOY STEELS , 27(9), 287-9 CODEN: TASTDL; ISSN: 0377-9408, 1993, XP009122240 * the whole document *	5-7,9-15	INV. C22C9/05 C22F1/08
X	MUKHERJEE, D. ET AL: "SRB-cidal properties of some copper-manganese alloys" BULLETIN OF ELECTROCHEMISTRY , 6(5), 499-500 CODEN: BUELE6; ISSN: 0256-1654, 1990, XP009122239 * the whole document *	5-7,9-15	
X	MUKHERJEE, D. ET AL: "Corrosion resistant and antifouling behavior of Cu-Mn alloys in sea-water" BULLETIN OF ELECTROCHEMISTRY , 9(8-10), 427-9 CODEN: BUELE6; ISSN: 0256-1654, 1993, XP009122244 * the whole document *	5-7,9-15	
	-/--		TECHNICAL FIELDS SEARCHED (IPC) C22C C22F

INCOMPLETE SEARCH

The Search Division considers that the present application, or one or more of its claims, does/do not comply with the EPC to such an extent that a meaningful search into the state of the art cannot be carried out, or can only be carried out partially, for these claims.

Claims searched completely :

Claims searched incompletely :

Claims not searched :

Reason for the limitation of the search:

see sheet C

1

Place of search	Date of completion of the search	Examiner
Munich	13 November 2009	Patton, Guy

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
.....
& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04E07)

Europäisches Patentamt
European Patent Office
Office européen des brevets

PARTIAL EUROPEAN SEARCH REPORT

Application Number
EP 09 00 8026

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (IPC)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	CA 964 408 A1 (OLIN CORP) 18 March 1975 (1975-03-18) * the whole document * -----	5-7,9-15	
X	DE 12 24 937 B (KURT DIES DR ING) 15 September 1966 (1966-09-15) * the whole document * -----	5-7,9-15	
A	EP 1 880 776 A (EUROPA METALLI S P A [IT]) 23 January 2008 (2008-01-23) * the whole document * -----	5-7,9-15	
A	WO 00/68447 A (OLIN CORP [US]) 16 November 2000 (2000-11-16) * the whole document * -----	5-7,9-15	TECHNICAL FIELDS SEARCHED (IPC)
A	US 3 725 052 A (MASUMOTO H ET AL) 3 April 1973 (1973-04-03) * the whole document * -----	5-7,9-15	
A	JP 60 072695 A (MARUYASU KOGYO) 24 April 1985 (1985-04-24) * abstract * -----	5-7,9-15	
A	US 5 725 682 A (HASHIMOTO AKIRA [JP]) 10 March 1998 (1998-03-10) * the whole document * -----	5-7,9-15	

1

EPO FORM 1503 03.82 (P04C10)

Europäisches Patentamt
European Patent Office
Office européen des brevets

INCOMPLETE SEARCH SHEET C

Application Number
EP 09 00 8026

Claim(s) not searched:
1-4,8

Reason for the limitation of the search:

The feature of claim 1 stating a
"use of a copper-based white alloy for producing articles"
does not indicate any clear and specific use.

Even the optional feature of claim 1 stating that the copper-based alloy is "to be employed in the health and/or food field" does not specify any clear application. The optional feature is so broadly worded that, even if it would be made mandatory, it could not help to depart the use claim from the prior art. Indeed, it is not clear what applications, i.e. uses, are meant under "health and/or food field".

In addition, there is no composition of the copper-based alloy given in claim 1.

The feature of claim 1 relating to
"the desired white colour is imparted by adding manganese to the alloy, and wherein the latter and possibly other alloying elements, except for impurities, are present in an amount such as to determine machinability, colour and surface properties of the alloy, similar to those of stainless steel, and simultaneously intrinsic antibacterial properties of the articles on corresponding exposed surfaces thereof"
relates to results to be achieved without specifying neither the means for achieving the results, i.e. the composition, nor the results themselves, i.e. "how white, how machinable" should the alloy be or "how its surface properties" should be.

As a result, in view of the lack of clarity, no significant search can be performed over the scope of claims 1-4 and 8. Present search is therefore limited to claims 5-7 and 9-15.

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 09 00 8026

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

13-11-2009

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CA 964408 A1	18-03-1975	BE 786013 A1	03-11-1972
		DE 2210432 A1	14-09-1972
		FR 2127826 A5	13-10-1972
		GB 1382201 A	29-01-1975
		GB 1382202 A	29-01-1975
		IT 948660 B	11-06-1973
		JP 54007730 B	10-04-1979
		JP 1012092 C	29-08-1980
		JP 52017320 A	09-02-1977
		JP 55004827 B	01-02-1980
DE 1224937 B	15-09-1966	NONE	
EP 1880776 A	23-01-2008	CN 101195134 A	11-06-2008
		US 2008060722 A1	13-03-2008
WO 0068447 A	16-11-2000	AT 243775 T	15-07-2003
		AU 4205300 A	21-11-2000
		CA 2307493 A1	05-11-2000
		CN 1353772 A	12-06-2002
		DE 20006294 U1	31-08-2000
		DE 60003555 D1	31-07-2003
		DE 60003555 T2	29-04-2004
		EP 1185718 A1	13-03-2002
		HK 1041297 A1	10-10-2003
		JP 3396658 B2	14-04-2003
		JP 2000345256 A	12-12-2000
		MX PA00003472 A	08-03-2002
US 3725052 A	03-04-1973	CH 552066 A	31-07-1974
JP 60072695 A	24-04-1985	NONE	
US 5725682 A	10-03-1998	JP 8206876 A	13-08-1996

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- EP 1306453 B1 **[0004]**
- US 6863746 B **[0004]**

Non-patent literature cited in the description

- **H. T. Michels.** *ASTM Standardization NEWS,* October 2006, 29-31 **[0002]**