

WHITE-COLORED COPPER ALLOY WITH REDUCED NICKEL CONTENT

[0001] The invention claims the benefit of priority of U.S. Provisional Patent Application No. 61/095,719, "WHITE-COLORED COPPER ALLOY WITH REDUCED NICKEL CONTENT", filed on September 10, 2008 and U.S. Provisional Patent No. 61/095,733 "IMPROVED WHITE-COLORED COPPER ALLOY WITH REDUCED NICKEL CONTENT" filed on September 10, 2008.

FIELD OF THE INVENTION

[0002] This invention relates to white- or silver-colored copper-based alloys with reduced nickel content compared to standard alloys of similar color.

BACKGROUND OF THE INVENTION

[0003] Copper base alloys are widely used for their combination of ease of fabrication, corrosion resistance, electrical and thermal conductivity, and availability in a wide range of attractive colors. They are the preferred material worldwide for circulating coinage, in many cases as part of multi-layer composite systems. In addition, recent research has shown copper and copper alloy surfaces can be manufactured to be antimicrobial, inactivating a variety of microorganisms in a matter of two hours or less.

[0004] Even though copper by itself is red in color, addition of most alloying elements results in more or less reddish or yellowish colors. These colors are typically well known, with descriptive names (brassy, golden, bronze, etc.). Alloys with a whiter color (reflecting all light wavelengths more uniformly) are also available, although it is generally difficult to achieve good white colors without strong reddish or yellowish overtones, particularly after the material has tarnished or partially oxidized. These whiter alloys are generally achieved using large additions of nickel (cupronickels and nickel silvers). Unfortunately, nickel is more expensive than most other alloying elements, and has been implicated as a major contributor to increased cases of allergic contact

dermatitis when used in contact with human skin and other tissue. The intent of this invention is to provide copper alloys with a good white color but using reduced nickel content.

[0005] Alloys consisting primarily of copper and nickel (with minor additions of other elements) are known as cupronickels or copper-nickels. As the nickel content increases, the color goes from copper red toward a pale reddish/purple at 10% Ni (C706) to a reasonably pure white at 25% Ni (C713). This white copper-nickel is used extensively for US circulating coinage as the material for the 5-cent coin and as the outside of the three-layer composite for the 10-cent, 25-cent and 50-cent coins. While attractive and durable, the alloy is expensive due to the high Ni content, since Ni is typically over twice the price of copper. The high cost of C713 is partially responsible for the use of composite coinage in the US; by substituting a core of less expensive copper surrounded by the silver-colored C713, the desired appearance can be achieved at lower cost. Another alternative to the high cost of white copper-nickels is to substitute zinc in the alloy for a portion of the copper, forming the alloys known as “nickel silvers” for their silvery color. Although less effective as a whitener for copper alloys than nickel, Zn reduces the need for Ni and is both less dense and less expensive than either Cu or Ni. Copper alloys of high manganese content (20% and more) are also reliably white but suffer from difficulties with hot working and very low electrical and thermal conductivity, so they have been used primarily as castings, where their lower melting point and increased fluidity compared to “nickel silvers” is an advantage.

[0006] By substituting a combination of Zn and Mn for most of the nickel in a white-colored copper alloy, a lower-cost alloy is possible with a similar appearance and other novel properties. While other white-colored copper base alloys superficially similar to the proposed alloys have been disclosed in the past, none match the composition range of this invention, as will be brought out below.

[0007] Numerous copper-nickels and nickel silvers are offered by various copper alloy producers with more or less white colors. Of 41 wrought copper-nickel alloys listed in the Copper Development Association (CDA) database, only two (C71640 and C72420) have a Mn content greater than 1%; neither of these alloys contains Zn greater than 1%. Of 25 wrought nickel silvers (Cu-Zn-Ni alloys) listed, only four have a minimum Mn content; all of these have Pb added to improve machining properties. Copper-aluminum alloys (aluminum bronzes) will contain either Zn or Mn, but not both. There are only two wrought Cu-Zn-Mn alloys listed in the CDA database, both nickel-free – C66900 and C66950. The first contains 0.25% max Fe (as an impurity) and 0.20% max other impurities with no other additions. The second (Wieland Alloy FX9) contains 14-15% Zn, 14-15% Mn, 1.0-1.5% Al, and the balance Cu.

[0008] Cast alloys listed in the CDA database show a similar trend; alloys which contain more than 1% of both Mn and Zn also contain at least 0.5% of Al. The one exception to this is an alloy known as “Bronwite” (C99750), which contains 17-23% Mn, 17-23% Zn, and at least 0.5% Pb with up to 5% Ni. Bronwite is very white, very fluid and has a relatively low melting temperature which makes it excellent for small, thin and

delicate castings such as costume jewelry, but it contains enough Pb to cause problems with current Restrictions on Hazardous Substances (RoHS) and Consumer Product Safety regulations.

[0009] A number of nickel-free white alloys have been disclosed in the past. Wieland Alloy FX9 (C66950) has been mentioned above. YKK Corporation of Tokyo, Japan holds a number of patents on nickel-free alloys. US Patent 5997663 covers two ranges: 1) 70-85% Cu, 5-22% Zn, 7-15% Mn and 0-4% of Al or Sn or a combination of both Al and Sn (with a white color); and 2) 70-85% Cu, 10-25% Zn, 0-7% Mn, and 0-3% of Al or Sn or a combination of both Al and Sn (with a distinctly yellow color). A second YKK patent (US 6340446) discloses nickel-free alloys containing 0.5-5% Zn, 7-17% Mn, 0.5-4% Al and the balance copper, which may also contain one or more of Cr, Si, and/or Ti up to 0.3%. A third such patent (EP1306453) teaches of Ni-free white alloys with 0.5-30% Zn and 1-7% Ti, optionally including up to 4% of a combination of one or more of Al, Sn, Mg, and/or Mn.

[0010] Another European patent (EP0685564) discloses a Ni-free alloy with generally lower copper (50-70% Cu) and higher Mn (8-25% Mn) than the YKK patents with the remainder zinc. Most of these previously disclosed Ni-free white alloys are intended to meet the EU regulations restricting Ni in jewelry, eyeglasses, and similar items in “direct and prolonged contact with human skin” (due to issues with allergies and sensitization) by completely eliminating Ni and are generally intended for use as cast articles or as wire products.

[0011] An alloy disclosed in US Patent 6432556 (Brauer, et. al) contains 5-10% Mn, 10-14% Zn, 3.5-4.5% Ni and less than 0.07% Al with the balance Cu. The alloy content of Patent 6432556 is specifically balanced so as to provide both a “golden visual appearance” and an electrical conductivity suitable for use as a replacement for standard alloy C713 (75 Cu-25 Ni) in both monolithic and clad form for use in circulating US coinage, particularly as a yellow alloy replacement for the Susan B. Anthony (SBA) dollar coin, and is currently in use as the outer clad layers of both the Sacajawea dollar and the US Presidential dollar series of circulating coins. A related earlier patent (US Patent 2445868, to Berwick and assigned to Olin Inc.) which is referred to in the application for Patent 6432556 teaches about quaternary (4-component) alloys of Cu-Zn-Ni-Mn type with 5% Ni minimum and essentially no other additions.

[0012] Another substantially Ni-free alloy is disclosed in US Patent 3778237 (Shapiro, et. al.) specifically as a substrate for silver plated articles such as flatware or hollow ware for food service. This alloy consists of 8-16% Mn, 20-31% Zn and the balance Cu with small additions of other elements (Al, Fe, Sn, Si, Co, Mg, Mo, Ni, P, As, Sb) permitted but not required. Nickel is permitted up to 0.3% but preferably no Ni is added. US Patent 3778236 (Goldman, et. al.) is a patent for an alloy containing 0.5-5% Ni, also restricted as a substrate for silver-plated articles. Other Ni-free Cu-Mn-Zn alloys are disclosed in US Patent 2772962 (Reichenecker, for a cast electrical-resistance alloy) and in US Patent 2479596 (Anderson and Jillson, et. al.).

[0013] US Pat. Nos. 5997663, 6340446, 6432556, 2445868, 3778236, 3778237, 2772962 and European Patent Nos. EP1306453 and EP0685564 are incorporated by reference in their entireties herein.

SUMMARY OF THE INVENTION

[0014] It is an object of at least one embodiment of the present invention to provide a copper-based alloy with a white- or silver-colored appearance and reduced nickel content compared to traditional copper alloys of similar appearance. A further object of at least one embodiment of the present invention is that the alloys of the invention exhibit tarnish resistance at least equal to other copper alloys of similar color. Yet a further object of at least one embodiment of the present invention is that the alloys of the invention exhibit resistance to staining (when subjected to repeated touch by human skin) at least equal to other copper alloys of similar color. A further object of at least one embodiment of the present invention is that alloys of the invention exhibit electrical conductivities substantially similar to those of stainless steels or similar to those of alloys currently used for circulating coinage. It is yet a further object of at least one embodiment of the present invention that these alloys exhibit antimicrobial properties such that bacteria exposed on the uncoated surface of the alloy exhibit inactivation rates equal to or superior to published data for copper-based alloys of similar color and significantly superior to stainless steels of similar color.

[0015] The above-stated objects, features and advantages will become more apparent from the specifications and drawings which follow.

(1) It is a feature of at least one embodiment of the present invention that the copper-base alloy claimed has a white- or silver-colored appearance making it suitable for the manufacture of decorative articles of various types, particularly (but not limited to) architectural and builders' hardware. It further may be used either in a monolithic form or as part of a composite system with other materials where the color, tarnish resistance and antimicrobial and other properties of the alloy of the invention permit creation of novel material systems with characteristics uniquely tailored to specific applications.

(2) Yet another feature of at least one embodiment of the present invention is that the alloy contains both zinc and manganese and a reduced level of nickel compared to traditional white-colored copper-base alloys.

(3) It is another feature of at least one embodiment of the present invention that iron may be used in place of or in addition to the nickel for improved color and

(4) tarnish resistance and

(5) stain resistance compared to alloys without either nickel or iron.

(6) Another feature of at least one embodiment of the present invention is that the alloy has a white visual appearance and an electrical conductivity similar to that of CDA Alloy C713 used in circulating US coinage.

(7) Yet another feature of at least one embodiment of the present invention is that the alloy has an appearance similar to that of stainless steel and also exhibits an electrical conductivity in the same range as stainless steel.

[0016] Among the advantages of at least one embodiment of the present invention is that the white-colored copper-base alloy of the invention has antimicrobial properties. The inactivation rate of bacteria placed on a surface composed of the alloy of at least one embodiment of the present invention is superior to that of other copper-based alloys of similar color, and is also superior to what would be expected from the rates found with commercial binary alloys of copper with components of the proposed alloy.

[0017] In accordance with the present invention there is provided a white-colored copper alloy comprising by weight up to 30% zinc, up to 20% manganese, up to 5% nickel with the balance copper. This alloy more preferably contains from 6% to 25% zinc, from 4% to 17% manganese, from 0.1% to 3.5% nickel and the balance copper. The balance copper in the alloy may further contain at least one of: up to 0.5% of at least one of the group which consists of Sn, Si, Co, Ti, Cr, Fe, Mg, Zr, and Ag; and up to 0.1% of at least one of the group which consists of P, B, Ca, Ge, Se, Te. This alloy preferably contains from 12% to 20% Zn, from 10% to 17% Mn, and from 0.5% to 3.5% Ni. It more preferably contains from 13% to 16% Zn, from 14% to 17% Mn, and from 1.5% to 2.5% Ni. It may also contain up to 0.3% Zr by weight.

[0018] There is also provided, in accordance with the present invention, a white-colored copper alloy comprising by weight up to 30% zinc, up to 20% manganese, up to

4% iron with the balance copper. This alloy more preferably contains from 6% to 25% zinc, from 4% to 17% manganese, from 0.1% to 2.5% iron and the balance copper. The balance copper in the alloy may further contain at least one of: up to 0.5% of at least one of the group which consists of Sn, Si, Co, Ti, Cr, Ni, Mg, Zr, and Ag; and up to 0.1% of at least one of the group which consists of P, B, Ca, Ge, Se, Te. This alloy preferably contains Ni only as an impurity (that is, less than about 0.1%), and consists of from 12% to 20% Zn, from 10% to 17% Mn, and from 0.5% to 2.5% Fe. It more preferably contains from 15% to 18% Zn, from 14% to 17% Mn, and from 0.5% to 1.5% Fe.

[0019] There is further provided, in accordance with the present invention, a white-colored copper alloy comprising by weight up to 30% zinc, up to 20% manganese, up to 6% nickel, up to 4% iron with the balance copper. This alloy more preferably contains from 6% to 25% zinc, from 4% to 17% manganese, from 0.1% to 5% nickel, from 0.05% to 2.5% iron and the balance copper. The balance copper in the alloy may further contain at least one of: up to 0.5% of at least one of the group which consists of Sn, Si, Co, Ti, Cr, Mg, Zr, and Ag; and up to 0.1% of at least one of the group which consists of P, B, Ca, Ge, Se, Te. This alloy preferably contains from 12% to 20% Zn, from 10% to 17% Mn, from 0.5% to 3.5% Ni, and from 0.1% to 1% Fe. It more preferably contains from 13% to 16% Zn, from 14% to 17% Mn, from 1.5% to 2.5% Ni, and from 0.2% to 0.6% Fe. This alloy may further contain up to 1.0% Al.

[0020] There is yet further provided, in accordance with the present invention, a white-colored copper alloy having an electrical conductivity greater than 2.5% IACS at

eddy current gauge exciting frequencies between 60kHz and 480 kHz comprising by weight up to 30% zinc, up to 20% manganese, up to 10% nickel, up to 4% iron, up to 1% Zr with the balance copper. This alloy more preferably contains from 6% to 25% zinc, from 4% to 17% manganese, from 0.1% to 9% nickel, up to 2.5% iron, up to 0.5% Zr and the balance copper. The balance copper in the alloy may further contain at least one of: up to 0.5% of at least one of the group which consists of Sn, Si, Co, Ti, Cr, Mg, and Ag; and up to 0.1% of at least one of the group which consists of P, B, Ca, Ge, Se, Te. This alloy preferably contains from 10% to 18% Zn, from 4% to 7% Mn, from 4% to 9% Ni, and from 0.05% to 0.2% Zr. It more preferably contains from 12% to 16% Zn, from 4% to 6% Mn, from 5% to 9% Ni, and from 0.05% to 0.15% Zr; the combination having an electrical conductivity between 4% IACS and 7% IACS.

BRIEF DESCRIPTION OF THE DRAWINGS

[0021] FIG. 1 graphically illustrates the CIELAB color chart attributes for lightness, hue and chroma as known from prior art.

[0022] FIG. 2 shows the alloys of the invention plotted on a 2-dimensional CIELAB color chart illustrating the desired color range, as well as comparative alloys.

[0023] FIG. 3 shows the same data as FIG 2, but focusing on the desired “white visual appearance” range.

[0024] FIG. 4 shows the antimicrobial effectiveness of alloys of the invention.

DEFINITIONS

[0025] For purposes of the claims listed below, the following definitions shall apply:

[0026] All compositions are given in percentages by weight. A composition listed as Cu-18Zn-17Ni will mean a nominal 18% by weight Zn, 17% by weight Ni and the remainder copper and inevitable impurities. Other compositions listed in similar form can be understood by analogy with this example.

[0027] “Copper-base alloy” shall hereafter be defined as: an alloy having a minimum of 50% by weight Cu with one or more elemental constituents, or a multi-component alloy where the percentage of Cu is greater than that of any other constituent.

[0028] “White visual appearance” shall hereafter be defined as: color (as measured with a spectrophotometer of d/8 sphere geometry (specular reflection included) with a D65 illuminant and 10° observer) meets $-2 \leq a^* \leq 3$ and $-2 \leq b^* \leq 10$ on the CIE 1976 $L^* a^* b^*$ (CIELAB) scale.

[0029] “Effectively antimicrobial” shall hereafter be defined as: 99.9% of bacteria in a suspension placed on an uncoated surface will be inactivated within 120 minutes exposure

[0030] “Time to complete inactivation” shall hereafter be defined as the time from placement of a bacteria on a surface until 99.9% of the bacteria is inactivated.

[0031] “Resistant to tarnishing” shall hereafter be defined as: after 30 days exposure in air at 20-25 °C without contact with human skin or body fluids, color change ΔE_{CMC} (as defined in ASTM D2244-07, pp.2-3) between initial color and final color is less than 1.

[0032] “Resistant to elevated temperature tarnishing” shall hereafter be defined as: after 24 hours exposure in air at 150 °C, color change ΔE_{CMC} (as defined in ASTM D2244-07, pp.2-3) between initial color and final color is less than 20.

DETAILED DESCRIPTION

[0033] Determination of color (of alloys or other materials) may be by spectroscopy or other objective means. Instruments such as those supplied by X-Rite, Inc. (Grand Rapids, MI) or Hunter Associates Laboratory, Inc. (Reston, VA) quantify color according to two chromatic attributes “hue” and “chroma” and a lightness attribute known as “value”. Hue is color perception, the recognition of an object as red, green, yellow, blue, etc. Chroma is the color concentration (intensity or saturation), ranging from gray to the pure hue. Value is a measure of the lightness of the color tone, ranging from pure white to pure black. A combination of these values gives a unique location in color space in polar coordinates, with hue denoting color tone (angular location), chroma denoting intensity (radial location), and value denoting lightness (vertical location) in Figure 1.

[0034] An alternative method of specifying color is by the CIELAB scale. CIE stands for Commission Internationale de l’ Eclairage (International Commission on Illumination) and LAB stands for the L^* , a^* , b^* coordinates of the scale; thus CIELAB is an abbreviation for CIE 1976 L^* a^* b^* color scale. On this scale, hue is expressed in terms of color pairs, with $+a^*$ being red, $-a^*$ being green, $+b^*$ being yellow, and $-b^*$

being blue. Chroma (intensity or saturation) is expressed as a value from the center of the coordinate system (0 being gray) to full intensity of the color component at ± 60 . Higher values of any component mean more intense colors, while lower values mean the material being measured is closer to colorless. The lightness value L^* ranges from 0 (pure black) to 100 (pure white). Once again, a specific combination of L^* , a^* , and b^* values identifies a unique location in color space and a specific color, saturation, and brightness.

[0035] Colors of all alloys were analyzed using an SP-62 spectrophotometer manufactured by X-Rite Inc. (Grand Rapids, MI). Analysis conditions were a d/8 sphere geometry (specular reflection included) with a D65 illuminant and 10° observer. All color measurements are reported on the CIE 1976 $L^* a^* b^*$ (CIELAB) scale. For initial color measurement, samples were prepared with the same surface finish (6-18 Ra; a measure of surface roughness) and cleaned to remove surface oxides, which can affect both initial color measurement and subsequent analysis of atmospheric tarnishing resistance.

Chemistry and color of alloys according to the invention are presented in Table 1 along with the same data for comparative copper alloys and selected stainless steels. Alloys according to the present invention are listed in the tables as I1, I2, I3, etc. Comparative copper alloys are listed as C1, C2, C3, etc. Comparative alloys which are not based on copper (carbon and stainless steel, zinc and aluminum alloys, pure metals other than copper, etc.) are listed as S1, S2, S3, and so forth.

[0036] Table 1. Chemistry and original (true metal) color

Table 1 - Chemistry and Color

Alloy	Actual Chemistry						Color				Electrical Conductivity at 240 kHz (%IACS)
	Cu	Zn	Mn	Ni	Fe	Other	L*	a*	b*	Visual	
C1	100						80.44	13.62	14.16	Red	100
C2	70	30					85.75	-1.44	21.74	Yellow	28.00
C3	77	12	7	4			80.41	2.30	10.27	Yellow	5.50
C4	88			10.5	1.5		79.96	3.65	8.18	Red	9.00
C5	75		0.5	24.5			78.79	1.00	5.26	White	5.60
C6	68.5		0.5	30	1		76.76	0.19	3.74	White	4.60
C7	71	11		18			79.30	0.84	6.74	White	6.80
C8	66	17		17			78.29	0.21	6.74	White	6.00
C9	91	6	3				82.03	7.49	13.99	Gold	13.25
C10	86	6	8				79.53	4.85	11.95	Gold	6.09
C11	82	6	12				79.48	3.04	9.09	Yellow	4.05
C12	78	6	16				78.61	1.99	6.95	White	3.05
C13	83	13	4				83.40	2.77	14.61	Yellow	10.34
C14	79	13	8				83.10	1.87	11.65	Yellow	5.60
C15	75	13	12				81.02	1.37	9.57	White	3.75
C16	71	14	15				80.70	0.88	7.13	White	2.82
C17	74	21	5				85.58	0.26	15.58	Yellow	9.31
C18	70	21	9				82.36	0.27	11.43	Yellow	5.17
C19	67	21	12				81.04	0.17	8.61	White	3.53
C20	63	21	16				80.24	0.15	6.66	White	2.72
C21	67	29	4				84.54	-0.64	17.59	Yellow	11.25
C22	63	29	8				83.36	-0.24	11.94	Yellow	5.10
C23	60	29	11				82.29	-0.19	10.52	Yellow	4.12
C24	56	28	16				82.78	-0.08	8.34	White	2.47
C25	88	6	4	2			77.37	5.63	12.19	Red	9.84
C26	69	15	15			1 Al	78.25	0.75	8.30	White	3.19

C28	97.8				2.2		80.67	11.05	12.06	Red	65.00
C29	85	15					84.19	4.36	19.14	Gold	37.00
C30	88		12				79.58	5.05	8.27	Red	4.15
C31	85			15			78.55	2.89	7.24	White	9.15
C32	90	10					81.54	6.44	17.58	Gold	44.00
I1	80	7	7	6			78.37	2.71	8.44	White	5.10
I2	74	9	14.5	2.5			78.49	1.53	6.92	White	3.10
I3	78.5	9	12	0.5			80.27	2.01	8.43	White	3.69
I4	76.5	9	12	2.5			78.39	1.82	7.69	White	3.61
I5	75.5	9	12.5	2.5	0.5		78.70	1.64	7.41	White	3.41
I6	75	8.5	11.5	2.5	2.5		78.79	1.65	7.28	White	3.26
I7	66	15	16	3			78.52	0.64	6.23	White	2.76
I8	66	17	16		1		79.09	0.49	6.98	White	2.96
I9	66	13	16	3	2		77.50	0.75	6.05	White	2.76
I10	77	14	4	3	2		80.16	2.07	11.65	Yellow	7.74
I11	53	25	17	3	2		77.76	0.09	5.32	White	2.52
S2			6.5	4	72	17 Cr, 0.25 N	77.18	0.30	4.64	White	2.50
S3				7	76	17 Cr	75.89	0.40	4.83	White	2.50

[0037] One of the difficulties with creating a “white” copper-base alloy is determining exactly what is meant by “white”. Many of the early applications for these alloys were as lower-cost alloys for coinage, flatware, and hollowware, so the desired color was similar to that of sterling and coin silver. More recently, “white” copper alloys are being considered as replacements for stainless steel or brushed nickel finishes in builder’s hardware and architectural applications, so that the antimicrobial properties of copper alloys are available with similar appearance to the modern look of stainless steel. A number of traditional “white” copper alloys were analyzed for color, along with other alloys which exhibited slight but distinct reddish or yellowish color overtones. Stainless

and carbon steel were also analyzed, along with pure nickel, zinc and tin such as would be found on the surface of white-colored plated products. These materials were compared to determine practical limits on CIELAB values for white alloys. Materials with measured values of both a^* and b^* close to zero appear nearly colorless and thus whiter than those with higher values of either a^* or b^* at the same overall lightness (L^*) value. Lightness values (L^*) for copper alloys typically range from 75 – 86 for surfaces free of oxide and a surface roughness of 6-18 Ra; this is true for all copper alloys measured, from bright yellow cartridge brass (Alloy C2, Cu-30Zn) to red pure copper (Alloy C1) to the strongly white copper-nickel used in circulating US coinage (Alloy C5).

[0038] For purposes of determining the desired white color, the upper limit of a^* is hereafter defined at the point where the visual appearance of the copper alloy is no longer primarily white and first becomes white with a distinctly red hue. This transition from white to red is defined by the a^* value of Alloy C31 (Cu-15Ni). Alloy C31 has an a^* value of 2.9. A comparable commercially available copper alloy (Alloy C4, Cu-10Ni-1Fe) is noticeably reddish and has an a^* value of 3.7. For the purposes of the present invention, it is proper to consider alloys with a^* values less than 3 and appropriate b^* values (on the CIELAB scale) to be white.

[0039] For copper alloys with a white visual appearance, the upper limit of b^* is defined at the point where the copper alloy is no longer primarily white and first becomes distinctly yellow (or white with a yellow hue). This transition from white to yellow is defined by the b^* value of comparative Alloy C3 (Cu-12Zn-7Mn-4Ni). This is a patented alloy with a “golden visual appearance” (as discussed in US 6,432,556 B1 to Brauer et

al.) and is specifically formulated to exhibit a color closer to that of 18K gold than to the white of Alloy C5 used for circulating US coinage; this alloy has a measured b^* value of 10.2. We set the upper limit for b^* at 10, so that only alloys less yellow than Alloy C3 are acceptable.

[0040] Lower limits for a^* and b^* were set based on the color of pure zinc (Alloy C35, a^* -1.7, b^* -1.9). Pure zinc subjectively appears white, although faint bluish and greenish overtones are visible on freshly cleaned and prepared surfaces. Therefore the lower limits for a^* and b^* were both set at -2 in order to include zinc in the white alloy zone. Copper alloys measured in our studies all had CIELAB values $a^* > -1.5$ and $b^* > 1.5$.

To be considered white the copper alloy must meet the constraints listed above for both a^* and b^* ; that is, a^* is preferably between about -2 and about +3, while b^* is preferably between about -2 and about +10. More preferably, a^* is between about -2 and about +2, while at the same time b^* is between about -2 and about +8. Most preferably, a^* is between about -2 and about +1 while at the same time b^* is between about -2 and about +7. Alloys meeting one or the other but not both are not considered white. For example, Alloy C2 (Cu-30Zn) has CIELAB a^* , b^* values of (-1.5, 21.5); although this falls within the a^* range for white (low redness), it exceeds the maximum allowable b^* to be considered white, therefore, Alloy C2 is a yellow copper alloy. A further example is Alloy C4 (Cu-10Ni-1Fe), with CIELAB a^* , b^* values of (3.7, 8.2); although the b^* value is within the white range (low yellowness) it exceeds the allowable a^* value, and is

visually reddish. Moreover, ranges having endpoints within the ranges discussed above are contemplated even if those endpoints or ranges are not specially set forth. For example, the range of values for a^* may have a lower endpoint of -1.9, -1.8, -1.7, etc. through +2.7, +2.8 and +2.9, while the upper endpoint may be +2.9, +2.8, +2.7, etc. through -1.7, -1.8 and -1.9. Similar endpoints for the values b^* are also contemplated. Also, it is also contemplated to combine any of the ranges for a^* with any of the ranges for b^* . For example, the range of values for a^* may be -2 to +2, while the range for the values of b^* may be -2 and about +10.

[0041] The present invention includes alloys that are, by weight, up to 30% zinc, up to 20% manganese, up to 5% nickel with the balance copper. These alloys more preferably contain from 6% to 25% zinc, from 4% to 17% manganese, from 0.1% to 3.5% nickel and the balance copper. The balance copper in the alloys may further contain at least one of: up to 0.5% of at least one of the group which consists of Sn, Si, Co, Ti, Cr, Fe, Mg, Zr, and Ag; and up to 0.1% of at least one of the group which consists of P, B, Ca, Ge, Se, Te. These alloys preferably contain from 12% to 20% Zn, from 10% to 17% Mn, and from 0.5% to 3.5% Ni. It more preferably contains from 13% to 16% Zn, from 14% to 17% Mn, and from 1.5% to 2.5% Ni. These alloys may also contain up to 0.3% Zr by weight. In a most preferred embodiment, the alloys of the above compositions are also white copper-based alloys; that is, they have CIELAB values where a^* is preferably between about -2 and about +3, while b^* is preferably between about -2 and about +10. More preferably, a^* is between about -2 and about +2, while at the same time b^* is

between about -2 and about +8. Most preferably, a^* is between about -2 and about +1 while at the same time b^* is between about -2 and about +7. It is contemplated that composition discussed above may be combined with each range of CIELAB values discussed above.

[0042] The present invention includes alloys that are, by weight, up to 30% zinc, up to 20% manganese, up to 4% iron with the balance copper. These alloys more preferably contains from 6% to 25% zinc, from 4% to 17% manganese, from 0.1% to 2.5% iron and the balance copper. The balance copper in the alloys may further contain at least one of: up to 0.5% of at least one of the group which consists of Sn, Si, Co, Ti, Cr, Ni, Mg, Zr, and Ag; and up to 0.1% of at least one of the group which consists of P, B, Ca, Ge, Se, Te. These alloys preferably contain Ni only as an impurity (that is, less than about 0.1%), and has from 12% to 20% Zn, from 10% to 17% Mn, and from 0.5% to 2.5% Fe. These alloys more preferably contain from 15% to 18% Zn, from 14% to 17% Mn, and from 0.5% to 1.5% Fe. In a most preferred embodiment, the alloys of the above compositions are also white copper-based alloys; that is, they have CIELAB values where a^* is preferably between about -2 and about +3, while b^* is preferably between about -2 and about +10. More preferably, a^* is between about -2 and about +2, while at the same time b^* is between about -2 and about +8. Most preferably, a^* is between about -2 and about +1 while at the same time b^* is between about -2 and about +7. It is contemplated that composition discussed above may be combined with each range of CIELAB values discussed above.

[0043] The present invention includes alloys that are, by weight, up to 30% zinc, up to 20% manganese, up to 6% nickel, up to 4% iron with the balance copper. These alloys more preferably contain from 6% to 25% zinc, from 4% to 17% manganese, from 0.1% to 5% nickel, from 0.05% to 2.5% iron and the balance copper. The balance copper in the alloys may further contain at least one of: up to 0.5% of at least one of the group which consists of Sn, Si, Co, Ti, Cr, Mg, Zr, and Ag; and up to 0.1% of at least one of the group which consists of P, B, Ca, Ge, Se, Te. These alloys preferably contain from 12% to 20% Zn, from 10% to 17% Mn, from 0.5% to 3.5% Ni, and from 0.1% to 1% Fe. These alloys more preferably contain from 13% to 16% Zn, from 14% to 17% Mn, from 1.5% to 2.5% Ni, and from 0.2% to 0.6% Fe. These alloys may further contain up to 1.0% Al. In a most preferred embodiment, the alloys of the above compositions are also white copper-based alloys; that is, they have CIELAB values where a^* is preferably between about -2 and about +3, while b^* is preferably between about -2 and about +10. More preferably, a^* is between about -2 and about +2, while at the same time b^* is between about -2 and about +8. Most preferably, a^* is between about -2 and about +1 while at the same time b^* is between about -2 and about +7. It is contemplated that composition discussed above may be combined with each range of CIELAB values discussed above.

[0044] In another embodiment of the invention, the alloys have an electrical conductivity greater than 2.5% IACS at eddy current gauge exciting frequencies between 60kHz and 480 kHz and that are, by weight, up to 30% zinc, up to 20% manganese, up to 10% nickel, up to 4% iron, up to 1% Zr with the balance copper. These alloys more

preferably contain from 6% to 25% zinc, from 4% to 17% manganese, from 0.1% to 9% nickel, up to 2.5% iron, up to 0.5% Zr and the balance copper. The balance copper in the alloys may further contain at least one of: up to 0.5% of at least one of the group which consists of Sn, Si, Co, Ti, Cr, Mg, and Ag; and up to 0.1% of at least one of the group which consists of P, B, Ca, Ge, Se, Te. These alloys preferably contain from 10% to 18% Zn, from 4% to 7% Mn, from 4% to 9% Ni, and from 0.05% to 0.2% Zr. The alloys more preferably contains from 12% to 16% Zn, from 4% to 6% Mn, from 5% to 9% Ni, and from 0.05% to 0.15% Zr. In a more preferred embodiment, each of the compositions discussed above also has an electrical conductivity between 4% IACS and 7% IACS. In a most preferred embodiment, the alloys of the above compositions are also white copper-based alloys; that is, they have CIELAB values where a^* is preferably between about -2 and about +3, while b^* is preferably between about -2 and about +10. More preferably, a^* is between about -2 and about +2, while at the same time b^* is between about -2 and about +8. Most preferably, a^* is between about -2 and about +1 while at the same time b^* is between about -2 and about +7. It is contemplated that composition discussed above may be combined with each range of CIELAB values discussed above as well as combined with each of the electrical conductivity characteristics discussed above.

[0045] Some specific examples of compositions contemplated include:

- 1) 6-25% zinc, 4-17% manganese, 0.1-3.5% nickel and balance Cu ; and
- 2) Same as 1), with 0.5% of at least one of Sn, Si, Co, Ti, Cr, Fe, Mg, Zr or Ag and up to 0.1% of P, B, Ca, Ge, Se or Te.

- 3) Same as 1) or 2), with 0.1-2.5% iron.
- 4) Same as 1) or 2), with 0.1-5% nickel and 0.05-2.5% iron.
- 5) 12-20% Zn, 10-17% Mn, and 0.5-3.5% Ni and balance Cu.
- 6) 13-16% Zn, 14-17% Mn, and 1.5-2.5% Ni and balance Cu.
- 7) Same as 1) with up to 0.3% Zr.
- 8) 12-20% Zn, 10-17% Mn, and 0.5-2.5% Fe and balance Cu.
- 9) 15-18% Zn, 14-17% Mn, and 0.5-1.5% Fe and balance Cu.
- 10) 13-16% Zn, 14-17% Mn, 1.5-2.5% Ni and 0.2-0.6% Fe and balance Cu.
- 11) 6-25% zinc , 4-17% manganese , 0.1-9.0% nickel and balance Cu.
- 12) Same as 11) with up to 0.3% Zr.
- 13) 10-18% Zn, 4-7% Mn, 4-9% Ni, 0.05-0.20% Zr and balance Cu.
- 14) 12-16% Zn, 4-6% Mn, 5-9% Ni, 0.05-0.15% Zr and balance Cu.

All of these examples may be combined with any combination of a* and b* values and any ranges of electrical conductivity.

[0046] For all the components in the compositions, ranges having endpoints within the ranges discussed above are also contemplated even if those endpoints or ranges are not specially set forth. For example, the range of values for Zn may have a lower endpoint of 6.1% 6.2%, 6.3%, etc. through 24.7%, 24.8% and 24.9%, while the upper endpoint may be 24.9%, 24.8%, 24.7%, etc. through 6.3%, 6.2% and 6.1%. Similar endpoints for the

ranges of the other components are also contemplated. Also, it also contemplated to combine any of the specially set forth ranges for Zn with any of the specifically set forth ranges for the other components. For example, ranges of from 6% to 25% zinc may be combined with ranges of from 10% to 17% Mn, and from 0.5% to 3.5% Ni.

[0047] A feature of the invention is that the alloys contain both Zn and Mn and lower levels of Ni than traditional “white” copper-based alloys. This results from synergistic effects of the alloying elements, where a combination of multiple components gives results not obtainable with simple binary alloys.

[0048] Nickel is a potent whitener in copper alloys. Addition of 10% Ni to Cu (Alloy C4) gives a pale alloy but still with a reddish-purple tinge. Additions of 15% Ni (Alloy C31) or more give distinctly white colors, and the alloys become more nearly colorless as the Ni content increases to 30% (Alloy C6). Increased Ni contributes to atmospheric tarnish resistance, inhibiting the formation of dark copper oxides. Unfortunately, Ni is also significantly more expensive than Cu (generally 2-3 times the cost), so there is a strong economic advantage to producing alloys similar in appearance but with less Ni. Higher additions of Ni also decrease the antimicrobial effectiveness of the alloys, so Ni should be held to a minimum consistent with the desired color and tarnish resistance. Nickel has been implicated as the major factor in metal-contact dermatitis, prompting the European Union to legislate Ni-free alloys for jewelry, eyeglasses, and similar items in “direct and prolonged contact with human skin” as seen in EP 0 635 564 B1

(Ammannati); “Copper-zinc-manganese alloy for the production of articles coming into direct and prolonged contact with the human skin”; Dec. 1, 2000; title, pg. 1-2.

[0049] Manganese is also an effective whitener in copper alloys, although binary alloys have had little commercial significance due to low strength, difficulties with ingot casting and hot rolling, and low and inconsistent ductility related to short-range ordering. Addition of 12% Mn or more to Cu give a relatively white alloy (Alloy C30, $[a^*, b^*] = [5.05, 8.27]$), but this is the range where short-range ordering becomes significant in binary alloys. Manganese is commonly used for strengthening at low levels in more complicated copper alloys containing Al, Zn, Si, Ni or combinations of these. These low-level Mn additions can also improve casting and hot rolling characteristics of these alloys.

[0050] Additions of Zn to copper alloys change the color strongly, but the alloys do not become “white” or colorless; instead, Cu-Zn alloys (“brasses”) become golden to yellow as the content increases to ~30% Zn. Beyond 33% Zn, the alloys turn reddish again with the formation of a new crystal structure. High Zn-brasses also exhibit short-range ordering under certain conditions, which can limit ductility and cause properties to change in service. Zinc can reduce the need for Ni in whitening copper-base alloys (the basis of the “nickel silver” Cu-Ni-Zn alloys). Appearance is close to the white Cu-Ni alloys, with a slight admixture of yellow due to the Zn content.

[0051] Iron additions to copper alloys are limited by low solubility. There is a miscibility gap above 3.5% Fe, preventing casting of higher-Fe alloys. Between 0.5% and

2.5%, Fe can be retained in solid solution by suitable heat treatment, and it is nearly as effective a whitener as Ni at the same levels. Fe can also be a potent strengthener, forming precipitates both directly and by reaction with P (phosphorus) in the alloy.

[0052] Zinc and aluminum are similar in copper alloys as far as color is concerned, but Al is significantly more effective at achieving golden-yellow colors. Addition of 6% Al (Alloy C32) gives a similar color to Cu-15Zn (Alloy C29). Over time, Cu-Al alloys (including those with other elements such as Zn, Mn and Fe) form tight passive oxide films which are beneficial for tarnish and corrosion resistance. This same effect reduces antimicrobial effectiveness of alloys of Cu with Al, so Al should be held to a minimum for antimicrobial applications. Hot- and cold-rolling and heat treatment of Al-containing alloys is more complicated than those without Al, due to interactions with many other alloying elements.

[0053] One of the primary objects of the invention is to provide a copper alloy of white visual appearance but with a reduced Ni content. The above description of the effects of alloying additions on the color of copper-base alloys point to methods for achieving this goal. By substituting Zn for a portion of the Ni, alloys of reduced Ni content can be created although the color tends to become yellower than Cu-Ni alloys of the same total Cu content. By further substituting Mn for some of the remaining Ni, alloys with much lower Ni content are possible with substantially white (colorless) appearance. We have found that retention of a low level of Ni (at a particular total alloy content) helps maintain the desired white color and also has benefits in terms of

atmospheric tarnish resistance and in decreasing staining due to contact with fluids from human skin. Thus, copper alloys of white visual appearance are found by substituting a combination of Zn and Mn for Ni in traditional alloys, along with maintaining a low level of Ni for improved color and tarnish resistance.

[0054] Another feature of the invention is that Fe may be used in place of Ni or in addition to Ni to improve the whiteness of Cu-Zn-Mn alloys. When measuring the color of commercial Cu-Ni alloys, we found that the whiteness of some of these alloys was better than expected from the Ni content alone. The alloys in question were found to contain significant amounts of Fe, added to improve casting and hot- and cold-working properties in these alloys. Further investigation of Cu-Fe alloys showed that while they are still distinctly red due to the low overall alloy content, they are closer to white (with a lower a^* value on the CIELAB scale) than expected for Cu-Zn or Cu-Mn of the same alloy content. Based on this, we added up to 2.5% Fe to alloys of the invention and found that the improved whiteness carried through even at total alloy content over 30%. Further, we found that the presence of Ni did not interfere with the effect of Fe so either or both may be used to improve the whiteness of Cu-Zn-Mn alloys. We also found that the presence of Fe in solid solution in the alloy (at a particular total alloy content) helps maintain the desired white color and also has benefits in terms of atmospheric tarnish resistance and in decreasing staining due to contact with fluids from human skin, similarly to the effects of low levels of Ni on these properties. These effects are also found when Fe or a combination of Fe and Ni are used in place of Ni alone. Thus, copper

alloys of white visual appearance are found by substituting a combination of Zn and Mn for Ni in traditional alloys, along with maintaining a low level of Ni or Fe or a combination of both Ni and Fe for improved color and tarnish resistance.

[0055] An important factor in selection of copper-base alloys for appearance (such as architectural and builder's hardware) is the stability of the appearance over time.

Stainless steels do not change appearance significantly when exposed to the atmosphere; this is due to formation of passive oxide layers preventing visible tarnish and corrosion and is why they are considered "stainless". Unfortunately, stainless steels are not available in the wide range of colors and tones that can be achieved with copper-base alloys, nor do stainless steels possess the antimicrobial characteristics of properly prepared copper alloys. Traditionally, Ni is added to copper alloys for improved resistance to atmospheric tarnishing, as Ni forms a passive oxide layer at the surface similar in function to the passive surface of stainless steels. We have found that it is possible to tailor the chemical composition of white copper alloys with reduced Ni content to give alloys with a desirable white appearance and resistance to atmospheric tarnishing substantially the same as traditional higher-Ni white copper-base alloys.

[0056] Tarnishing in copper alloys is the result of the formation of oxide films over time by reaction with oxygen from the atmosphere. It generally shows up as a darkening of the surface, although the different colors of the oxides formed from the base material (as well as interference-layer effects) can also introduce differences in hue and chroma compared to the original appearance of the material. By comparing colors before and

after exposure, the magnitude of tarnishing can be quantified and objective comparisons made between different alloys.

[0057] Color differences between samples with measured CIELAB values are readily calculated; a variety of color-difference and color-tolerance equations are given in ASTM Standard D2244-07^{ε1} “Standard Practice for Calculation of Color Tolerances and Color Differences from Instrumentally Measured Color Coordinates”; ASTM International; May 1, 2007. The total color difference ΔE^*_{ab} between two colors each given in terms of L^* , a^* , b^* can be calculated as:

$$\Delta E^*_{ab} = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

[0058] ΔE^*_{ab} provides the magnitude of the color difference but gives no indication of the character of the difference since it does not indicate the relative quantity and direction of hue, chroma, and lightness differences. (ASTM Standard D2244-07^{ε1}, Section 6.2.2). It is most useful when the color change is dominated by one of the three factors and the nature of the color change is easily understood but less useful when two or three components are significant contributors to the measured color change. It is also possible to transform the L^* , a^* , b^* rectangular coordinates into L^* , C^* , H^* cylindrical coordinates to better understand the relative differences in lightness L^* , chroma C^* and hue H^* . The equivalent total color difference equation is then:

$$\Delta E^*_{ab} = [(\Delta L^*)^2 + (\Delta C^*)^2 + (\Delta H^*)^2]^{1/2}$$

[0059] An alternate calculated color difference ΔE_{CMC} (as defined by the Colour Measurement Committee (CMC) of the Society of Dyers and Colourists in England) is intended to be used as a single-number shade-passing equation (also defined in ASTM D2244-07^{e1}). It was developed as a tolerancing system based on CIELCH cylindrical coordinates and defines ellipsoids around a standard color (specific point in color space) within which the difference from the standard is acceptable for the intended application. The color difference ΔE_{CMC} is given by:

$$\Delta E_{CMC}^* = cf [(\Delta L^*/(l \cdot S_L))^2 + (\Delta C^*/(c \cdot S_C))^2 + (\Delta H^*/(S_H))^2]^{1/2}$$

[0060] Parameters in the equation account for differences in spectral sensitivity and relative importance of the lightness versus chroma and hue, so that there is better agreement between numeric tolerances and the actual range of colors visually acceptable to human perception. In particular, the commercial factor cf can be varied to match the desired range for a given application. A $\Delta E_{cmc}=1$ is assumed to represent a just perceptible difference in color.

[0061] For purposes of comparing resistance to color change due to atmospheric exposure, ΔE_{CMC} was calculated based on the actual color difference between the samples before exposure (time = 0) and after exposure at a given time and temperature. Lower values of ΔE_{CMC} (less color change due to exposure) are considered a measure of superior atmospheric tarnish resistance.

[0062] Table 2: Atmospheric Tarnishing Table – Room Temperature

Table 2. Atmospheric Tarnishing - Room Temperature

Alloy	Initial Color			15 Days		30 Days	
	L*	a*	b*	ΔE^*_{ab}	ΔE_{cmc}	ΔE^*_{ab}	ΔE_{cmc}
C3	80.41	2.30	10.27	1.04	0.69	1.25	0.80
C4	79.96	3.65	8.18	1.02	0.56	1.33	0.76
C5	78.79	1.00	5.26	0.43	0.27	0.51	0.37
C6	76.76	0.19	3.74	0.32	0.32	0.43	0.45
C7	79.30	0.84	6.74	0.84	0.48	0.93	0.58
C8	78.29	0.21	6.74	0.48	0.29	0.46	0.31
C11	79.48	3.04	9.09	0.77	0.52	1.30	1.05
C12	78.61	1.99	6.95	1.27	0.71	2.32	1.44
C14	83.10	1.87	11.65	2.08	0.99	2.32	1.11
C15	81.02	1.37	9.57	0.78	0.57	1.95	1.31
C16	80.70	0.88	7.13	1.01	0.50	1.15	0.72
C17	85.58	0.26	15.58	2.75	1.35	3.09	1.54
C19	81.04	0.17	8.61	0.86	0.66	0.92	0.72
C20	80.24	0.15	6.66	0.88	0.74	1.45	1.04
C23	82.29	-0.19	10.52	0.94	0.75	1.05	0.87
C24	82.78	-0.08	8.34	0.59	0.53	0.80	0.71
C26	78.25	0.75	8.30	0.84	0.73	0.90	0.83
I1	78.37	2.71	8.44	0.45	0.34	0.66	0.48
I2	78.49	1.53	6.92	0.80	0.72	0.91	0.85
I3	80.27	2.01	8.43	0.81	0.56	0.85	0.63
I4	78.39	1.82	7.69	0.45	0.41	0.53	0.48
I5	78.70	1.64	7.41	0.60	0.46	0.71	0.52
I6	78.79	1.65	7.28	0.67	0.45	0.72	0.54
I7	78.52	0.64	6.23	0.57	0.58	0.76	0.73
I8	79.09	0.49	6.98	0.68	0.66	0.88	0.79
I9	77.50	0.75	6.05	0.86	0.76	0.97	0.83
S2	77.18	0.30	4.64	0.39	0.16	0.51	0.22
S3	75.89	0.40	4.83	0.27	0.15	0.21	0.14

[0063] Color change due to atmospheric tarnishing is given in Table 2. After 30 days at room temperature, many of the nickel-free comparative alloys (Alloys C11-C24) show $\Delta E_{CMC} > 1$. Nickel-containing comparative alloys C3-C8 (with Ni content >4%) all show less color change, with $\Delta E_{CMC} < 1$. Alloys of the invention (Alloys I1-I9) also show $\Delta E_{CMC} < 1$, even with Ni <3.5%. Comparing Alloy C16 with Alloy I8, it is expected that

one would see that adding 1% Fe (to a color-balanced Cu-Zn-Mn alloy) may not decrease tarnish resistance and may move the visual appearance closer to colorless. Similarly comparing Alloy I7 to Alloy C16, it is expected that one would see that addition of 3% Ni also may give a whiter alloy and significantly improves tarnish resistance. Addition of both Ni and Fe (Alloy I9) is expected to show that the color and tarnishing benefits of both elements are independent and may not interfere with each other.

Table 3. Atmospheric Tarnishing - Elevated Temperature

Alloy	Initial Color			150°C for 7 Hours		150°C for 24 Hours	
	L*	a*	b*	ΔE^*_{ab}	ΔE_{cmc}	ΔE^*_{ab}	ΔE_{cmc}
C3	80.41	2.30	10.27	18.2	12.4	20.9	14.4
C4	79.96	3.65	8.18	52.4	31.5	46.9	40.3
C5	78.79	1.00	5.26	16.7	14.9	30.3	26.7
C6	76.76	0.19	3.74	13.2	13.3	21.1	23.0
C7	79.30	0.84	6.74	19.4	15.3	29.6	22.9
C8	78.29	0.21	6.74	16.9	14.2	16.9	14.2
C11	79.48	3.04	9.09	18.3	13.8	28.5	21.5
C14	83.10	1.87	11.65	20.8	13.9	28.1	19.1
C16	80.70	0.88	7.13	13.4	11.5	17.6	15.6
C26	78.25	0.75	8.30	12.9	10.5	16.6	13.9
I2	78.49	1.53	6.92	12.4	10.8	15.9	14.0
I3	80.27	2.01	8.43	15.1	12.2	21.2	17.5
I4	78.39	1.82	7.69	13.3	10.9	16.8	12.7
I5	78.70	1.64	7.41	13.0	11.0	19.1	16.1
I6	78.79	1.65	7.28	13.0	10.9	18.0	15.1
I7	78.52	0.64	6.23	6.6	5.4	9.3	9.1
I8	79.09	0.49	6.98	9.1	8.4	12.7	11.9
I9	77.50	0.75	6.05	8.0	7.4	10.4	9.9
S2	77.18	0.30	4.64	3.1	2.9	4.0	3.8
S3	75.89	0.40	4.83	2.5	2.4	3.0	2.8

[0064] Elevated temperatures are often used to simulate longer-term exposures for purposes of oxidation or corrosion studies. It is important to select temperature-time

regimes where the nature of the oxides or corrosion products is the same as under the conditions being simulated. For example, at moderately elevated temperatures in air (200°C and above), the direct formation of black CuO is preferred over red Cu₂O which later transforms to CuO; this affects the nature of the color change during atmospheric tarnishing in terms of all three components (hue, chroma, and lightness). These exposures also indicate how materials will respond when used at moderately elevated temperatures (such as panels on kitchen appliances) or when subjected to automatic dishwashing or autoclave sterilization cycles.

[0065] Color change due to elevated-temperature atmospheric exposure is shown in Table 3. Alloy samples (also called coupons) were cleaned and prepared by the same procedure as other color samples and the CIELAB color measured before exposure. Color was reevaluated after exposure and ΔE_{CMC} calculated. After furnace treatment at 150°C for either 7 or 24 hours, the alloys of the invention (Alloys I2-I9) showed the same or less color change as any of the comparative copper alloys listed in Table 3 (Alloys C3-C26). The preferred embodiments of the invention (Alloys I7-I9) showed the least color change of any copper alloy listed. Of particular interest is a comparison between Alloy C16 and these preferred embodiments. Alloy C16 is essentially the same as these embodiments, but without either Ni or Fe; after 24 hours at 150°C, color change ΔE_{CMC} =15.6. For the same alloy with 1% Fe (Alloy I8), ΔE_{CMC} =11.9, illustrating that addition of Fe not only improved whiteness of the alloy but enhanced tarnish resistance as well. The same is true (but more so) for Alloys I7 and I9 (ΔE_{CMC} =9.1-9.9); addition of Ni (or

Ni plus Fe) to the basic Cu-Zn-Mn alloy dramatically improved tarnish resistance as well as whiteness of the alloy.

[0066] Touch surfaces (handrails, door hardware, countertops, appliance panels, hospital equipment, etc.) are in repeated contact with films of water, sweat, sebum, and other body fluids as part of their function. These body fluids contain complex mixtures of substances, many of which are noticeably corrosive to copper and copper alloys. An evaluation of how the appearance of these alloys changes after repeated contact with human skin is important not only in selection of these alloys for touch surface applications but also useful to determine the frequency of cleaning necessary to maintain their appearance. From a functional standpoint, cleaning and sanitizing cycles ranging from once per week to multiple times each day are recommended for stainless steel and similar hospital surfaces to minimize cross-contamination in healthcare situations.

Table 4. Touch Tarnishing - Room Temperature

Alloy	Initial Color			3 Days		7 Days	
	L*	a*	b*	ΔE^*_{ab}	ΔE_{cmc}	ΔE^*_{ab}	ΔE_{cmc}
C3	80.41	2.30	10.27	6.92	3.70	8.79	4.37
C4	79.96	3.65	8.18	3.49	2.00	7.05	3.35
C5	78.79	1.00	5.26	1.93	1.68	4.55	2.88
C6	76.76	0.19	3.74	3.05	1.77	6.25	2.90
C7	79.30	0.84	6.74	4.49	2.46	6.45	3.60
C8	78.29	0.21	6.74	5.31	2.83	6.27	3.38
C11	79.48	3.04	9.09	4.80	2.74	6.96	3.93
C12	78.61	1.99	6.95	2.51	1.69	5.63	3.38
C14	83.10	1.87	11.65	3.17	1.86	9.90	4.78
C15	81.02	1.37	9.57	4.02	2.30	5.58	3.35
C16	80.70	0.88	7.13	4.22	2.56	5.85	3.30
C17	85.58	0.26	15.58	4.98	2.62	9.74	4.85

C19	81.04	0.17	8.61	2.14	1.87	6.13	4.04
C20	80.24	0.15	6.66	1.52	1.24	5.47	3.23
C23	82.29	-0.19	10.52	1.39	0.89	7.68	4.12
C24	82.78	-0.08	8.34	1.09	0.76	7.47	4.40
C26	78.25	0.75	8.30	2.62	1.66	4.75	3.03
I1	78.37	2.71	8.44	3.22	1.99	7.91	4.18
I2	78.49	1.53	6.92	4.26	2.68	6.72	3.72
I3	80.27	2.01	8.43	3.01	1.80	7.56	4.54
I4	78.39	1.82	7.69	2.75	1.84	6.72	4.49
I5	78.70	1.64	7.41	2.27	1.54	4.91	3.28
I6	78.79	1.65	7.28	1.20	0.91	3.33	2.34
I7	78.52	0.64	6.23	1.72	1.16	2.93	1.90
I8	79.09	0.49	6.98	3.70	2.24	5.67	3.50
I9	77.50	0.75	6.05	2.03	1.37	3.18	2.06
S2	77.18	0.30	4.64	0.46	0.48	2.19	1.67
S3	75.89	0.40	4.83	2.29	1.67	3.93	2.75

[0067] Coupons of the alloys of interest were cleaned and prepared with the desired surface finish (6-18 Ra). Initial color was determined before any contact with human skin and/or fluids. The coupons were contacted daily, and the change in color determined and calculated for comparison. Results are given in Table 4. After three days of repeated skin contact, all white alloys showed little difference in stain resistance; ΔE_{CMC} was 1.2-2.8. There did not seem to be any strong correlation with content of any particular alloying element or combination of elements. After seven days of repeated exposure, the differences between alloys were even less although total color change was greater; ΔE_{CMC} was 2.9-4.4. Alloys of the invention were no worse than conventional alloys in terms of resistance to color change due to contact with human skin and/or body fluids, even though content of Ni and/or Fe was significantly lower than the Ni content of conventional white copper-base alloys.

[0068] Many of the applications for copper-based alloys involve conduction of electricity or resistance to such conduction. For example, controlled electrical

conductivity or resistivity is used as a security feature in discriminating between legal circulating coinage or tokens and invalid “slugs”, where a particular combination of color and electrical properties are desired. It is also used to control the activity of electrical equipment such as fuses and circuit breakers. Conductivity is controlled primarily by alloy content; addition of different alloying elements to pure copper (with 100% IACS conductivity) will cause more or less reduction in the conductivity. Conductivity of comparative alloys as well as alloys according to the invention is listed in Table 1.

[0069] Comparing Alloy C29 (Cu-15Zn, 37% IACS), Alloy C31 (Cu-15Ni, 9.15% IACS) and Alloy C30 (Cu-12Mn, 4.15% IACS), we see that various alloying elements have different effects on electrical conductivity. Taking advantage of this, it is possible to design alloys for a specific conductivity while maintaining a particular visual appearance. Alloy I1 has a white visual appearance and electrical conductivity (5.1% IACS) similar to that of Alloy C5 but it contains only 6% Ni compared to the 24.5% Ni in C5, which could result in a significant cost savings if substituted in circulating US coinage.

[0070] Among the advantages of the invention is that the white-colored copper-base alloy of the invention has antimicrobial properties. Copper and many copper-base alloys, when properly prepared, decrease the viability of bacteria and other microorganisms exposed on surfaces of these alloys. The effectiveness of the alloy surface at inactivating bacteria is related to alloy chemistry as well as other factors, such as surface roughness as demonstrated in PCT Application _PCT/US 2007/069413. The exposure time necessary to inactivate 99.9% of bacteria on the surface is a useful measure of the antimicrobial

properties of the alloys under consideration, and a test procedure based on that in the November 2003 study sponsored by the Copper Development Association (Wilks, et. al) was used for comparison with their published values.

[0071] Coupons (~22 mm square) of the alloys of interest were prepared and sterilized prior to exposure. The prepared coupons were placed in Petri dishes on sterilized filter paper. A 5-20 μ l aliquot of a suspension of active bacterial culture (E. Coli, American Type Culture Collection [ATCC] strain 11229, Gram-negative) in nutrient broth was applied onto the surface of the coupon; this inoculum contained a minimum of 10^6 - 10^8 colony-forming units per milliliter (CFU/ml). After the desired exposure time, the coupons were placed in tubes containing 20 ml of sterilized Butterfield's buffer (3.1×10^{-4} M K_2HPO_4 in filtered deionized/reverse osmosis laboratory-grade water) and ultrasonically agitated for 5 minutes to suspend any surviving bacterial colonies from the surface of the coupons. The suspension of surviving bacterial colonies was serially diluted four times (1/10, 1/100, 1/1000, and 1/10000). A 20 μ l aliquot of this original suspension and of each dilution was plated onto nutrient agar and incubated at 35-37 °C for 48 hours to count the surviving colonies. To check the baseline (the number of colonies in the original inoculum exposed on the coupons), a 20 μ l aliquot of the original inoculum was placed into a tube containing 20 ml of sterile buffer directly without exposure on a metal coupon and this was then treated in identical fashion to the suspension of survivors from the coupons (ultrasonically agitated, diluted, placed on agar plates and incubated before counting). Duplicate coupons were exposed and the dilutions

plated in duplicate to average out statistical variation common in biological testing. The number of colonies present on each agar plate was counted and the number of colony-forming units (CFU) per ml in the original baseline and the suspension from the exposed coupons calculated, accounting for all dilutions. Only plates exhibiting between 5 and 400 colonies were used for the final calculations, in order to minimize statistical variability. The exposure time required to achieve a 99.9% reduction in bacteria count ($3\log_{10}$ reduction in CFU) and time to complete inactivation are the primary measures of antimicrobial effectiveness.

[0072]

[0073] Results of antimicrobial testing of alloys of the invention challenged with E. Coli are presented in Table 5 and Figure 4. Published information on commercial alloys challenged with E. Coli (from Wilks and Keevil) is included below for comparison.

Table 5. Antimicrobial Effectiveness of Copper Alloys

Sample ID (Wilks and Keevil)	Equivalent Alloy (from Table 1)	Time to 99.9% Reduction	Time to Complete Inactivation
110 CDA	C1	75-90	90
220 CDA	C32	90-105	105
260 CDA	C2	90-105	120
706 CDA	C4	90-105	105
713 CDA	C5	90-105	120
752 CDA	C8	90-105	105
Y90 CDA	C3	90	120
	I1	45-60	60
	I2	45-60	60

[0074] Comparative Alloy C32 (Cu-10Zn) shows a 99.9% reduction in bacteria count after exposures between 90 and 105 minutes and complete inactivation after 105 minutes.

Alloy C4 (Cu-10Ni-1Fe) has essentially the same effectiveness as Alloy C32. Similar alloys with higher alloy content (C2 [Cu-30Zn] and C5 [Cu-25Ni-0.5Fe]) show slightly less effectiveness, with 99.9% reduction between 90 and 105 minutes and complete inactivation only after 120 minutes. Alloy C8 (Cu-17Zn-18Ni) is intermediate in chemistry between these alloys and shows intermediate antimicrobial effectiveness, just slightly less than C22000 Alloy C32 and Alloy C4. A commercial coinage alloy (Y90 from Olin Brass, Comparative Alloy C3, Cu-12Zn-4Ni-7Mn) also contains Mn like the alloys of the invention, but is balanced to have a “golden visual appearance” rather than the substantially white color of the invention. Antimicrobial effectiveness of C3 is slightly better than alloys without Mn, with 99.9% reduction near 90 minutes exposure and complete inactivation after 120 minutes. Alloy C1 (commercially pure copper) shows a 99.9% reduction in bacteria count after exposures between 75 and 90 minutes, with complete inactivation after 90 minutes.

[0075] Based on these published results, we expected antimicrobial effectiveness of the alloys of the invention to be similar to that of Alloy C3 (Y90). The zinc is somewhat higher (making for longer times, from a comparison of Alloy C32 and Alloy C2) and the nickel is slightly lower (shorter times, comparing Alloy C4 and C5). Comparing Alloy C8 and C3, the Mn did not seem to have a strong effect on antimicrobial effectiveness, although there was a more gradual and earlier drop in bacterial count rather than the sharp drop seen with most alloys. Unexpectedly, initial testing showed 99.9% reduction in CFU counts between 45 and 60 minutes (40% faster than other alloys) and complete

inactivation after 60 minutes (40-50% faster). Subsequent testing showed a 99.9% reduction at times as short as 10 minutes or less and complete inactivation between 15 and 30 minutes, and similar results for the same alloys challenged with the Gram-positive bacteria Staph. Aureus [ATCC 6538] using the same sample preparation and procedures. The mechanism responsible for the increased kill rates in our modified higher-Mn alloys is unclear, although it seems to be related to suppression of passivating oxide layers present on alloys of Cu with Zn and Ni.

[0076] It is apparent that there has been provided in accordance with this invention a copper alloy which fully satisfies the objects, features, and advantages of the invention as set forth herein. While the invention has been described in combination with specific embodiments thereof, it is evident that there are many alternatives, modifications and variations based on these descriptions which will be apparent to those skilled in the art. Accordingly, this invention is intended to embrace all such alternatives, modifications and variations as fall within the broad spirit and scope of the appended claims, and not be restricted to the specific examples set forth herein.

[0077] It will be further appreciated that functions or structures of a plurality of components or steps may be combined into a single component or step, or the functions or structures of one-step or component may be split among plural steps or components. The present invention contemplates all of these combinations. Unless stated otherwise, dimensions and geometries of the various structures depicted herein are not intended to be restrictive of the invention, and other dimensions or geometries are possible. Plural

structural components or steps can be provided by a single integrated structure or step. Alternatively, a single integrated structure or step might be divided into separate plural components or steps. In addition, while a feature of the present invention may have been described in the context of only one of the illustrated embodiments, such feature may be combined with one or more other features of other embodiments, for any given application. It will also be appreciated from the above that the fabrication of the unique structures herein and the operation thereof also constitute methods in accordance with the present invention. The present invention also encompasses intermediate and end products resulting from the practice of the methods herein. The use of “comprising” or “including” also contemplates embodiments that “consist essentially of” or “consist of” the recited feature.

[0078] The explanations and illustrations presented herein are intended to acquaint others skilled in the art with the invention, its principles, and its practical application. Those skilled in the art may adapt and apply the invention in its numerous forms, as may be best suited to the requirements of a particular use. Accordingly, the specific embodiments of the present invention as set forth are not intended as being exhaustive or limiting of the invention. The scope of the invention should, therefore, be determined not with reference to the above description, but should instead be determined with reference to the appended claims, along with the full scope of equivalents to which such claims are entitled. The disclosures of all articles and references, including patent applications and publications, are incorporated by reference for all purposes.

CLAIMS

What is claimed is:

- 1) An effectively antimicrobial copper alloy with a visual appearance similar to one of stainless steel and “nickel silver”, the copper alloy comprising :
 - a) 6-25% zinc (Zn)
 - b) 4-17% manganese (Mn),
 - c) 0.1-3.5% nickel (Ni),
 - d) a balance of substantially Cu ; and
 - e) the combination of a-d exhibiting a white visual appearance and is effectively antimicrobial.
- 2) The copper alloy of Claim 1 wherein the balance of substantially Cu also contains up to at least one of:

0.5% of at least one of the following group which consists of: Sn, Si, Co, Ti, Cr, Fe, Mg, Zr, Ag; and

up to 0.1% of at least one the following group which consists of: P, B, Ca, Ge, Se, Te;

and said alloy has a time to complete inactivation of less than 60 minutes.
- 3) A copper alloy of white visual appearance similar to one of stainless steel and “nickel silver” the copper alloy consisting essentially of :
 - a) 6-25% zinc (Zn),

- b) 4-17% manganese (Mn),
 - c) 0.1-2.5% iron (Fe),
 - d) a balance of substantially Cu
 - e) wherein the combination of a-d exhibits a white visual appearance and is effectively antimicrobial.
- 4) The copper alloy of Claim 3 wherein the balance of substantially copper also contains at least one of:
- up to 0.5% of at least one of the following group which consist of: Sn, Si, Co, Ti, Cr, Ni, Mg, Zr, Ag, and
 - up to 0.1% of at least one of the following group consisting of : P, B, Ca, Ge, Se, .
- 5) A copper alloy of white visual appearance similar to one of stainless steel and “nickel silver”; the copper alloy consisting essentially of :
- a) 6-25% zinc (Zn),
 - b) 4-17% manganese (Mn),
 - c) 0.1-5% nickel (Ni),
 - d) 0.05-2.5% iron (Fe), and
 - e) a balance of substantially Cu;
 - f) where the combination of a-e is effectively antimicrobial and has a white visual appearance.
- 6) The copper alloy of Claim 5 which also contains at least one of:

up to 0.5% of at least one of the following group which consists of : Sn, Si, Co, Ti, Cr, Mg, Zr, Ag, and

up to 0.1% of at least one of the group consisting of : P, B, Ca, Ge, Se, Te.

- 7) The copper alloy of Claim 1 which combination is resistant to tarnishing on room temperature exposure in air and has a time to complete inactivation of less than 60 minutes.
- 8) The copper alloy of Claim 7 which contains 12-20% Zn, 10-17% Mn, and 0.5-3.5% Ni
- 9) The copper alloy of Claim 8 which contains 13-16% Zn, 14-17% Mn, and 1.5-2.5% Ni, and wherein said time to complete inactivation is less than 20 minutes.
- 10)The copper alloy of Claim 1 which contains up to 0.3% Zr by weight.
- 11)The copper alloy of Claim 3 which is effectively antimicrobial and contains Ni only as an impurity.
- 12)The copper alloy of Claim 11 which contains 12-20% Zn, 10-17% Mn, and 0.5-2.5% Fe.
- 13)The copper alloy of Claim 12 which contains 15-18% Zn, 14-17% Mn, and 0.5-1.5% Fe.
- 14)The copper alloy of Claim 5 which is resistant to elevated temperature tarnishing.
- 15)The copper alloy of Claim 14 which contains 12-20% Zn, 10-17% Mn, 0.5-3.5% Ni and 0.1-1.0% Fe.
- 16)The copper alloy of claim 15 which contains 13-16% Zn, 14-17% Mn, 1.5-2.5% Ni and 0.2-0.6% Fe.

17) The copper alloy of Claim 14 which contains at least one of:

up to 1.0% Al ; and

and at least one of:

up to 0.5% of at least one of the following group consisting of: Sn, Si, Co, Ti, Cr, Mg, Zr, Ag, and;

up to 0.1% of at least one of the group consisting of : P, B, Ca, Ge, Se, Te.

18) A copper alloy of white visual appearance and resistant to touch tarnishing to be used for coinage applications as a direct replacement for C713, the copper alloy comprising :

a) 6-25% zinc (Zn),

b) 4-17% manganese (Mn),

c) 0.1-9.0% nickel (Ni),

d) a balance of substantially Cu; and

e) said combination of a-d having a white visual appearance, is effectively antimicrobial and has an electrical conductivity greater than 2.5% IACS at eddy current gauge exciting frequencies between 60 kHz and 480 kHz.

19) The copper alloy of Claim 18 wherein the balance of substantially Cu also contains up to at least one of:

0.5% of at least one of the following group which consists of: Sn, Si, Co, Ti, Cr, Fe, Mg, Zr, Ag; and

up to 0.1% of at least one the following group which consists of: P, B, Ca, Ge, Se, Te.

20) The copper alloy of Claim 19 wherein said electrical conductivity is between 4% IACS and 7% IACS;

and further having a time to complete inactivation of less than 60 minutes.

21) The copper alloy of Claim 19 containing up to 0.3% Zr by weight; and the time to complete inactivation is less than 30 minutes.

22) The copper alloy of Claim 21 containing 10-18% Zn, 4-7% Mn, 4-9% Ni and 0.05-0.20% Zr; and

the time to complete inactivation is less than 20 minutes.

23) The copper alloy of Claim 22 which contains 12-16% Zn, 4-6% Mn, 5-9% Ni and 0.05-0.15% Zr; and

the time to complete inactivation is less than 15 minutes.

24) The copper alloy of Claim 18 which has been formed into a planchet.