

LEAD-FREE SOLDER WITH LOW COPPER DISSOLUTION

CROSS REFERENCES TO RELATED APPLICATIONS

- This application claims priority from and is related to commonly owned U.S.
- 5 Provisional Patent Application Serial No. 60/761,400 filed January 23, 2006, entitled: Lead-Free Solder With Low Copper Dissolution, this Provisional Patent Application incorporated by reference herein.

FIELD OF THE INVENTION

- 10 The present invention relates to low-cost solder compositions for bonding electronic devices or parts to printed wiring boards (PWBs). In particular, the present invention relates to solder compositions that prevent or minimize the dissolution of copper into the solder during the soldering process.

BACKGROUND OF THE INVENTION

- Electronic assemblies are composed of a printed wiring board (PWB), sometimes also known as a printed circuit board (PCB), which is constructed of an insulating board, such as glass-epoxy or paper-epoxy, on which copper circuitry is formed on one or both sides. Electronic components, wires, or other devices with
- 20 metal terminations are joined to the copper circuitry with solder. Though some of the soldering of electronic assemblies is being done by hand with soldering irons, the much larger percentage of production is being accomplished with automated soldering machines. U.S. Patent 2,993,272 discloses one of the earliest wave soldering processes for soldering electrical and mechanical portions of a circuit
- 25 board, a process still in present use.

Automated soldering machines, often also known as mass soldering machines, employ a conveyor to transport a printed circuit board assembly first across a fluxing unit that applies soldering flux to the bottom side of the printed circuit board and component terminations, then across a preheating unit, and then
5 across the solder station. The solder station consists of an iron or steel heated pot that maintains the solder in a melted condition, usually 50-100°C above the liquidus melting point of the solder composition. The printed circuit assembly may be transported across the surface of the melted solder, known as drag soldering, or, more commonly, across a standing wave of molten solder, the wave being generated by a
10 pumping system contained in the melted solder.

Solders for joining electronic parts to copper terminations of a printed wiring board traditionally have been composed of tin and lead of about 60% to 63% tin (Sn) and the balance lead (Pb). More recently, international environmental regulations are restricting the use of lead (Pb) in solders for electronic products; so, solder
15 technologists and manufacturing personnel have been evaluating and using alternative solders for soldering electronic assemblies. The process of automated soldering results in dissolution of copper from the printed circuit board and component terminations into the melted solder. Copper is very soluble in melted tin, a primary component in solders used for electronic assembly. Copper is particularly
20 susceptible to dissolving in lead-free solders because the lead-free solders melt at higher temperatures than tin-lead solder and consist of more than 95% tin. As copper dissolves into the lead-free solder, the liquidus melting point of the solder alloy increases dramatically. For example, the eutectic melting temperature (solidus and liquidus points are the same) for tin containing 0.7% copper is 227°C. Because
25 of the superheating required for automated wave soldering, the solder may be heated to above 300°C for reliable soldering. During the soldering process, the melted tin-

copper solder can dissolve additional copper from the assembly being soldered. A very small increase in copper from 0.7% to 1.0% will raise the liquidus melting point of the tin-copper solder alloy to 239°C, while an increase in copper to only 1.5% results in a liquidus melting point of 260°C. One solution would be to increase the solder temperature to accommodate the increased amount of copper, but this would not be acceptable because of the damage caused by excessive heating of the electronic devices being soldered.

A common practice by those using automated dip or wave soldering machines, to adjust for the increasing copper percentage in the solder, is to use a second alloy with reduced copper percentage for replacement additions of solder to the pot. For example, where a solder composition of 0.7% copper in tin is the most economical lead-free solder of choice in the automated soldering machine, additions of solder to replace expended solder and dilute dissolved copper may contain only from 0% to 0.5% copper. This adjustment is not precise and can affect the quality of the soldering process and the reliability of the soldered electronic assembly. A significant advantage of the present invention is that the dissolution rate of copper into the melted solder is sufficiently low that the use of another solder alloy is not necessary.

A solder wave is formed by pumping molten solder, contained within a solder pot, up through a nozzle to provide a standing wave. Usually, only one wave is employed, but dual waves are also employed, particularly when surface mounted devices are being soldered to the bottom side of printed circuit boards. Solder cascades and solder jets also find application as wave soldering. Alternatively, the solder may be maintained in an open solder pot where an electronic assembly may be dragged across the melted solder surface to accomplish the soldering. One of the problems encountered with automated soldering processes is that the molten solder

oxidizes when exposed to the oxygen in the air. The oxidized solder forms a surface oxide layer, which must be removed by a flux before the components being soldered will wet with solder. Particularly with wave soldering, the surface oxide layer is continually broken by the flow of solder in the wave. This exposes fresh solder
5 which, in turn, is also oxidized. A mixture of oxide and solder, thus, collects within the solder pot. This mixture is known as dross, which must be removed and disposed. Dross generation adds to the cost of the process due to the lost value of the solder and the maintenance time required to remove it and repair mechanical parts of the wave soldering apparatus damaged by the abrasive action of the dross.

10 One method employed to minimize the formation of oxide on the solder in a wave soldering machine is to cover the surface of the melted solder with an oil. This is effective in protecting the solder from atmospheric oxygen, but the oil degrades and must be replaced periodically. Furthermore, the oils commonly used are difficult to clean off of the components being soldered and can produce a great deal of smoke
15 at wave soldering temperatures. A solution for this problem for over three decades is to add phosphorus to the solder. U.S. Patent 5,240,169 describes the use of known low dross solder containing 10 to 1000 parts per million (ppm) phosphorus.

More recently, concerns about safety and environmental pollution caused by lead (Pb) in the solder used for assembling electronic products has resulted in the
20 development of environmentally acceptable, substitute solder compositions where the lead (Pb) has essentially been replaced with tin (Sn). There are a variety of other metals -- such as silver (Ag), copper (Cu), antimony (Sb), zinc (Zn), indium (In), and bismuth (Bi) -- that can be added to tin (Sn) either individually or in combination to reduce the melting temperature, improve the ductility and strength of the solder joint,
25 and/or improve wetting to the metal surfaces being soldered.

Some examples are described by the patents referenced in Table 1 below:

TABLE 1 - (Prior Art) Values Given in Weight Percent

U.S. Patent Number	Sn	Ag	Cu	Sb	Zn	In	Bi	Ni	P	Other
1,239,195	Balance	0.5-1	0.5-1	—	—	—	—	—	—	—
1,437,641	85-95	0.5-4.5	0.5-4.5	—	0.5-9.5	—	—	—	—	—
4,193,530	Balance	—	—	—	—	0.1-0.5	0.1-0.5	—	—	—
4,670,217	90.0-98.5	0.5-2	—	0.5-4.0	0.5-4.0	—	—	—	—	—
4,758,407	92.5-96.9	0.1-0.5	3.0-5.0	—	—	—	—	0.1-2.0	—	—
4,879,096	88-99.35	0.05-3	0.5-6	—	—	—	0.1-3	—	—	—
4,929,423	Balance	0.01-1.5	0.02-1.5	—	—	—	0.08-20	—	0.10	Rare Earth 0-0.2
5,094,813	95.68	0.08-0.16	2.8-3.5	—	0.2-0.5	—	—	0.08-0.16	—	—
5,352,407	93-98	1.5-3.5	0.2-2.0	0.2-2.0	—	—	—	—	—	—
5,817,194	Balance	≤10	≤3	—	—	—	—	0.5-5.0	0.05-1.5	—
5,837,191	Balance	0.05-0.6	0.05-0.6	0.75-2	—	—	—	0.05-0.6	—	—
5,863,493	91.5-96.5	2.0-5	0-2	—	—	—	—	0.1-2	—	—
5,980,822	81.4-99.6	0.1-5.0	0.1-5.5	0.1-3.0	—	—	0.1-5.0	—	0.001-0.01	Ge 0.01-0.1
5,985,212	>75.0	—	0.01-9.5	—	—	0-6.0	—	—	—	Ga 0.01-5.0
6,139,979	Balance	—	0.7-2*	3.0-5.0*	—	—	—	0.01-0.5	—	*at least one
6,179,935	Balance	>0-4.0	<0-2.0	—	—	—	—	>0-1.0	—	Ge >0-1
6,180,055	Balance	—	0.1-2	—	—	—	—	0.002-1	—	Ge 0-1
6,296,722	Balance	—	0.1-2	—	—	—	—	0.002-1	—	Ga 0.001-1
6,365,097	Balance	<4	<2	—	—	—	≤21	<0.2	—	Ge ≤0.1
6,440,360	Balance	—	0.8	—	—	—	—	0.9	—	—
6,488,888	Balance	0.1-3.5*	0.1-3*	—	7-10	—	—	0.01-1	0.001-1	*at least one
6,649,127	Balance	—	0.3-3	—	0.5-10	—	0.5-8	—	—	Ge 0.005-0.05
6,660,226	>88.0	0.5-9	0.5-2	—	—	—	—	—	—	Co 0.1-2.0
6,702,176	Balance	1.0-4.0	0.2-1.3	—	—	—	—	—	—	Co 0.02-0.06
6,843,862	88.5-93.2	3.5-4.5	0.3-1.0	—	—	2.0-6.0	—	—	0.01	—

There are specific problems with the above listed solder alloy compositions that make them not as desirable for soldering of electronic assemblies as the tin-lead solder compositions they are intended to replace.

Tin without the addition of other metals is unacceptable for soldering electronic assemblies for several reasons. First, soldering temperatures required for using tin (Sn) with its high melting point (232°C) may damage electronic

components. Second, the wetting ability is poor because of the high surface tension of the melted tin. Third, the tensile strength and ductility are unacceptably low because of the coarse grain structure of the solidified metal. Adding other metals, such as lead, silver, copper, and/or zinc will decrease the surface tension and the melting points of the solder alloys, while increasing the tensile strengths and ductility. U.S. Patent 1,239,195 describes the addition of copper and/or silver to tin to harden the composition.

U.S. Patent 1,437,641 describes the improvement of mechanical properties of tin-silver by adding copper to tin-silver solder compositions. Tin (Sn) solders containing 3.5% or less silver, such as SnAg3.5 or SnAg3.0Cu0.5, have an acceptable melting temperature (217 to 221°C) and higher mechanical strength than the tin-lead solders. U.S. Patent 5,863,493 describes the addition of small amounts of copper (0-2.9%) and nickel (0.1-3%) to SnAg3.5 solder compositions to provide resistance to grain growth of tin-silver intermetallic compound in the tin matrix, especially during thermal cycling of the solder joints. Nevertheless, the ability of these solders to wet or bond to copper is impaired by the high surface tension and slow wetting speed of tin-silver solders on copper. Also, silver is too costly for large scale manufacturing of electronic products, and the appearance of the completed solder joints is dull or frosty, unlike the acceptable appearance of tin-lead solder.

Tin-copper solders, such as the SnCu0.7 eutectic composition, melt at an acceptable temperature (227°C) for hand or automated soldering, but the surface tension of the solder alloy is still high compared to the conventional tin-lead solder, resulting in inferior wetting ability compared to that of the tin-lead solder. The dissolved tin-copper intermetallic compound (primarily Cu₆Sn₅) crystallizes and causes a grainy, dull appearance on the solidified solder.

Tin-antimony solder, such as the well-known composition SnSb05, provides solder joints with acceptable tensile strength, but the melting temperature (232-240°C) is higher than alloys of tin and copper or silver, and therefore too high of a melting temperature for heat-sensitive electronic components. Also, antimony seriously reduces the ability of the solder to spread on a copper surface because of the formation of a copper-antimony intermediate phase between the copper and the solder alloy. Antimony is considered the most toxic metal in this grouping of solder compositions. As antimony has been added to tin-lead solder to improve strength, so to is antimony added to other tin compositions incorporating silver, copper, bismuth, and zinc, as shown in Table 1.

U.S. Patent 1,437,641 describes a well-known tin-zinc solder alloy with acceptable melting temperature, but unacceptably rapid oxidation and corrosion problems. U.S. Patent 4,670,217 describes solder compositions for joining copper that contain up to 4% zinc added to solder compositions containing tin, silver, and antimony. However, for automated applications, such as wave soldering, tin alloys containing zinc (Zn) are subject to very rapid oxidation while being pumped to generate a standing wave of solder, resulting in a large production of dross, *i.e.*, a mixture of metal oxides and metal particles that float on the surface of the melted solder. There is also much concern about the potential galvanic corrosion of solder joints made with solders containing zinc.

U.S. Patent 4,193,530 describes the addition of small amounts (0.1% to 0.5%) of bismuth and indium to tin metal to improve the corrosion resistance of the tin. U.S. Patent 4,879,096 describes adding 0.1% to 3% bismuth to solder compositions containing tin, silver, and copper, to increase the strength of the solder joints. U.S. Patent 5,980,822 describes adding 0.1% to 5.0% bismuth to reduce the solidus melting temperature of the solder alloy that contains tin, silver, copper, and antimony.

U.S. Patent 4,929,423 describes adding up to 20% bismuth, preferably 3% to 6%, to solders containing tin, silver, and copper. U.S. Patent 6,649,127 describes the addition of bismuth up to 8% to tin-copper solder composition containing up to 10% zinc, for the purpose of reducing the melting temperature and improving the wetting
5 speed when soldering to copper surfaces.

These described solders are designed for copper pipe plumbing applications. However, for soldering electronic components to a printed circuit board, solder alloys that contain more than about 2% to 5% bismuth (Bi) are incompatible with lead (Pb) that may be contained on the electronic component terminations, resulting in
10 potential cracked solder joints. Nevertheless, bismuth can be added in small amounts to certain lead-free solder alloy compositions to improve the wetting ability and slightly reduce the melting temperature of the solder. As much as 1% bismuth is soluble in solid tin. The much lower surface tension of bismuth compared to tin would help wetting.

15 Tin alloys containing indium (In) have the same high cost problem as those with silver, even though indium additions are able to improve the wetting ability of the solder. Though U.S. Patent 6,843,862 describes lead-free solders containing 4% indium as dissolving the copper substrate metal at a reduced rate compared to lead-free solders that do not contain indium, there is no significant difference when
20 bismuth is added to these alloys. U.S. Patent 5,985,212 also describes the addition of gallium (Ga) to lead-free solders containing tin, copper, and indium with the purpose of increasing strength and reducing the melting point of the resulting solder composition.

Tin-nickel compositions with as little as 4 weight % nickel (Ni) melt above
25 400°C, which is too high of a temperature for electronic soldering applications. However, the addition of nickel in smaller amounts (0.1% to 2.0%) to tin alloys

containing 3% to 5% copper is described in U.S. Patent 4,758,407 as improving wettability and increasing strength of the solder composition. Nevertheless, while acceptable for plumbing applications, the specified solder compositions have high liquidus temperatures exceeding 600°F (315°C), which is exceedingly high for
5 soldering of electronic assemblies. Subsequent patents, as shown in Table 1, have incorporated nickel as an additive to lead-free solders also to improve the solderability and reduce the melting point of the specified solder compositions. U.S. Patent 5,863,493 teaches that tin-silver solder alloys experience grain growth coarsening during thermal cycling, resulting in decreased creep and fatigue
10 resistance, and the additions of nickel and copper to the tin-silver solder composition improves both properties.

Alternatively, U.S. Patent Nos. 6,660,226 and 6,702,176 describe the addition of cobalt (Co) to lead-free solders to prevent leaching by the lead-free solder of certain transition metals, such as copper, silver, gold, palladium, platinum, nickel,
15 and zinc. Yet another U.S. Patent 6,702,176 describes the addition of cobalt to a tin-based, lead-free solder to prevent leaching of copper metal being soldered.

U.S. Patent 5,980,822 describes the addition of germanium (Ge) in combination with phosphorus (P) to prevent the formation of metal oxide and improve the thermal fatigue of the solder. Subsequent patents, as shown in Table 1,
20 have incorporated germanium (Ge) with nickel (Ni) to enhance the wettability and tensile strength of a variety of lead-free solders containing tin, silver, copper, and/or zinc. The use of germanium in price competitive solder compositions is precluded because of the very high cost of germanium.

Phosphorus is commonly added to bulk molten metal, such as copper and
25 solder, to remove oxides. The addition of phosphorus to tin solder alloys is recognized by those skilled in the art as a standard method for deoxidizing metals

during the manufacture of solder or while using the solder for joining electronic assemblies. Because the Gibb's Free Energy of Formation of phosphorus oxide (P_2O_5) is much lower than that of tin, copper, bismuth, nickel, silver, or lead oxides, the oxygen affinity of phosphorus is higher. So, phosphorus oxide preferentially
5 forms on the melted solder surface during the solder processing. The resulting phosphorus oxide (specific gravity 2.4) floats on the surface of the solder (specific gravity 7.3). U.S. Patent 6,488,888 describes adding phosphorus to reduce drossing or oxide formation resulting from using tin-zinc solders. U.S. Patent 5,817,194 describes the addition of phosphorus to soldering/brazing material in the range of
10 0.05% to 1.5% to act as a fluxing agent to improve the wettability of the solder/brazing material to stainless steel. Also stated is that phosphorus addition must exceed 0.05% to exhibit fluxing properties, and that the nickel addition must be greater than 0.05% to be effective.

Therefore, there is a need for improving lead-free solder compositions.

15 Nothing in the prior art provides the benefits attendant with the present invention.

Therefore, it is an object of the present invention to provide an improvement which overcomes the inadequacies of the prior art devices and which is a significant contribution to the advancement of the solder art.

20 It is another object of the present invention to form solder compositions that will result in smooth, shiny solder connections equivalent to those obtained when using tin-lead solder.

Another object of the present invention is to provide lead-free solder compositions for use in joining electronic components and other parts to printed
25 wiring boards.

Yet another object of the present invention is to provide a lead-free solder composition containing 0.2 to 0.9% by weight of copper, 0.006 to 0.07% by weight of nickel, 0.03 to 0.08% by weight of bismuth, less than 0.5% by weight of silver, less than 0.010% by weight of phosphorus, and the balance of tin.

5 Still yet another object of the present invention is to provide a solder paste composition comprising a powder containing 0.2 to 0.9% by weight of copper, 0.006 to 0.07% by weight of nickel, 0.03 to 0.08% by weight of bismuth, less than 0.5% by weight of silver, less than 0.010% by weight of phosphorus, and the balance of tin; a rosin-based resin; an activating agent, and a solvent.

10 Another object of the present invention is to provide a soldered article comprising a workpiece containing a transition metal conductor capable of readily diffusing into melted tin; and a lead-free solder composition containing 0.2 to 0.9% by weight of copper, 0.006 to 0.07% by weight of nickel, 0.03 to 0.08% by weight of bismuth, less than 0.5% by weight of silver, less than 0.010% by weight of
15 phosphorus, and the balance of tin, the lead-free solder composition bonded to the workpiece so as to be electrically and mechanically bonded to the transition metal conductor.

Yet another object of the present invention is to provide a lead-free solder composition containing 0.2 to 0.9% by weight of copper, 0.006 to 0.07% by weight
20 of nickel, 0.03 to 0.08% by weight of bismuth, and the balance of tin.

The foregoing has outlined some of the pertinent objects of the present invention. These objects should be construed to be merely illustrative of some of the more prominent features and applications of the intended invention. Many other beneficial results can be attained by applying the disclosed invention in a different
25 manner or modifying the invention within the scope of the disclosure. Accordingly, other objects and a fuller understanding of the invention may be had by referring to

the summary of the invention and the detailed description of the preferred embodiment in addition to the scope of the invention defined by the claims.

SUMMARY OF THE INVENTION

5 According to the present invention, the melted solder compositions dissolve copper from electronic components, printed wiring boards and wires at a rate slower than that experienced in the same applications with 63% tin, 37% lead solder alloy. Additionally, the need to attempt to balance the solder composition in a solder pot by adding another solder composition with reduced copper content is eliminated. Still
10 further, the solder compositions of the present invention are low cost, exhibit good wetting properties, have acceptably low melting temperatures, and result in the formation of reflective solder joints with a shiny appearance similar to that experienced in the same applications with 63% tin, 37% lead solder alloy.

 It was discovered that a very small amount of bismuth added to tin-based
15 solder containing copper and nickel can significantly reduce the dissolution rate of copper into the solder when compared to tin-lead and tin-copper solder alloys. Further, the synergistic effect of adding nickel and bismuth improves the cosmetic appearance of the solder joint.

 A feature of the present invention is to provide a lead-free solder composition
20 containing copper, nickel, bismuth, silver, phosphorus, tin and inevitable impurities. The range of copper in the lead-free solder composition can be between 0.2 to 0.9% by weight or, in a preferred embodiment, between 0.5% and 0.7% by weight. The range of nickel in the lead-free solder composition can be between 0.006 to 0.07% by weight or, in a preferred embodiment, between 0.04% by weight and 0.06% by
25 weight. The range of bismuth in the lead-free solder composition can be between 0.03 to 0.08% by weight or, in a preferred embodiment, between 0.05% by weight

and 0.07% by weight. The range of silver in the lead-free solder composition is less than 0.5% by weight. The range of phosphorus in the lead-free solder composition is less than 0.010% by weight. The balance of the lead-free solder composition is of tin.

5 The lead-free solder composition of the present invention containing 0.2 to 0.9% by weight of copper, 0.006 to 0.07% by weight of nickel, 0.03 to 0.08% by weight of bismuth, less than 0.5% by weight of silver, less than 0.010% by weight of phosphorus, and the balance of tin can be formed into a solder bar where the solder bar can be used in electronic assembly solder machines.

10 The lead-free solder composition of the present invention containing 0.2 to 0.9% by weight of copper, 0.006 to 0.07% by weight of nickel, 0.03 to 0.08% by weight of bismuth, less than 0.5% by weight of silver, less than 0.010% by weight of phosphorus, and the balance of tin can be formed into a solder ingot where the solder ingot can be used in electronic assembly.

15 The lead-free solder composition of the present invention containing 0.2 to 0.9% by weight of copper, 0.006 to 0.07% by weight of nickel, 0.03 to 0.08% by weight of bismuth, less than 0.5% by weight of silver, less than 0.010% by weight of phosphorus, and the balance of tin can be formed into a solder wire where the solder wire can be used in electronic assembly.

20 The lead-free solder composition of the present invention containing 0.2 to 0.9% by weight of copper, 0.006 to 0.07% by weight of nickel, 0.03 to 0.08% by weight of bismuth, less than 0.5% by weight of silver, less than 0.010% by weight of phosphorus, and the balance of tin can be formed into a solder chip where the solder chip can be used in electronic assembly.

25 The lead-free solder composition of the present invention containing 0.2 to 0.9% by weight of copper, 0.006 to 0.07% by weight of nickel, 0.03 to 0.08% by

weight of bismuth, less than 0.5% by weight of silver, less than 0.010% by weight of phosphorus, and the balance of tin can be formed into a solder ribbon where the solder ribbon can be used in electronic assembly.

The lead-free solder composition of the present invention containing 0.2 to
5 0.9% by weight of copper, 0.006 to 0.07% by weight of nickel, 0.03 to 0.08% by weight of bismuth, less than 0.5% by weight of silver, less than 0.010% by weight of phosphorus, and the balance of tin can be formed into a solder powder where the solder powder can be used in electronic assembly.

The lead-free solder composition of the present invention containing 0.2 to
10 0.9% by weight of copper, 0.006 to 0.07% by weight of nickel, 0.03 to 0.08% by weight of bismuth, less than 0.5% by weight of silver, less than 0.010% by weight of phosphorus, and the balance of tin can be employed in hot air leveling of printed circuit boards.

The lead-free solder composition of the present invention containing 0.2 to
15 0.9% by weight of copper, 0.006 to 0.07% by weight of nickel, 0.03 to 0.08% by weight of bismuth, less than 0.5% by weight of silver, less than 0.010% by weight of phosphorus, and the balance of tin can be employed in assembling surface mounted printed circuit boards.

The lead-free solder composition of the present invention containing 0.2 to
20 0.9% by weight of copper, 0.006 to 0.07% by weight of nickel, 0.03 to 0.08% by weight of bismuth, less than 0.5% by weight of silver, less than 0.010% by weight of phosphorus, and the balance of tin can be employed in the solder coating of printed circuit boards.

The lead-free solder composition of the present invention containing 0.2 to
25 0.9% by weight of copper, 0.006 to 0.07% by weight of nickel, 0.03 to 0.08% by

weight of bismuth, less than 0.5% by weight of silver, less than 0.010% by weight of phosphorus, and the balance of tin can be employed in roll tinning of circuit boards.

The lead-free solder composition of the present invention containing 0.2 to 0.9% by weight of copper, 0.006 to 0.07% by weight of nickel, 0.03 to 0.08% by weight of bismuth, less than 0.5% by weight of silver, less than 0.010% by weight of phosphorus, and the balance of tin can be employed in surface mount assembly of electronic components onto a printed circuit board.

The lead-free solder composition of the present invention containing 0.2 to 0.9% by weight of copper, 0.006 to 0.07% by weight of nickel, 0.03 to 0.08% by weight of bismuth, less than 0.5% by weight of silver, less than 0.010% by weight of phosphorus, and the balance of tin can be formed into a solder preform where the solder preform can be used in electronic assembly. The solder preform can be fluxed or unfluxed.

Another feature of the present invention is to provide a solder paste composition comprising a powder containing 0.2 to 0.9% by weight of copper, 0.006 to 0.07% by weight of nickel, 0.03 to 0.08% by weight of bismuth, less than 0.5% by weight of silver, less than 0.010% by weight of phosphorus, and the balance of tin; a rosin-based resin; an activating agent, and a solvent.

Yet another feature of the present invention is to provide a soldered article comprising a workpiece containing a transition metal conductor capable of readily diffusing into melted tin; and a lead-free solder composition containing 0.2 to 0.9% by weight of copper, 0.006 to 0.07% by weight of nickel, 0.03 to 0.08% by weight of bismuth, less than 0.5% by weight of silver, less than 0.010% by weight of phosphorus, and the balance of tin. The lead-free solder composition is bonded to the workpiece so as to be electrically and mechanically bonded to the transition metal

conductor. The transition metal conductor is selected from the group consisting of copper, silver, nickel, gold, palladium, platinum, zinc and an alloy thereof.

Still yet another feature of the present invention is to provide a lead-free solder composition containing copper, nickel, bismuth, tin and inevitable impurities.

5 The range of copper in the lead-free solder composition can be between 0.2 to 0.9% by weight or, in a preferred embodiment, between 0.5% and 0.7% by weight. The range of nickel in the lead-free solder composition can be between 0.006 to 0.07% by weight or, in a preferred embodiment, between 0.04% by weight and 0.06% by weight. The range of bismuth in the lead-free solder composition can be between
10 0.03 to 0.08% by weight or, in a preferred embodiment, between 0.05% by weight and 0.07% by weight. The balance of the lead-free solder composition of the present invention is of tin. In addition, silver can be added to the lead-free solder composition in an amount no greater than 0.5% by weight. In addition, phosphorus can be added to the lead-free solder composition in an amount no greater than
15 0.010% by weight.

The foregoing has outlined rather broadly the more pertinent and important features of the present invention in order that the detailed description of the invention that follows may be better understood so that the present contribution to the art can be more fully appreciated. Additional features of the invention will be described
20 hereinafter which form the subject of the claims of the invention. It should be appreciated by those skilled in the art that the conception and the specific embodiment disclosed may be readily utilized as a basis for modifying or designing other structures for carrying out the same purposes of the present invention. It should also be realized by those skilled in the art that such equivalent constructions do not
25 depart from the spirit and scope of the invention as set forth in the appended claims.

DETAILED DESCRIPTION OF THE INVENTION

The solder alloy compositions of the present invention are essentially free of potentially toxic metals including antimony, arsenic, cadmium, cobalt, gallium, mercury, and thallium. The term “essentially free” is used in the context to mean that
5 if any of these metals are present in the composition, the included concentration is so low that the expected health or environmental effects are insignificant.

According to one preferred embodiment of the present invention, the solder compositions comprise, as essential ingredients, from about 0.2% to about 0.9% by weight copper (Cu), from about 0.006% to about 0.07% by weight nickel (Ni), from
10 about 0.03% to about 0.08% by weight bismuth (Bi), less than about 0.5% by weight silver (Ag) and the balance tin (Sn), together with incidental impurities. Optionally, to reduce drossing in automatic soldering machines, phosphorus (P) may be added from about 0.001% to about 0.010%.

The alloy compositions of the present invention may be prepared by
15 techniques known in the art by melting the tin metal and then adding the remaining elements while mixing until all added elements are dissolved into the tin. The alloy compositions can then be cast into billets or continuous wire, and subsequently manufactured into ingots, bars, wire, or other predetermined shapes. Though primarily intended for use as bar or solid wire form in automatic wave or dip
20 soldering machines, the alloy compositions can also be manufactured as solid or flux cored wire solder for hand soldering.

The following formulation examples and tests performed are intended to enable those skilled in the art to apply the principles of this invention in practical embodiments, but are not intended to limit the scope of the invention.

TABLE 2
Solder Alloy Compositions (weight percentages)

Solder Sample Number	Sn	Pb	Ag	Cu	Bi	Ni	P	Melting Temp. (°C)	Time (seconds) to dissolve copper at 300°C
1	Balance	37	---	---	---	---	---	183	954.3
2	Balance	37	---	---	---	---	0.010	183	945.6
3	Balance	---	3.5	---	---	---	---	221	421.2
4	Balance	---	3.5	---	---	---	0.010	221	405.6
5	Balance	---	3.5	0.7	---	---	---	217	468.6
6	Balance	---	3.5	0.7	---	---	0.010	217	445.3
7	Balance	---	3.0	0.5	---	---	---	217-219	444.3
8	Balance	---	0.9	0.7	---	---	---	217-225	488.7
9	Balance	---	0.4	0.7	---	---	---	219-225	602.9
10	Balance	---	0.4	0.7	---	---	0.010	219-225	596.7
11	Balance	---	0.3	0.7	0.1	---	0.012	219-225	609.5
12	Balance	---	0.3	0.7	---	0.036	0.007	220-225	628.8
13	Balance	---	0.03	0.7	---	0.041	0.010	227	833.3
14	Balance	---	0.001	0.7	---	0.005	---	227	635.3
15	Balance	---	0.001	0.7	---	0.057	0.010	227	850.8
16	Balance	---	0.001	0.7	0.06	0.005	---	227	750.4
17	Balance	---	0.46	0.7	0.054	0.05	0.008	219-225	1187.9
18	Balance	---	0.1	0.7	0.054	0.05	0.008	227	1196.7
19	Balance	---	0.08	0.7	0.054	0.05	0.008	227	1205.4
20	Balance	---	0.04	0.7	0.06	0.05	0.010	227	1274.6
21	Balance	---	0.001	0.7	0.06	0.06	0.010	227	1347.5

Samples were taken from each alloy melt and submitted for analysis using a spark emission spectrograph. Individual solder alloys were cast into small ingots for testing of properties.

The eutectic composition for tin-lead solder is Sn61.9Pb38.1 weight % (Sn70.9Pb29.1 atomic %), melting at 183°C, but the convention in the solder industry is to refer to the eutectic composition as either 63/37 or Sn63Pb37 (weight %). The eutectic composition for tin-silver is Sn96.5Ag3.5 weight % (Sn96.2Ag3.8 atomic %), melting at 221°C. The eutectic composition for tin-copper is Sn99.3Cu0.7 weight % (Sn98.7Cu1.3 atomic %) melting at 227°C. The melting points of these standard industry solder alloys and the other alloys shown in Table 1 were verified by measurement with a differential scanning calorimeter (DSC).

The choice of solder compositions is very limited for use as alternative alloys to the tin-lead solders that are no longer acceptable for assembly of electronic

products. More recently, lead-free solders have been used for automated soldering, including dip, wave, and reflow soldering techniques, as well as for hand soldering applications. The commonly acceptable lead-free solders contain more than 95% tin in combination primarily with silver and/or copper. The higher tin percentage and
5 higher melting temperature of the lead-free solder alloys result in an increase in the rate of copper dissolution during soldering. Consequently, the small copper traces on a printed wiring board, small copper electrical wires, or the coatings on component terminations may completely dissolve into the solder, rendering the soldered product useless.

10 To determine the comparative rate of copper dissolution for the solder compositions listed in Table 2, each solder alloy composition was heated in a temperature controlled solder pot that maintained the temperature of the solder at $300^{\circ}\text{C} \pm 5^{\circ}\text{C}$. One end of a copper wire measuring 0.6 mm diameter and 25 mm long was suspended vertically from a holder over the solder pot. The suspended lower end
15 of the copper wire was dipped into a mildly activated rosin soldering flux, Kester #186, to a depth of 10 mm. The solder pot was raised mechanically at a speed of 2 mm/second by means of an electric elevator until 5 mm of the wire was immersed into the solder, immediately followed by starting the timer. The end of the test was determined by observing the number of seconds required for the immersed 5 mm of
20 the copper wire to dissolve into the melted solder. The test results are shown in Table 2 for each solder alloy composition.

As shown in the above Table 2, the rate of dissolution of copper into the known lead-free solder alloy compositions increases dramatically compared to the electronics industry standard tin-lead solder. Solder samples 3 to 8, containing silver
25 as the main element added to the tin, were found to dissolve copper at about two times the rate compared to tin-lead solder samples 1 and 2. This is the case even with

the addition of copper to the test compositions, as shown with samples 5 to 8. Only when the silver is reduced to less than 0.5% as in samples 9 and 10 does the rate of dissolution of copper from the substrate surface become appreciably slower. As one objective of the present invention is to reduce the cost of the solder composition, experiments continued with the very low silver content with solder compositions essentially consisting of the tin-copper eutectic base alloy.

The addition of bismuth in sample 11 results in only minimal improvement in the rate of copper dissolution. The solubility of copper in bismuth is about 0.15 weight % at 270°C and is expected to have minimal effect on the rate of copper dissolution. However, bismuth additions to tin solder alloys are known to improve the wetting ability of the solder because of the low surface tension property of bismuth.

The addition of nickel to the solder compositions without the addition of bismuth in samples 12 to 15 also shows some reduction in the rate of copper dissolution. Sample 14 is an example demonstrating the minimum nickel that has any effect. However, sample 15 with the higher amount of nickel resulted in approaching the low rate of copper dissolution experienced with the conventional tin-lead solder. Copper-nickel alloys are a metallurgical example of an isomorphous binary system in which only a single type of crystal structure is observed for all ratios of the components. Copper and nickel combine to form only a single liquid phase and a single solid phase. Therefore, copper and nickel dissolve in each other in all percentages to form a solid solution. During soldering of a copper surface with a tin-copper solder containing nickel, the tin in the solder composition will dissolve some copper at the surface of the copper substrate, and, because the nickel-copper solid solution melts above 1000°C, a nickel-copper compound is formed as a barrier on the copper to prevent additional dissolution of the copper.

As shown for solder sample 16, and especially samples 17 to 21, the combination of bismuth and nickel acts synergistically to greatly reduce the copper dissolution rate. The solubility of bismuth in tin at 25°C is about 1.2 weight %, so the bismuth addition less than 1 weight % to the tin-copper composition is not
5 expected to result in any crystallization problem as might be experienced with higher amounts of bismuth. However, the solubility of copper in bismuth is only about 0.15 weight % at 270°C, the normal wave solder temperature for soldering electronic assemblies, which allows the nickel to form the nickel-copper compound on the copper substrate surface. Bismuth additions also have the effect of reducing the
10 surface tension of the solder alloy composition.

The electronics industry bases its inspection quality standards on the appearance of solder joints. Compared to the normally bright, smooth, and shiny appearance of tin-lead solder joints, the known lead-free solders by their crystalline nature solidify with a frosty or dull surface caused by precipitation of tin-silver or tin-
15 copper intermetallics during solidification of the tin alloys. The specific gravities of these intermetallic crystals results in their rising to the surface of the solder to make the surface frosty or grainy. This visible grainy surface is also a sign that the grainy structure also may exist in the solder composition matrix, a potential mechanism for cracking of the solder joints over time with thermal cycling of the electronic
20 assembly.

For this test, a deoxidized copper coupon of dimensions 50 mm x 50 mm x 0.3 mm was prepared by polishing the copper with #1500 abrasive paper, washing the copper coupon with alcohol, and then heating the copper coupon in a furnace at 150°C for one hour. Precisely 1.0 gram of the solder sample was placed on the
25 copper coupon, and then 100 micro liters of mildly activated rosin soldering flux (Kester #186) was placed with a micropipette onto the solder sample. The copper

coupon was then placed onto a hotplate with temperature controlled at $270^{\circ}\text{C} \pm 5^{\circ}\text{C}$. When the solder melted and spread out onto the copper coupon, the coupon was removed, allowed to cool to room temperature (25°C), and the rosin flux residue removed with alcohol. The cosmetic appearance of the solidified solder is recorded in Table 3.

TABLE 3
Cosmetic Appearance of the Solidified Solder Surface

Solder Sample Number	Shine of Solder Surface		Texture of Solder Surface	
	Quality Rating	Observation	Quality Rating	Observation
1	1	Shiny, reflective	1	Smooth
2	1	Shiny, reflective	1	Smooth
3	4	Dull, 100% frosty	4	Crystalline, granular
4	4	Dull, 100% frosty	4	Crystalline, granular
5	4	Dull, 100% frosty	4	Crystalline, granular
6	4	Dull, 100% frosty	4	Crystalline, granular
7	4	Dull, 90% frosty	4	Crystalline, granular
8	3.5	Dull, 70% frosty	4	Crystalline, granular
9	3.5	Dull, 70% frosty	4	Crystalline, granular
10	3.5	Dull, 66% frosty	4	Crystalline, granular
11	3.5	Dull, 60% frosty	3.5	Crystalline, some dewetting
12	3	Dull, 50% frosty	3	Crystalline, granular
13	1	Shiny, reflective	1	Smooth
14	1.5	Shiny, reflective	2	Small rough spot
15	1	Shiny, reflective	1	Smooth
16	1.5	Shiny, reflective	2	Small rough spot
17	2	Dull, 10% frosty	2	Crystalline, granular
18	1	Shiny, reflective	1	Smooth
19	1	Shiny, reflective	1	Smooth
20	1	Shiny, reflective	1	Smooth
21	1	Shiny, reflective	1	Smooth

The quality ratings in Table 3 are based on the overall shine and texture of the solder surface. The shine varies from completely reflective which is a rating of 1, down to completely dull or frosty which is a rating of 4. The amount of frosty or dull appearance of the solder surface becomes a spot or spots of increasing size as the rating goes from 1 to 4. The solder with the best rating of 1 is equivalent in shininess and smoothness to that experienced with the standard tin-lead solder Sn63Pb37. A rating of 4 is completely frosty or grainy looking and not acceptable for quality

inspection and reliability. The texture column rating is the observed appearance of the frosty area.

During the formation of the solder joint on copper substrate surfaces, the tin in the solder composition will dissolve some copper from the surface. The tin in the solder can readily dissolve copper with the formation of a low-melting temperature (221°C) tin-copper eutectic composition. The microstructure consists of the copper-tin intermetallic compound Cu_6Sn_5 needles contained along the grain boundaries of the solidified tin. The solid solubility of copper in tin at the solidification point 227°C is very low (about 0.006 weight %).

When soldering with tin-lead solder (samples 1, 2), as the copper tin intermetallic Cu_6Sn_5 forms between the solder and the copper surface, the residual lead (Pb) in the solder composition forms a barrier to prevent further copper dissolution by the tin. Most electronic circuitry and component termination metallization is designed with copper dissolution considerations. However, as printed wiring circuitry becomes more fine-lined or when very small copper wires are being soldered, the dissolution of the copper becomes more problematic.

When soldering with lead-free solders, such as tin-silver solder compositions (samples 3, 4), the combination of the higher melting point of the solder alloy and much higher tin content compared to that of the tin-lead compositions, results in much more rapid dissolution of the copper surface. Upon solidification of the tin-silver solder, the silver is present as tin-silver intermetallic platelets Ag_3Sn contained in the tin matrix. Reducing the amount of silver improves the appearance of the solidified solder. There is no residual metal barrier formed, as with tin-lead solders, so copper continues to dissolve into the solder, and will also migrate under solid state diffusion after the solder solidifies, resulting in brittle, failed solder joints.

Adding copper to the tin-silver alloys (samples 5, 6, 7) reduces the melting point and slightly reduces the rate of dissolution of the copper surface being soldered. Additionally, reducing the silver content (samples 8, 9, 10) results in further reduction in the rate of copper dissolution from the substrate. The addition of bismuth (sample 11) has little improved effect on the rate of copper dissolution, but the addition of nickel (samples 12, 13, 14, 15), even in small amounts, reduces the rate of copper dissolution.

In addition to the nickel participating in the reduction of the dissolution of the copper substrate, the remaining nickel contained in the solder composition will solidify in the tin matrix with intermetallic compound Ni_3Sn containing some copper in a solid solution. The tin-nickel-copper compound precipitates along the grain boundaries in the tin crystals, thereby reducing the size and subsequent growth of the tin-copper crystals.

Sample 16 exhibits the effect of adding a small amount of bismuth to the sample 14 with the result being a significant reduction in the rate of copper dissolution, but not as good as sample 15 with the larger amount of nickel content. Adding bismuth or nickel to the solder compositions containing 0.3 weight % silver slightly improves the appearance (samples 11 to 15), and the combined addition of bismuth and nickel (samples 16 to 21) further improves the appearance.

A further observation during this melting test is that the additions of bismuth and nickel to the primarily tin-copper compositions had very little affect, if any, on the wetting or spreading properties of the solder compositions on the copper substrate. All of the test samples wet out and spread on the copper test coupon, indicating the low copper dissolution rate of the solder composition of the present invention does not affect the soldering ability of the alloy.

Phosphorus content in solder compositions up to 0.010 weight % (100 parts per million) is known to reduce drossing (oxide formation) on the surface of the solder in automated wave or dip soldering machines, but over 0.010 weight % is known to cause dewetting (pulling back of the solder) on the copper surface, as
5 experienced with sample 11. Phosphorus content in tin-lead or tin-copper solder compositions only slightly increases the rate of dissolution of the copper substrate without affecting the wetting properties of the solder or the appearance of the solder joint. Phosphorus content in alloys containing more than about 0.3 weight % silver causes a slight increase in the rate of dissolution of the copper substrate.

10 The most remarkable discovery was the synergistic effect of adding both bismuth and nickel to the tin-copper alloy to reduce the rate of dissolution of the copper surface by more than half, while also improving the cosmetic appearance of the solder joints. There is also a significant reduction in the copper dissolution by the solder compositions of the present invention compared with the conventional tin-lead
15 solder alloy. Additionally, as the weight percentage of silver is reduced from about 0.5% to about 0.001%, the reduction in the rate of copper dissolution is further improved.

The present disclosure includes that contained in the appended claims, as well as that of the foregoing description. Although this invention has been described in its
20 preferred form with a certain degree of particularity, it is understood that the present disclosure of the preferred form has been made only by way of example and that numerous changes in the details of construction and the combination and arrangement of parts may be resorted to without departing from the spirit and scope of the invention.

25 Now that the invention has been described,

What is claimed:

1. A lead-free solder composition containing 0.2 to 0.9% by weight of copper, 0.006 to 0.07% by weight of nickel, 0.03 to 0.08% by weight of bismuth, less
5 than 0.5% by weight of silver, less than 0.010% by weight of phosphorus, and the balance of tin.

2. The lead-free solder composition according to Claim 1, wherein the copper content falls within a range of between 0.5% by weight and 0.7% by weight.
10

3. The lead-free solder composition according to Claim 1, wherein the nickel content falls within a range of between 0.04% by weight and 0.06% by weight.

4. The lead-free solder composition according to Claim 1, wherein the bismuth content falls within a range of between 0.05% by weight and 0.07% by weight.
15

5. A lead-free solder composition containing 0.2 to 0.9% by weight of copper, 0.006 to 0.07% by weight of nickel, 0.03 to 0.08% by weight of bismuth, and
20 the balance of tin.

6. The lead-free solder composition according to Claim 5, further containing silver in an amount not larger than 0.5% by weight.

7. The lead-free solder composition according to Claim 5, further containing phosphorus in an amount not larger than 0.010% by weight.
25

8. The lead-free solder composition according to Claim 5, wherein the copper content falls within a range of between 0.5% by weight and 0.7% by weight.

5 9. The lead-free solder composition according to Claim 5, wherein the nickel content falls within a range of between 0.04% by weight and 0.06% by weight.

10 10. The lead-free solder composition according to Claim 5, wherein the bismuth content falls within a range of between 0.05% by weight and 0.07% by weight.