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(54) Title: CONDUCTIVE PASTE COMPRISING COPPER PARTICLES AND USE THEREOF TO PRODUCE ELECTRONIC COMPONENTS

(57) Abstract: Provided herein is a conductive paste comprising copper particles, glass frit, and an organic vehicle. The conductive paste is useful as a precursor to electronic components, such as dielectric filters. Further provided herein is a method of manufacture for electronic components, such as dielectric filters.

Title of the Invention

CONDUCTIVE PASTE COMPRISING COPPER PARTICLES AND USE THEREOF TO PRODUCE ELECTRONIC COMPONENTS

Field of Invention

The present invention relates to the field of electronic components, particularly to electrodes deposited on a substrate and components manufactured with such electrodes, such as dielectric filters.

Background of the Invention

Several patents and publications are cited in this description in order to more fully describe the state of the art to which this invention pertains. The entire disclosure of each of these patents and publications is incorporated by reference herein.

Radio waves with a variety of frequencies are used in communication systems. Depending on the application, a specific range of frequencies is allocated.

Band filters select a range of frequencies for which they are designed, and reject non-selected frequencies. Several types of filter are known, including metal cavity filters and dielectric filters. Dielectric filters have the advantage of permitting downsizing and weight saving, high reliability and relatively low cost of manufacture.

A need exists for dielectric filters made a with a variety of materials, giving flexibility of manufacture and possibly cost reduction.

Summary of the Invention

In a first aspect, the invention provides a conductive paste, wherein the conductive paste comprises: (i) Cu powder having a D_{50} from 0.8 to 2.6 μm, (ii) glass frit, and (iii) an organic vehicle.

In a second aspect, the invention provides a method of manufacturing an electronic component, comprising the steps of: (a) preparing a ceramic substrate; (b) applying a conductive paste on the ceramic substrate, wherein the conductive paste comprises, (i) Cu powder having a D_{50} from 0.8 to 2.6 μm, (ii) glass frit, and (iii) an organic vehicle; and (c) firing the ceramic substrate and the applied conductive paste.

Detailed Description of the Invention

The inventors have surprisingly found that conductive pastes made with copper particles having a D_{50} from 0.8 to 2.6 μm give good results when sintered onto a ceramic substrate, particularly as measured by quality factor.

In one embodiment, the invention provides a conductive paste, wherein the conductive paste comprises: (i) Cu powder having a D_{50} from 0.8 to 2.6 μm, (ii) glass frit, and (iii) an organic vehicle. The sum of the weight percentages of the copper powder, the glass frit, and the organic vehicle is 100 wt%, based on the total weight of the conductive paste.

Copper powder

The copper powder is preferably a pure copper powder. Also suitable are copper powders that are wholly or partially coated by organic materials, and copper powders that are wholly or partially coated by oxidized copper. The pure copper powder, whether coated, uncoated, or partially coated, preferably comprises at least 99.0 wt%, at least 99.5 wt%, at least 99.9 wt%, or at least 99.99 wt% of elemental copper.

Any copper powder is suitable for use in the invention, provided it has a D_{50} from 0.8 to 2.6 μm as measured by laser diffraction according to the method ASTM B822-20, using water as the suspending medium and calculations based on MIE theory.

In a preferred embodiment, the copper powder has a D_{50} from 0.8 to 2.5 μm, more preferably from 0.9 to 2.5 μm, more particularly preferably from 1.0 to

2.4 μm, as measured by laser diffraction, using water as the suspending medium.

In a preferred embodiment, the copper powder has an average particle size of from 1 to 2.6 μm, as measured by laser diffraction, using water as the suspending medium. The method of measuring the particle size is the same as described above to determine the D_{50} of the copper powder.

In another preferred embodiment, the copper powder has from 2.9 to 39.8% of particles having a size of less than 1 μm, as measured by laser diffraction, using water as the suspending medium.

In another preferred embodiment, the copper powder has from 36 to 98% of particles having a size of less than 2 μm, as measured by laser diffraction, using water as the suspending medium.

In a preferred embodiment, the copper powder has less than 50% of particles having a size of less than 1 μm.

In another preferred embodiment, the copper powder has greater than 32% of particles having a size of less than 2 μm.

In another preferred embodiment, the copper powder has a D_5 from 0.5 to 1.0 μm, as measured by laser diffraction, using water as the suspending medium.

In another preferred embodiment, the copper powder has a D_{10} from 0.6 to 1.2 μm, as measured by laser diffraction, using water as the suspending medium.

In another preferred embodiment, the copper powder has a D_{90} from 1.2 to 4.5 μm, preferably 1.5 to 4.3 μm, as measured by laser diffraction, using water as the suspending medium.

In another preferred embodiment, the copper powder has a D_{95} from 1.5 to 5.5 µm, preferably 1.7 to 5.1 µm, as measured by laser diffraction, using water as the suspending medium.

In another preferred embodiment, the copper powder has an average particle size of from 1.0 to 2.6 µm.

In a particularly preferred embodiment, the copper powder has a D_{50} from 0.8 to 2.6 µm as measured by laser diffraction, using water as the suspending medium and less than 50 % of particles having a size of less than 1 µm.

In another particularly preferred embodiment, the copper powder has a D_{50} from 0.8 to 2.6 µm as measured by laser diffraction, using water as the suspending medium and greater than 32 % of particles having a size of less than 2 µm.

In another particularly preferred embodiment, the copper powder has a D_{50} from 0.8 to 2.6 µm as measured by laser diffraction, using water as the suspending medium, less than 50 % of particles having a size of less than 1 µm, and greater than 32 % of particles having a size of less than 2 µm.

In a particularly preferred embodiment, the copper powder has a D_{50} from 0.8 to 2.6 µm and a D_{90} from 1.2 to 4.5 µm, as measured by laser diffraction, using water as the suspending medium.

In another preferred embodiment, the copper powder has a D_5 of 0.5 to 1.0 µm and a D_{50} of from 1.0 to 2.4 µm, as measured by laser diffraction, using water as the suspending medium.

In another preferred embodiment, the copper powder has a D_{10} of 0.6 to 1.2 µm and a D_{50} of from 1.0 to 2.4 µm, as measured by laser diffraction, using water as the suspending medium.

In another preferred embodiment, the copper powder has a D_{90} of 1.5 to 4.3 μm and a D_{50} of from 1.0 to 2.4 μm, as measured by laser diffraction, using water as the suspending medium.

In another preferred embodiment, the copper powder has a D_{95} of 1.7 to 5.1 μm and a D_{50} of from 1.0 to 2.4 μm, as measured by laser diffraction, using water as the suspending medium.

In another preferred embodiment, the copper powder has a D_5 of 0.5 to 1.0 μm, a D_{10} of 0.6 to 1.2 μm and a D_{50} of from 1.0 to 2.4 μm, a D_{90} of 1.5 to 4.3 μm, a D_{95} of 1.7 to 5.1 μm and a D_{50} of from 1.0 to 2.4 μm, as measured by laser diffraction, using water as the suspending medium.

The copper powder particles are not particularly limited in shape, although spherical particles are preferred. By spherical is meant particles that appear generally isometric (i.e. having approximately the same dimensions in any axis) under a scanning electron microscope at 400- to 5500X magnification, preferably at 5000X magnification. Preferably the particles also have an aspect ratio of 1 to 1.2, more preferably 1 to 1.1.

The specific surface area (SA) of the copper powder is preferably 0.1 to 8.0 m^2/g, more preferably 0.3 to 4.0 m^2/g, particularly preferably 0.5 to 2.0 m^2/g. The specific surface area can be measured by a BET method such as ASTM B922-22 with a device such as Monosorb™ from Quantachrome Instruments Corporation.

If the copper particle size is too small, cracks are prone to occur due to sintering occurring too quickly during the firing process. If the cracks are severe enough, the sintered copper film may peel off, or its conductivity may be substantially decreased. If the copper particle size is too large, the sintering may not occur to a sufficient degree for the sintered copper film to attain adequate conductivity, or the sintered copper film may develop internal voids to an extent that interferes with its conductivity.

The copper powder is preferably used at 40 to 95 weight percent (wt%), more preferably 52 to 93 wt%, particularly preferably 65 to 92 wt%, based on the weight of the conductive paste.

Suitable copper powders are commercially available from a number of well-known suppliers.

Glass frit

The glass frit functions to increase adhesion of the sintered conductive paste to the ceramic substrate. Any glass that fulfills this function is suitable for use in the conductive paste described herein. Its chemical composition is not otherwise limited.

In one embodiment, the glass frit is produced from a metal oxide selected from the group consisting of bismuth oxide (Bi_2O_3), boron oxide (B_2O_3), zinc oxide (ZnO), aluminum oxide (Al_2O_3), silicon oxide (SiO_2) and mixtures of two or more thereof.

In another embodiment, the glass frit is a Si -B -Zn glass, a Bi -B -Zn glass, or a mixture thereof.

In one embodiment, no lead (Pb) or lead oxide is intentionally added to the glass frit. In another embodiment, the glass frit comprises less than 100 ppm, less than 50 ppm, less than 5 ppm, or less than 1 ppm of lead.

The softening point of the glass frit is preferably at least about 350°C, 400°C, 450°C, 500°C, or 550°C. In addition, the softening point of the glass frit is preferably no greater than about 900°C, 875°C, 850°C, 750°C, or 700°C. In some preferred embodiments, the softening point of the glass frit is about 524°C.

In a preferred embodiment, the glass frit is prepared from a mixture comprising SiO_2, B_2O_3, Al_2O_3, Bi_2O_3, CaO and ZnO.

In a particularly preferred embodiment, the glass frit is prepared from a mixture comprising 5 to 9 wt% SiO_2, 5 to 12 wt% B_2O_3, 1 to 3 wt% Al_2O_3, 65 to 75 wt% Bi_2O_3, 0.1 to 1 wt% CaO and 8 to 16 wt% ZnO, based on the total weight of the glass frit. In a more preferred embodiment, the glass frit is prepared from a mixture comprising 7.1 wt% SiO_2, 8.4 wt% B_2O_3, 2.1 wt% Al_2O_3, 69.8 wt% Bi_2O_3, 0.5 wt% CaO and 12.0 wt% ZnO, based on the total weight of the glass frit. The sum of the weight percentages of the components from which the glass frit is produced is 100 wt%.

The particle diameter (D_{50}) of the glass frit is preferably 0.1 to 15 μm, more preferably 0.5 to 11 μm, more particularly preferably 1.0 to 6.8 μm, and 1.5 to 4.5 μm in another embodiment. The particle diameter (D_{50}) can be measured by laser scattering method, for example with Microtrac model S-3500, with water as suspending medium. The method of measuring the particle size is the same as described above to determine the D_{50} of the copper powder.

The glass frit is preferably used in the conductive paste at a level of 0.5 to 2 wt%, more preferably at 0.7 to 1.8 wt%, particularly preferably at 0.8 to 1.5 wt%, based on the total weight of the conductive paste.

Suitable glass frits may be prepared by methods that are well-known in the art, for example the methods described in U.S. Patent No. 5,439,852, issued to Jacob Hormadaly. Some, but not all, of the glass frits described herein may be commercially available from well-known suppliers.

Organic vehicle

The conductive powder and the glass frit are dispersed in an organic vehicle to form a conductive paste. Preferably, the conductive paste has a suitable viscosity for application to a substrate by conventional means such as, for example, screen-printing, spraying or dipping.

The organic vehicle preferably comprises an organic polymer and a solvent, or at least one organic polymer and at least one organic solvent. In certain

embodiments, the organic polymer(s) can be selected from the group consisting of ethyl cellulose, ethylhydroxyethyl cellulose, wood rosin, phenolic resin, polymethacrylate of a lower (C_{1-6}) alcohol, and mixtures of two or more thereof.

The organic polymer(s) are preferably used at a level of 0.1 to 50 wt%, 0.5 to 42 wt%, 1 to 35 wt%, 2 to 27 wt%, and particularly preferably 3 to 15 wt%, based on the weight of the organic vehicle.

The solvent(s) are preferably selected from the group consisting of texanol (2,2,4-trimethyl-1,3-pentanediol monoisobutyrate), ester alcohol, terpineol, kerosene, dibutylphthalate, butyl carbitol, butyl carbitol acetate, dibutyl carbitol, hexylene glycol, dibasic ester, and mixtures of two or more thereof. The solvent(s) are chosen so that the organic polymer(s) are readily soluble therein.

The solvent(s) are used at a level of 50 to 99.9 wt%, 48 to 99.5 wt%, 65 to 99 wt%, 73 to 98 wt%, preferably 75 to 95 wt%, more preferably 80 to 93 wt%, more particularly preferably at 85 to 93 or 97 wt%, based on the weight of the organic vehicle.

In a preferred embodiment, the organic vehicle comprises a mixture of ethyl cellulose and texanol. Particularly preferably the organic vehicle comprises 3 to 15 wt% ethyl cellulose and 85 to 93 or 97 wt% texanol, based on the weight of the organic vehicle.

The organic vehicle may optionally comprise an organic additive. The organic additive can be one or more of a thickener, stabilizer, viscosity modifier, surfactant and thixotropic agent in an embodiment. The amount of the organic additive(s) depends on the desired characteristics of the resulting electrically conductive paste.

When present, the optional organic additives(s) are preferably used at a level of up to 25 wt%, up to 10 wt%, up to 5 wt%, up to 2 wt%, or up to 1 wt%,

based on the total weight of the organic vehicle. The sum of the weight percentages of the organic polymer, the solvent, and the optional organic additive(s), if present, is 100 wt%, based on the total weight of the organic vehicle.

The organic vehicle preferably is used at a level of 5 to 30 wt%, more preferably 6 to 15 wt%, particularly preferably 7 to 10 wt%, based on the weight of the conductive paste.

Other Components

The conductive pastes may further comprise one or more other components. Materials suitable for use as other components and suitable amounts of the other components are described in U.S. Patent No. 11,228,080, issued to Yusuke Tachibana. Briefly, the other components include organic materials and inorganic additives. Preferred organic materials include, without limitation, thickeners, stabilizers, viscosity modifiers, surfactants, and thixotropic agents. Preferred inorganic additives include, without limitation, metal oxides selected from the group consisting of copper oxide (CuO, Cu2O), iron oxide (FeO, Fe2O3), zinc oxide (ZnO), titanium oxide (TiO2), lithium ruthenate oxide (Li2RuO3), and combinations of two or more of these oxides. Also preferably, the metal oxide(s) are powders having a D50 of 0.1 to 10 um.

Method of manufacture of the conductive paste

The conductive pastes of the invention are manufactured by dispersing the copper powder, the glass frit, and the other component(s), if present, in the organic vehicle in a mixer, such as a dispersator, and homogenizing the mixture, for example using a three-roll mill.

Electronic component and method of manufacture

The invention also provides a method of manufacturing an electronic component, comprising the steps of: (a) preparing a ceramic substrate; (b) applying a conductive paste on the ceramic substrate, wherein the conductive paste comprises (i) copper powder having a D_{50} from 0.8 to 2.6 μm, (ii) glass

frit, and (iii) an organic vehicle; and (c) firing the ceramic with the applied conductive paste.

The ceramic substrate preferably has a dielectric constant, ε_Y, of 9 to 50, more preferably 15 to 45, particularly preferably 20 to 40. The dielectric constant of the ceramic substrate can be measured by a known method, for example by the method of ASTM Standard D2520(2013) at 5 GHz. Such ceramic substrates are suitable, for example, for ceramic filters used in the radio frequency range. More specifically, such ceramic substrates are suitable for use in the range of 1 GHz to 10 GHz.

Preferred ceramic substrates include those made with certain metal oxide components.

Metal components of the ceramic substrate are, for example, selected from the group consisting of Al, Ba, Ca, La, Mg, Mn, Nb, Nd, Ni, Pb, Sm, Sn, Sr, Ta, Ti, Zn, Zr, and mixtures of two or more thereof. In some embodiments, the ceramic substrate comprises at least 60 mol %, at least 70 mol %, at least 80 mol %, at least 90 mol %, at least 95 mol%, or 100 mol % of one or more metal components selected from this group. In an embodiment, other metal(s) are included in the metal component of the ceramic substrate.

The ceramic substrate is not particularly limited, and may be selected from, for example, Al_2O_3, $BaTi_4O_9$, $Ba_2Ti_9O_{20}$, $BaSnO_3$, $BaMgO_3$, $BaTaO_3$, $BaZrO_3$, $Ba(ZrTi)O_3$, $Ba(NiTa)O_3$, $Ba(ZrZnTa)O_3$, $Ba(Mg_{1/3}Ta_{2/3})O_3$, $Ba(Mg_{1/3}Nb_{2/3})O_3$, $Ba(Zn_{1/3}Ta_{2/3})O_3$, $Ba(Zn_{1/3}Nb_{2/3})O_3$, $Ba(Mn_{1/3}Ta_{2/3})O_3$, $CaTiO_3$, $(CaSrBa)ZrO_3$, $MgTiO_3$, $(Mg_{0.95}Ca_{0.05})TiO_3$, $SrZrO_3$, $Sr(Zn_{1/3}Nb_{2/3})O_3$, $Sr(Zn_{1/3}Ta_{2/3})O_3$, $ZrTiO_2$, $(Zr_{0.8}Sn_{0.2})TiO_4$, and mixtures of two or more thereof. In a preferred embodiment, the ceramic substrate is selected from the group consisting of Al_2O_3, $MgTiO_3$, $(Mg_{0.95}Ca_{0.05})TiO_3$, $Ba(Mg_{1/3}Ta_{2/3})O_3$, $BaTi_4O_9$, $Ba_2Ti_9O_{20}$, $Ba(Zn_{1/3}Ta_{2/3})O_3$ and $Ba(Zn_{1/3}Nb_{2/3})O_3$, $(Zr_{0.8}Sn_{0.2})TiO_4$.

The ceramic substrate may be surface treated. For example, it may be smoothed or roughened. A primer layer may also be used. A primer layer may be formed, for example, by chemical vapor deposition or by plating.

The conductive paste of the invention is applied on the ceramic substrate. The conductive paste may be applied, for example, by screen-printing, spraying or dipping. The conductive paste is applied by screen-printing in another embodiment.

The conductive paste may be applied on the entire surface of the ceramic substrate, or on a portion of the surface.

The conductive paste viscosity can be adjusted to be suitable for the applying method chosen. Suitable methods for adjusting the viscosity include adjusting the amount of organic vehicle in the conductive paste, adjusting the ratio of solvent and organic polymer in the organic vehicle, adjusting the molecular weight of the organic polymer, selecting a different organic polymer, or selecting a different solvent. Two or more of these methods may be used in combination.

For application by printing, the preferred viscosity range is from 200 to 450 Pa·s. For application by dipping, the viscosity is preferably in the range of 4 to 10 Pa·s. For application by spraying the preferred viscosity range is 0.5 to 4 Pa·s.

Preferably, the viscosity of the conductive paste is from 0.5 to 450 Pa·s, 1 to 400 Pa·s in another embodiment, 5 to 350 Pa·s in another embodiment, 10 to 300 Pa·s in another embodiment, as measured by Brookfield HBT with a spindle SC4-14 at 10 rpm, RVT with a spindle SC4-14 at 10 rpm or LVT with a spindle SC4-14 at 10 rpm.

The conductive paste is typically applied at 5 to 40 μm thick in an embodiment, 7 to 30 μm thick in another embodiment, 10 to 20 μm thick in another embodiment, or 7 to 16 μm in another embodiment. If the thickness is

significantly less than 5 μm the quality factor drops. If the thickness is significantly more than 40 μm peeling may be a problem.

The conductive paste may optionally be dried after application to the ceramic substrate and before the firing step. Typical drying conditions are 50 to 250°C, or 100 to 150°C for 3 to 30 minutes. Drying serves to remove volatile elements and improves the conductive layer. Firing without drying can lead to blistering or the formation of voids.

The ceramic substrate with the applied conductive paste is fired to sinter the paste on the substrate. This process produces the electronic component. During the firing process, the glass frit softens gradually with increasing the temperature and eventually flows. In parallel, the glass frit helps to sinter copper powder during the process, so that an electrically conductive layer is formed. Furthermore, the melted glass reacts with the ceramic substrate. Thus, a glass layer is formed between the ceramic substrate and the copper metal rich upper layer of the sintered conductive paste.

The firing peak temperature is preferably 600 to 1100°C, 650 to 1050°C in another embodiment, 800 to 1000°C in another embodiment. Firing time at the peak temperature is preferably 3 to 30 minutes, 5 to 20 minutes, or 7 to 15 minutes. Firing is preferably carried out under oxygen-poor conditions, for example, under a blanket of nitrogen or argon, or under vacuum.

The electronic component is used, for example, in the radio frequency range. More specifically, the electronic component is suitable for filters used in 1 GHz to 10 GHz. In a preferred embodiment, the electronic component is a dielectric filter.

When the ceramic substrate is Al_2O_3, and the quality factor is measured at 2.7 GHz according to the method used in the Examples, the quality factor is preferably greater than 2,550, more preferably greater than 2,600, more particularly preferably greater than 2,750, or greater than 2,800.

When the ceramic substrate is $Mg_{0.95}Ca_{0.05}TiO_3$, and the quality factor is measured at 2.6 GHz according to the method used in the Examples, the quality factor is preferably greater than 2,200, more preferably greater than 2,300.

Particularly preferred embodiments

1. A conductive paste, wherein the conductive paste comprises: (i) Cu powder having a D_{50} from 0.8 to 2.6 μm, (ii) glass frit, and (iii) an organic vehicle.
2. A method of manufacturing an electronic component, comprising the steps of: (a) preparing a ceramic substrate; (b) applying a conductive paste on the ceramic substrate, wherein the conductive paste comprises, (i) Cu powder having a D_{50} from 0.8 to 2.6 μm, (ii) glass frit, and (iii) an organic vehicle; and (c) firing the applied conductive paste.
3. Embodiment 1 or 2, wherein the copper powder has less than 50 % of particles having a size of less than 1 μm.
4. Embodiment 1, 2 or 3, wherein the copper powder has greater than 32 % of particles having a size of less than 2 μm.
5. Any one preceding embodiment, wherein the copper powder has a D_{90} from 1.2 to 4.5 μm.
6. Any one preceding embodiment, wherein the copper powder has a D_{95} from 1.5 to 5.5 μm.
7. Any one preceding embodiment, wherein the copper powder has an average particle size of from 0.8 to 2.8 μm.
8. Any one preceding embodiment, wherein the copper powder has a D_{50} from 0.8 to 2.6 μm as measured by laser diffraction, using water as the suspending medium and less than 50 % of particles having a size of less than 1 μm.
9. Any one preceding embodiment, wherein the copper powder has a D_5 from 0.5 to 1.0 μm, as measured by laser diffraction, using water as the suspending medium.
10. Any one preceding embodiment, wherein the copper powder has a D_{10} from 0.6 to 1.2 μm, as measured by laser diffraction, using water as the suspending medium.

11. Any one preceding embodiment, wherein the copper powder has a D_{90} from 1.2 to 4.5 μm, preferably 1.5 to 4.3 μm, as measured by laser diffraction, using water as the suspending medium.
12. Any one preceding embodiment, wherein the copper powder has a D_{95} from 1.5 to 5.5 μm, preferably 1.7 to 5.1 μm, as measured by laser diffraction, using water as the suspending medium.
9. Any one preceding embodiment, wherein the copper powder has a D_5 of 0.5 to 1.0 μm and a D_{50} of from 1.0 to 2.4 μm, as measured by laser diffraction, using water as the suspending medium.
10. Any one preceding embodiment, wherein the copper powder has a D_{10} of 0.6 to 1.2 μm and a D_{50} of from 1.0 to 2.4 μm, as measured by laser diffraction, using water as the suspending medium.
11. Any one preceding embodiment, wherein the copper powder has a D_{90} of 1.5 to 4.3 μm and a D_{50} of from 1.0 to 2.4 μm, as measured by laser diffraction, using water as the suspending medium.
12. Any one preceding embodiment, wherein the copper powder has a D_{95} of 1.7 to 5.1 μm and a D_{50} of from 1.0 to 2.4 μm, as measured by laser diffraction, using water as the suspending medium.
13. Any one preceding embodiment, wherein the copper powder has a D_5 of 0.5 to 1.0 μm, a D_{10} of 0.6 to 1.2 μm and a D_{50} of from 1.0 to 2.4 μm, a D_{90} of 1.5 to 4.3 μm, a D_{95} of 1.7 to 5.1 μm and a D_{50} of from 1.0 to 2.4 μm, as measured by laser diffraction, using water as the suspending medium.
14. Any one preceding embodiment, wherein the copper powder has spherical particles.
15. Any one preceding embodiment, wherein the copper particles have an aspect ratio of 1 to 1.2, preferably 1 to 1.1.
16. Any one preceding embodiment, wherein the specific surface area of the copper powder is 0.1 to 8.0 m^2/g, more preferably 0.3 to 4.0 m^2/g, particularly preferably 0.5 to 2.0 m^2/g.
17. Any one preceding embodiment, wherein the copper powder is used at 40 to 95 weight percent (wt%), more preferably 52 to 93 wt%, particularly preferably 65 to 92 wt%, based on the weight of the conductive paste.

18. Any one preceding embodiment, wherein the glass frit comprises a metal oxide selected from the group consisting of bismuth oxide (Bi_2O_3), boron oxide (B_2O_3), zinc oxide (ZnO), aluminum oxide (Al_2O_3), silicon oxide (SiO_2) and mixtures thereof.
19. Any one preceding embodiment, wherein the glass frit is a Si -B -Zn glass, a Bi -B -Zn glass or a mixture thereof.
20. Any one preceding embodiment, wherein the glass frit is lead-free.
21. Any one preceding embodiment, wherein the glass frit has a softening point of at least about 350°C, 400°C, 450°C, 500°C, or 550°C. In addition, the softening point of the glass frit is preferably no greater than about 900°C, 875°C, 850°C, 750°C, or 700°C. In some preferred embodiments, the softening point of the glass frit is about 524°C.
22. Any one preceding embodiment, wherein the glass frit comprises SiO_2, B_2O_3, Al_2O_3, Bi_2O_3, CaO and ZnO.
23. Any one preceding embodiment wherein the glass frit comprises 5 to9 wt% SiO_2, 5 to 12 wt% B_2O_3, 1 to 3 wt% Al_2O_3, 65 to 75 wt% Bi_2O_3, 0.1 to 1 wt% CaO and 8 to 16 wt% ZnO.
24. Any one preceding embodiment, wherein the glass frit comprises 7.1 wt% SiO_2, 8.4 wt% B_2O_3, 2.1 wt% Al_2O_3, 69.8 wt% Bi_2O_3, 0.5 wt% CaO and 12.0 wt% ZnO. The glass frit has a softening point of 524°C.
28. Any one preceding embodiment, wherein the particle diameter (D_{50}) of the glass frit is 0.1 to 15 μm, more preferably 0.5 to 11 μm, more particularly preferably 1.0 to 6.8 μm, and 1.5 to 4.5 μm.
29. Any one preceding embodiment, wherein the glass frit is used in the conductive paste at 0.5 to 2 wt%, more preferably at 0.7 to 1.8 wt%, particularly preferably at 0.8 to 1.5 wt%, based on the total weight of the conductive paste.
30. Any one preceding embodiment, wherein the organic vehicle comprises an organic polymer selected from the group consisting of ethyl cellulose, ethylhydroxyethyl cellulose, wood rosin, phenolic resin, polymethacrylate of a lower (C_{1-6}) alcohol, and mixtures thereof.

31. Embodiment 30, wherein the organic polymer is preferably used at 0.1 to 50 wt%, 0.5 to 42 wt%, 1 to 35 wt%, 2 to 27 wt%, and particularly preferably 3 to 15 wt% based on the weight of the organic vehicle.
32. Any one preceding embodiment, wherein the organic vehicle comprises a solvent selected from the group consisting of texanol (2,2,4-Trimethyl-1,3-pentanediol monoisobutyrate), ester alcohol, terpineol, kerosene, dibutylphthalate, butyl carbitol, butyl carbitol acetate, dibutyl carbitol, hexylene glycol, dibasic ester, and mixtures thereof.
33. Embodiment 32, wherein the solvent is used at 75 to 95 wt%, more preferably 80 to 93 wt%, more particularly preferably at 85 to 93 wt%, based on the weight of the organic vehicle.
34. Any one preceding embodiment, wherein the organic vehicle comprises a mixture of ethyl cellulose and texanol.
35. Any one preceding embodiment, wherein the organic vehicle comprises 3 to 15 wt% ethyl cellulose and 85 to 93 wt% texanol, based on the weight of the organic vehicle.
36. Any one preceding embodiment, wherein the organic vehicle is used at 5 to 30 wt%, more preferably 6 to 15 wt%, particularly preferably 7 to 10 wt%, based on the weight of the conductive paste.
37. Embodiment 2, and any one preceding embodiment as it relates to Embodiment 2, wherein the ceramic substrate has a dielectric constant, ε_r, of 9 to 50, more preferably 15 to 45, particularly preferably 20 to 40.
38. Embodiment 2, and any one preceding embodiment as it relates to Embodiment 2, wherein the ceramic substrate is selected from Al_2O_3, $BaTi_4O_9$, $Ba_2Ti_9O_{20}$, $BaSnO_3$, $BaMgO_3$, $BaTaO_3$, $BaZrO_3$, $Ba(ZrTi)O_3$, $Ba(NiTa)O_3$, $Ba(ZrZnTa)O_3$, $Ba(Mg_{1/3}Ta_{2/3})O_3$, $Ba(Mg_{1/3}Nb_{2/3})O_3$, $Ba(Zn_{1/3}Ta_{2/3})O_3$, $Ba(Zn_{1/3}Nb_{2/3})O_3$, $Ba(Mn_{1/3}Ta_{2/3})O_3$, $CaTiO_3$, $(CaSrBa)ZrO_3$, $MgTiO_3$, $(Mg_{0.95}Ca_{0.05})TiO_3$, $SrZrO_3$, $Sr(Zn_{1/3}Nb_{2/3})O_3$, $Sr(Zn_{1/3}Ta_{2/3})O_3$, $ZrTiO_2$, $(Zr_{0.8}Sn_{0.2})TiO_4$, and mixtures thereof.
39. Embodiment 2, and any one preceding embodiment as it relates to Embodiment 2, wherein the ceramic substrate is selected from the group consisting of Al_2O_3, $MgTiO_3$, $(Mg_{0.95}Ca_{0.05})TiO_3$, $Ba(Mg_{1/3}Ta_{2/3})O_3$, $BaTi_4O_9$, $Ba_2Ti_9O_{20}$, $Ba(Zn_{1/3}Ta_{2/3})O_3$ and $Ba(Zn_{1/3}Nb_{2/3})O_3$, $(Zr_{0.8}Sn_{0.2})TiO_4$.

40. Embodiment 2, and any one preceding embodiment as it relates to Embodiment 2, wherein the conductive paste is applied by screen-printing, spraying or dipping.
41. Embodiment 2, and any one preceding embodiment as it relates to Embodiment 2, wherein the conductive paste is dried before the firing step.
42. Embodiment 2, and any one preceding embodiment as it relates to Embodiment 2, wherein the firing step is carried out at 600 to 1100°C, 650 to 1050°C in another embodiment, 800 to 1000°C.
43. Embodiment 2, and any one preceding embodiment as it relates to Embodiment 2, wherein the firing step is carried out under an oxygen-poor atmosphere, such as nitrogen, argon or under a vacuum.
44. Embodiment 2, and any one preceding embodiment as it relates to Embodiment 2, wherein firing is carried out for 3 to 30 minutes, 5 to 20 minutes, or 7 to 15 minutes.
45. Embodiment 2, and any one preceding embodiment as it relates to Embodiment 2, wherein the electronic component is a dielectric filter.

EXAMPLES

The following examples are provided to describe the invention in further detail. These examples, which set forth a preferred mode presently contemplated for carrying out the invention, are intended to illustrate and not to limit the invention.

100 parts by weight of Cu powder and 1.6 parts by weight of the glass frit were dispersed in 10 parts by weight of organic vehicle in a mixer and homogenized by a three-roll mill.

The particle size distributions of the various Cu powders are shown in Table 1.

The glass frit was prepared by methods described in U.S. Patent No. 5,439,852, cited above. The composition of the mixture from which the glass frit was prepared was 7.1 wt% SiO_2, 8.4 wt% B_2O_3, 2.1 wt% Al_2O_3, 69.8

wt% Bi_2O_3, 0.5 wt% CaO and 12.0 wt% ZnO. The glass frit had a softening point of 524°C.

The organic vehicle was a mixture of 6 wt% of an organic polymer, 91 wt% of a solvent and 34 wt% of organic additives based on the weight of the organic vehicle.

The paste viscosity was about 250 to 400 Pa·s measured by Brookfield HBT with a spindle SC4-14 at 10 rpm.

The conductive paste was screen printed on Al_2O_3 and $Mg_{0.95}Ca_{0.05}TiO_3$ substrates (25 mm long, 25 mm wide, 0.6 mm thick) in a ring pattern (2.5 mm wide, 10 μm thick, 80 mm round length).

Dielectric constants of the substrates were 9.6 for Al_2O_3 and 21 for $Mg_{0.95}Ca_{0.05}TiO_3$. The electrodes were formed by firing the ring pattern at peak temperature of 900°C for 10 minutes under N_2 after drying at 150°C for 10 minutes.

The results are shown in Table 2. The conductive paste comprising Cu powder with D_{50} between 0.8 and 2.6 μm show higher quality factor Q. The quality factor Q was determined according to methods that are set forth in U.S. Patent No. 11,228,080, cited above. Briefly, the ring pattern that was formed on the fired substrates was connected to a network analyzer (Keysight, E5063A). The Q value and the associated frequency were measured and recorded.

While certain of the preferred embodiments of this invention have been described and specifically exemplified above, it is not intended that the invention be limited to such embodiments. Various modifications may be made without departing from the scope and spirit of the invention, as set forth in the following claims.

Table 1. Particle size distribution of copper powders used (measured by laser diffraction, in water)

Reference	D_5 (µm)	D_{10} (µm)	D_{50} (µm)	D_{90} (µm)	D_{95} (µm)	Ave, (µm)	Percentage less than 1 µm (%)	Percentage less than 2 µm (%)
A	2.1	2.5	4.6	7.7	8.8	4.9	0.0	4
B	1.9	2.3	4.4	7.3	8.2	4.6	0.1	6
C	1.4	1.6	3.0	5.1	6.0	3.2	0.7	18
D	1.2	1.5	2.9	5.1	5.9	3.1	1.3	22
E	1.1	1.3	2.7	6.1	7.6	3.3	2.4	30
F	1.0	1.2	2.4	4.3	5.1	2.6	2.9	36
G	0.8	0.9	1.6	3.6	4.7	2.0	9.1	64
H	0.9	1.0	1.6	2.6	2.9	1.7	4.5	72
I	0.7	0.8	1.3	2.2	2.6	1.4	15.1	84
J	0.7	0.8	1.2	1.8	2.1	1.3	18.0	94
K	0.5	0.6	1.0	1.5	1.7	1.0	39.8	98
L	0.3	0.4	0.6	1.0	1.2	0.7	81.9	100

Table 2. Quality factor of pastes with different Cu powders

		CE1	CE2	CE3	CE4	CE5	E1	E2	E3	E4	E5	E6	CE7
Glass frit		1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6
Organic vehicle		10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
Cu powder	A	100											
	B		100										
	C			100									
	D				100								
	E					100							
	F						100						
	G							100					
	H								100				
	I									100			
	J										100		
	K											100	
	L												100
Quality factor on Al_2O_3 at 2.7 GHz		2409	2470	2550	2248	2408	2855	2903	2967	3277	2920	2945	2520
Qualify factor on $Mg_{0.95}Ca_{0.05}TiO_3$ at 2.6 GHz		1857	1889	2026	1638	1927	2356	2367	2719	2709	2543	2827	2132

Claims

1. A conductive paste, wherein the conductive paste comprises: (i) Cu powder having a D_{50} from 0.8 to 2.6 μm, (ii) glass frit, and (iii) an organic vehicle.
2. The paste of Claim 1, wherein the copper powder has less than 50 % of particles having a size of less than 1 μm.
3. The paste of Claim 1 or 2, wherein the copper powder has greater than 32 % of particles having a size of less than 2 μm.
4. The paste of any one preceding claim, wherein the copper powder has a D_{90} from 1.2 to 4.5 μm.
5. The paste of any one preceding claim, wherein the copper powder has a D_{95} from 1.5 to 5.5 μm.
6. The paste of any one preceding claim, wherein the copper powder has an average particle size of from 0.8 to 2.8 μm.
7. The paste of any one preceding claim, wherein the copper powder has a D_{50} from 0.8 to 2.6 μm as measured by laser diffraction, using water as the suspending medium and less than 50 % of particles having a size of less than 1 μm.
8. The paste of any one preceding claim, wherein the copper powder has spherical particles.
9. The paste of Claim 8, wherein the particles have an aspect ratio of 1 to 1.2, preferably 1 to 1.1.
10. The paste of any one preceding claim, wherein the specific surface area of the copper powder is 0.1 to 8.0 m^2/g, more preferably 0.3 to 4.0 m^2/g, particularly preferably 0.5 to 2.0 m^2/g.
11. The paste of any one preceding claim, wherein the copper powder is used at 40 to 95 weight percent (wt%), more preferably 52 to 93 wt%, particularly preferably 65 to 92 wt%, based on the weight of the conductive paste.
12. The paste of any one preceding claim, wherein the glass frit is produced from a metal oxide selected from the group consisting of bismuth oxide (Bi_2O_3), boron oxide (B_2O_3), zinc oxide (ZnO), aluminum oxide (Al_2O_3), silicon oxide (SiO_2), and mixtures of two or more thereof.

13. The paste of any one preceding claim, wherein the glass frit is a Si -B - Zn glass, a Bi -B -Zn glass or a mixture thereof.
14. The paste of any one preceding claim, wherein the glass frit is lead-free.
15. The paste of any one preceding claim, wherein the glass frit has a softening point of at least about 350°C, 400°C, 450°C, 500°C, or 550°C; and wherein the softening point of the glass frit is no greater than about 900°C, 875°C, 850°C, 750°C, or 700°C.
16. The paste of any one preceding claim, wherein the glass frit is produced from a mixture comprising SiO_2, B_2O_3, Al_2O_3, Bi_2O_3, CaO and ZnO.
17. The paste of any one preceding claim wherein the glass frit is produced from a mixture comprising 5 to 9 wt% SiO_2, 5 to 12 wt% B_2O_3, 1 to 3 wt% Al_2O_3, 65 to 75 wt% Bi_2O_3, 0.1 to 1 wt% CaO and 8 to 16 wt% ZnO.
18. The paste of any one preceding claim, wherein the glass frit comprises 7.1 wt% SiO_2, 8.4 wt% B_2O_3, 2.1 wt% Al_2O_3, 69.8 wt% Bi_2O_3, 0.5 wt% CaO and 12.0 wt% ZnO.
19. The paste of any one preceding claim, wherein the particle diameter (D_{50}) of the glass frit is 0.1 to 15 μm, more preferably 0.5 to 11 μm, more particularly preferably 1.0 to 6.8 μm, and 1.5 to 4.5 μm.
20. The paste of any one preceding claim, wherein the glass frit is used in the conductive paste at 0.5 to 2 wt%, more preferably at 0.7 to 1.8 wt%, particularly preferably at 0.8 to 1.5 wt%, based on the total weight of the conductive paste.
22. The paste of any one preceding claim, wherein the organic vehicle comprises an organic polymer selected from the group consisting of ethyl cellulose, ethylhydroxyethyl cellulose, wood rosin, phenolic resin, polymethacrylate of a lower (C_{1-6}) alcohol, and mixtures thereof.
23. The paste of Claim 22, wherein the organic polymer is preferably used at 0.1 to 50 wt%, 0.5 to 42 wt%, 1 to 35 wt%, 2 to 27 wt%, and particularly preferably 3 to 15 wt% based on the weight of the organic vehicle.

24. The paste of any one preceding claim, wherein the organic vehicle comprises a solvent selected from the group consisting of texanol (2,2,4-trimethyl-1,3-pentanediol monoisobutyrate), ester alcohol, terpineol, kerosene, dibutylphthalate, butyl carbitol, butyl carbitol acetate, dibutyl carbitol, hexylene glycol, dibasic ester, and mixtures of two or more thereof.
25. The paste of Claim 24, wherein the solvent is used at 75 to 95 wt%, more preferably 80 to 93 wt%, more particularly preferably at 85 to 93 wt%, based on the weight of the organic vehicle.
26. The paste of any one preceding claim, wherein the organic vehicle comprises a mixture of ethyl cellulose and texanol.
27. The paste of any one preceding claim, wherein the organic vehicle comprises 3 to 15 wt% ethyl cellulose and 85 to 93 wt% texanol, based on the weight of the organic vehicle.
28. The paste of any one preceding claim, wherein the organic vehicle is used at 5 to 30 wt%, more preferably 6 to 15 wt%, particularly preferably 7 to 10 wt%, based on the weight of the conductive paste.
29. A method of manufacturing an electronic component, comprising the steps of: (a) preparing a ceramic substrate; (b) applying the conductive paste of any of claims 1 to 30 on the ceramic substrate; and (c) firing the ceramic substrate with the applied conductive paste.
30. The method of claim 29, wherein the ceramic substrate has a dielectric constant, ε_Y, of 9 to 50, more preferably 15 to 45, particularly preferably 20 to 40.
31. The method of claim 29 or 30, wherein the ceramic substrate is selected from Al_2O_3, $BaTi_4O_9$, $Ba_2Ti_9O_{20}$, $BaSnO_3$, $BaMgO_3$, $BaTaO_3$, $BaZrO_3$, $Ba(ZrTi)O_3$, $Ba(NiTa)O_3$, $Ba(ZrZnTa)O_3$, $Ba(Mg_{1/3}Ta_{2/3})O_3$, $Ba(Mg_{1/3}Nb_{2/3})O_3$, $Ba(Zn_{1/3}Ta_{2/3})O_3$, $Ba(Zn_{1/3}Nb_{2/3})O_3$, $Ba(Mn_{1/3}Ta_{2/3})O_3$, $CaTiO_3$, $(CaSrBa)ZrO_3$, $MgTiO_3$, $(Mg_{0.95}Ca_{0.05})TiO_3$, $SrZrO_3$, $Sr(Zn_{1/3}Nb_{2/3})O_3$, $Sr(Zn_{1/3}Ta_{2/3})O_3$, $ZrTiO_2$, $(Zr_{0.8}Sn_{0.2})TiO_4$, and mixtures of two or more thereof.

32. The method of any one of claims 29 to 31, wherein the ceramic substrate is selected from the group consisting of Al_2O_3, $MgTiO_3$, $(Mg_{0.95}Ca_{0.05})TiO_3$, $Ba(Mg_{1/3}Ta_{2/3})O_3$, $BaTi_4O_9$, $Ba_2Ti_9O_{20}$, $Ba(Zn_{1/3}Ta_{2/3})O_3$ and $Ba(Zn_{1/3}Nb_{2/3})O_3$, $(Zr_{0.8}Sn_{0.2})TiO_4$, and mixtures of two or more thereof.
33. The method of any one of claims 29 to 32, wherein the conductive paste is applied by screen-printing, spraying or dipping.
34. The method of any one of claims 29 to 33, wherein the conductive paste is dried before the firing step.
35. The method of any one of claims 29 to 34, wherein the firing step is carried out at 600 to 1100°C, 650 to 1050°C, or 800 to 1000°C.
36. The method of any one of claims 29 to 35, wherein the firing step is carried out under an oxygen-poor atmosphere, such as nitrogen, argon or under a vacuum.
37. The method of any one of claims 29 to 36, wherein firing is carried out for 3 to 30 minutes, 5 to 20 minutes, or 7 to 15 minutes.
38. The method of any one of claims 29 to 37, wherein the electronic component is a dielectric filter.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2022/072979

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01B1/22 H05K3/12
ADD. H01P1/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01B H01P H05K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2020/144691 A1 (TACHIBANA YUSUKE [JP]) 7 May 2020 (2020-05-07) column 4, line 20 - line 44; claims 1-20; examples 1-11; tables 1-2	1-37
X	EP 2 822 000 A1 (HERAEUS PRECIOUS METALS NORTH AMERICA CONSHOHOCKEN LLC [US]) 7 January 2015 (2015-01-07)	1-18, 20-27
A	claims 1-33; example 1; tables 1-5	28-37
X	US 2013/026424 A1 (KUROKI MASAKATSU [JP]) 31 January 2013 (2013-01-31)	1-11, 20-27
Y	claims 1-6; example 1	12-19
A		28-37
Y	US 2018/240576 A1 (MURAKAMI MAMORU [JP] ET AL) 23 August 2018 (2018-08-23) paragraph [0029] - paragraph [0031]	12-19

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[x] Further documents are listed in the continuation of Box C.

[x] See patent family annex.

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"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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Date of the actual completion of the international search	Date of mailing of the international search report
22 August 2022	30/08/2022

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2022/072979

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2019/005452 A1 (HERAEUS PRECIOUS METALS NORTH AMERICA CONSHOHOCKEN LLC [US]) 3 January 2019 (2019-01-03) paragraph [0028] - paragraph [0034]; example 1; table 1	12-19
A	CN 112 289 482 A (XIAN HONGXING ELECTRONIC PASTE CO LTD) 29 January 2021 (2021-01-29) the whole document	1-37

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2022/072979

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2020144691 A1	07-05-2020	CN 111161905 A	15-05-2020
		US 2020144691 A1	07-05-2020
EP 2822000 A1	07-01-2015	NONE	
US 2013026424 A1	31-01-2013	NONE	
US 2018240576 A1	23-08-2018	CN 108470614 A	31-08-2018
		US 2018240576 A1	23-08-2018
WO 2019005452 A1	03-01-2019	EP 3645474 A1	06-05-2020
		US 2020013522 A1	09-01-2020
		WO 2019005452 A1	03-01-2019
CN 112289482 A	29-01-2021	NONE	