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IMPROVED SINTER PASTE WITH PARTIALLY OXIDISED METAL PARTICLES

10 The present invention relates to a sinterable mixture, and to a method for the connecting of components, in which said mixture is used. Moreover, the invention relates to a method for producing the sinterable mixture.

15 In power electronics, the connecting of components, such as LEDs or very thin silicon chips, comprising high pressure and temperature resistance, is particularly challenging. For this reason, said pressure- and temperature-sensitive components are often connected to each other by means of gluing. However, adhesive technology is associated with a disadvantage in that it produces contact sites between the components that comprise only insufficient heat conductivity and/or electrical conductivity. In order to solve this problem, the components to
20 be connected are often subjected to sintering. Sintering technology is a very simple method for the connecting of components in stable manner and utilises sinter pastes.

For example, US-B-7,766,218 describes the use of sinter pastes containing silver particles that are coated, at least in part, with fatty acids or fatty acid derivatives and a volatile disper-
25 sion agent for improving the sintering process and the electrical and thermal conductivity.

WO-A-2011/026624 discloses sinter pastes containing metal particles, metal precursors, solvents, and sintering aids.

30 According to EP-A-2425290, at least one aliphatic hydrocarbon compound is added to the sinter pastes in order to ensure a low sintering temperature.

However, it has been evident that continues to be a need to improve the sinterability of cus-
tomary pastes or mixtures, in particular at low process pressures, despite the use of various
35 sintering aids.

In the scope of the present invention, sinterability comprises the ability of the metal particles-
containing mixture to diffuse as well as the bonding of the contacts the mixture was used to
connect.

Moreover, there continues to be a need for sinterable mixtures that can be used in a broader temperature and pressure range than is feasible at this time. Moreover, it would be desirable to have sinterable mixtures that comprise improved diffusability and whose use under comparable conditions leads to improved bonding of the sintered contacts as compared to previously customary pastes.

The present invention is therefore based on the object to provide a sinterable mixture, in particular a sinter paste, which possesses improved sinterability, in particular when applied to a copper surface. It is another object of the present invention to provide a sinterable mixture that allows the sintering process to proceed at milder conditions, mainly at lower temperatures and lower pressures, then is allowed according to the prior art. Accordingly, the use of said mixture needs to an energy saving method for the connecting of contacts.

The object is met through the features of the independent claims of the present invention.

Accordingly, a subject matter of the present invention is a mixture containing

(a) metal particles and

(b) an organic compound represented by Formula I: R^1-COR^2 (I),

whereby R^1 is an aliphatic residue having 8 to 32 carbon atoms, and R^2 comprises either the -OM moiety or the $-X-R^3$ moiety, whereby M is a cation and whereby X is selected from the group consisting of O, S, N- R^4 , and whereby R^3 is a hydrogen atom or an aliphatic residue, and R^4 is a hydrogen atom or an aliphatic residue,

whereby the molar ratio of carbon present in organic compound (b) to oxygen present in metal particles (a) is in the range of 3 to 50.

Moreover, the present invention relates to a method for the connecting of at least two components, comprising providing a sandwich arrangement that comprises at least a first component, a second component, and the mixture according to the invention, whereby the mixture is situated between the first and second component, and the sintering of said sandwich arrangement.

The mixtures of the present invention can be sintered and are present, preferably, as sinter pastes, in particular as printable sinter pastes.

The present invention is based on the surprising finding that the molar ratio of carbon in organic compound b) to oxygen in metal particles a) has a significant influence on the sinterability of the mixtures produced from them. It has been found, surprisingly, that only a relatively narrow range of ratios leads to improved sintering properties.

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Metal particles (a)

The mixture according to the invention contains metal particles.

10 In the scope of the invention, the term, "metal", refers to an element in the periodic system of the elements that is in the same period as boron, but to the left of boron, in the same period as silicon, but to the left of silicon, in the same period as germanium, but to the left of germanium, and in the same period as antimony, but to the left of antimony, as well as all elements having an atomic number of more than 55. According to the invention, the term, "metal", also
15 includes alloys and inter-metallic phases.

The purity of the metal preferably is at least 95 % by weight, more preferably at least 98 % by weight, even more preferably at least 99 % by weight, and yet more preferably at least 99.9 % by weight.

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In the scope of the present invention, metal particles also include metal particles that are partially oxidised, for example are surface-oxidised.

According to a preferred embodiment, the metal is selected from the group consisting of
25 copper, silver, nickel, and aluminium as well as from alloys and mixtures thereof. According to a particularly preferred embodiment, the metal is silver.

In another preferred embodiment, at least one metal of the metal particles (a) is selected from the group consisting of silver, copper, and mixtures thereof.

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The metals of the metal particles (a) preferably consist essentially of silver or copper or mixtures of copper and silver.

In this context, "essentially" shall mean that at least 95 % by weight and specifically at least
35 97.5 % by weight of the metal particles (a) consist of the corresponding metal or mixture of metals.

According to the invention, metal alloys shall be understood to be metallic mixtures of at least two components of which at least one is a metal.

According to a preferred embodiment, the scope of the invention involves using an alloy containing copper, aluminium, nickel and/or precious metals as metal alloy. The metal alloy preferably comprises at least one metal selected from the group consisting of copper, silver, gold, nickel, palladium, platinum, and aluminium. Particularly preferred metal alloys contain at least two metals selected from the group consisting of copper, silver, gold, nickel, palladium, platinum, and aluminium. Moreover, it can be preferred that the fraction of metals selected from the group consisting of copper, silver, gold, nickel, palladium, platinum, and aluminium accounts for at least 90 % by weight, preferably at least 95 % by weight, more preferably at least 99 % by weight, and even more preferably 100 % by weight of the metal alloy. The alloy can, for example, be an alloy that contains copper and silver, copper, silver and gold, copper and gold, silver and gold, silver and palladium, platinum and palladium or nickel and palladium.

The metal particles according to the scope of the present invention can just as well be particles consisting of multiple phases. Accordingly, the metal particles can, for example, comprise a core made of at least one metallic phase that is coated with at least one further metallic phase. Silver-coated copper particles shall be mentioned for exemplary purposes in this context as they are included in the definition of metal particles according to the invention. Moreover, the metal coating can just as well be applied to a non-metallic core.

In an alternative embodiment, the metal particles comprise two or more different metals. Also preferred are metal particles comprising a metal core made of a non-precious metal and a coating made of a precious metal, e.g. silver-coated copper particles.

The mixture according to the invention can contain, as metal, a pure metal, multiple types of pure metals, a type of metal alloy, multiple types of metal alloys or mixtures thereof. The metal is present in the mixture in the form of particles.

The metal particles can differ in shape. The metal particles can be present, for example, in the form of flakes or be of a spherical (ball-shaped) shape. According to a particularly preferred embodiment, the metal particles take the shape of flakes. However, this does not exclude a minor fraction of the particles employed being of different shape. However, preferably at least 70 % by weight, more preferably at least 80 % by weight, even more preferably at least 90 % by weight or 100 % by weight, of the particles are present in the form of flakes.

The metal particles present in the mixture according to the invention can be homogeneous or heterogeneous in terms of their composition. In particular, the mixture can contain particles made of different metals.

5 The mixture according to the invention preferably contains 60 - 99.7 % by weight, more preferably 77 - 89 % by weight, and even more preferably 80 - 88 % by weight metal particles, relative to the total weight of the mixture. For sinterable mixtures according to the invention, the amount of metal particles a) can be in the range of 96 - 99.7 % by weight, preferably 96.5 - 99.5 % by weight, more preferably 97 - 99.3 % by weight, and in particular in the range of
10 97.5 - 99.0 % by weight, each relative to the total weight of metal particles a) and organic compound b).

Preferably, the metal particles are partially oxidised. Alternatively, mixtures made of metal particles can be present, whereby a part of the particles is non-oxidised and a part of the
15 particles is partially or fully oxidised.

The oxygen content of metal particles (a) in the mixture according to the invention preferably is in the range of 0.01 to 0.15 % by weight, in particular between 0.05 and 0.10 % by weight relative to the total weight of the metal particles.

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The determination of the oxygen content of the metal particles can be done, for example, according to analytical procedures known to a person skilled in the art by hot extraction of carrier gas using the TC 436 analyser from Leco (USA), whereby the oxygen content is determined indirectly through conversion to CO₂, whereby the CO₂ gas is detected by a CO₂
25 infrared measuring cell. The determination of the oxygen content can be based on the ASTM E1019-03 standard. The conditioning of the device for ensuring that the measurements are reproducible is done by gas calibration with a known amount of CO₂ gas and by testing certified steel standards of Leco, whose oxygen content is approximately on the order of magnitude of the expected oxygen content of the sample to be tested. For sample preparation, 100
30 to 150 mg of the metal powder are weighed into a tin capsule of Leco. The sample and the tin capsule are then placed into a graphite crucible of Leco at 2,000°C, which had been purged twice before-hand for approximately 30 seconds each at 2,500°C. The oxygen of the sample reacts with the carbon of the graphite to form carbon monoxide (CO). The latter, in turn, is oxidised on a copper oxide column (Cu(II)O) from Leco to form carbon dioxide (CO₂),
35 whereby the column has a device-specific temperature of approximately 600°C. The CO₂ thus generated is detected by means of an infra-red cell and the oxygen content of the sample is determined accordingly. The blank value of an unfilled tin capsule needs to be deter-

mined under the same conditions before the actual measurement on the sample is performed. The device subtracts this blank value from the measured value (tin capsule and sample) during the actual measurement.

5 *Organic compound (b)*

Moreover, the sinter paste of the present invention contains an organic compound that is represented by Formula I: R^1COR^2 (I), whereby R^1 is an aliphatic residue having 8 to 32, preferably 10-24, particularly preferably 12 to 18, carbon atoms and can be branched or non-
 10 branched. In addition, R^1 can contain hetero atoms. R^2 comprises either the -OM moiety or the $-X-R^3$ moiety, whereby M is a cation and whereby X is selected from the group consisting of O, S, and N- R^4 , whereby R^3 is a hydrogen atom or an aliphatic residue, and R^4 is a hydrogen atom or an aliphatic residue. In this context, X is preferred to be O, N or S, particularly preferably O.

15 Preferably R^3 and/or R^4 is/are an aliphatic residue having 1 to 32, more preferably 10 to 24, and in particular 12 to 18, carbon atoms, whereby the residue can be linear or branched. Moreover, the residue can comprise, in addition, one or more hetero atoms. The aliphatic residue can be saturated or unsaturated.

20 The organic compound preferably is a compound selected from the group consisting of fatty acids ($X = O$ and $R^3 = H$), fatty acid salts ($M = \text{cation}$), and fatty acid esters.

The free fatty acids, fatty acid salts, and fatty acid esters preferably are non-branched.

25 Moreover, the free fatty acids, fatty acid salts, and fatty acid esters preferably are saturated.

According to a preferred embodiment, the organic compound is fatty mono-acids, salts of fatty mono-acids or fatty mono-acid esters.

30 In a preferred embodiment, organic compound (b) is a C_8 - C_{30} fatty acid, preferably a C_8 - C_{24} fatty acid, in particular a C_{12} - C_{18} fatty acid.

Conceivable fatty acid salts are preferably salts whose anionic component is the deprotonated fatty acid and whose cationic component M is selected from the group consisting of ammonium ions, monoalkylammonium ions, dialkylammonium ions, trialkylammonium ions, lithium ions, sodium ions, potassium ions, copper ions, and aluminium ions.
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Preferred fatty acid esters are derived from the corresponding fatty acids, whereby methyl, ethyl, propyl or butyl esters are preferred.

5 According to a preferred embodiment, the organic compound is selected from the group consisting of caprylic acid (octanoic acid), capric acid (decanoic acid), lauric acid (dodecanoic acid), myristic acid (tetradecanoic acid), palmitic acid (hexadecanoic acid), stearic acid (octadecanoic acid), mixtures thereof, as well as the corresponding esters and salts, and mixtures thereof.

10 According to a particularly preferred embodiment, the organic compound is selected from the group consisting of lauric acid (dodecanoic acid), stearic acid (octadecanoic acid), sodium stearate, potassium stearate, aluminium stearate, copper stearate, sodium palmitate, and potassium palmitate and any mixtures thereof.

15 Moreover, organic compound (b) is preferably selected from the group consisting of octanoic acid, stearic acid, lauric acid, palmitic acid, and any mixtures thereof.

For example a mixture of lauric acid and stearic acid is a particularly preferred mixture. Preferred mixtures have a weight ratio of stearic acid to lauric acid above 1:1.

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Preferably, organic compound (b) is present in the form of a coating on the metal particles (a).

25 The term, coating of particles, shall be understood to refer to a firmly adhering layer on the surface of particles. A firmly adhering layer shall be understood to mean that the layer does not detach from the metal particles simply by the effect of gravity.

30 The metal particles used in this context are commercially available. The corresponding organic compounds can be applied to the surface of the metal particles by means of conventional methods that are known from the prior art.

It is feasible, for example, to slurry the organic compound, in particular the stearic acid and/or lauric acid mentioned above, in solvents and to triturate it together with the metal particles in ball mills. After trituration, the coated metal particles are dried and then dust is removed.

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Preferably, the fraction of organic compounds (b), in particular the fraction of compounds selected from the group consisting of free fatty acids, fatty acid salts or fatty acid esters that

preferably comprise 8 to 24, more preferably 10 to 24, and even more preferably 12 to 18 carbon atoms, of the entire coating is at least 60 % by weight, more preferably at least 70 % by weight, even more preferably at least 80 % by weight, yet more preferably at least 90 % by weight, in particular at least 95 % by weight, at least 99 % by weight or 100 % by weight.

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According to a preferred embodiment, the content of organic compound (b) is 0.1 to 4.0 % by weight, more preferably between 0.3 and 3.0 % by weight, particularly between 0.4 and 2.5 % by weight, in particular between 0.5 % by weight to 2.2 % by weight, and specifically between 0.8 and 2.1 % by weight, relative to the total weight of particles (a) and compound (b).

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The degree of coating, defined as the ratio of the mass of organic compound (b) to the surface of the metal particles (a), preferably is 0.003 to 0.03 g, more preferably 0.007 to 0.02 g, and even more preferably 0.01 to 0.015 g of organic compound per square metre (m²) of surface of the metal particles.

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According to a preferred embodiment, the mixture according to the invention contains 0.05 to 3.5 % by weight or 0.08 to 2.5 % by weight, more preferably 0.25 to 2.2 % by weight, and even more preferably 0.5 to 2 % by weight of organic compound (b), which preferably is selected from the group consisting of fatty acids, fatty acid salts, and fatty acid esters, each relative to the total weight of the mixture according to the invention.

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In a preferred embodiment, the molar ratio of carbon contained in organic compound (b) and oxygen contained in the metal particles is in the range of 4 to 45, preferably of 5 to 40, more preferably of 10 to 35, in particular of 12 to 30, and specifically of 15 to 25 or in the range of 12 to 45, with 15 to 14 being preferred.

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It has been found, surprisingly, that establishing a certain molar ratio of carbon contained in organic compound (b) and oxygen contained in the metal particles allows the sinterability of the pastes to be improved, which is expressed in improved strength of the components connected to each other by means of sintering. In this context, the ratio, at which said improvement of the sinterability can be observed, is in the range of 3 to 50, preferably of 4 to 45. If the ratio is outside of the specified range, no improvement of the sinterability can be obtained. Likewise, an excessive content of organic compound (b) has a negative effect on the application properties of the mixture.

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The carbon content of the organic compound (b) can be calculated from the added amount of organic compound (b). Alternatively, the carbon content can also be determined analytically by means of methods known to a person skilled in the art, such as elemental analysis, for examples in accordance with the ASTM D 529102 standard. The carbon content of organic compound (b) present in the mixture can be determined, for example, by first removing all carbon-containing compounds of the mixture according to the invention with the exception of organic compound (b) from the mixture and by then determining the carbon content of the remaining mixture (e.g. by means of elemental analysis). The carbon-containing compounds can also be removed, for example, by heating the mixture for a sufficient period of time to a temperature below the boiling point of organic compound (b), but above the boiling point of all other carbon-containing compounds of the mixture.

Presumably, carbon monoxide is released during the sintering process. Carbon monoxide is a reducing agent and as such is capable of reducing the metal oxide present on the surface of the metal particles. Removing the metal oxide ensures unimpeded diffusion and ensuing increase in the diffusion rate. Said reduction of the metal oxide is also associated with the generation of *in situ* reactive metal that further favours the sintering process. Moreover, said reactive metal can fill voids between the metal atoms of the metal particles during the sintering process and can thus significantly decrease the porosity of the contact site of the two components to be connected. As a result, extremely stable and heat-conductive as well as electrically conductive contact sites are being generated.

Dispersing agent (c)

The sinterable mixtures according to the invention can be present as sinter pastes and then usually contain an additional dispersing agent (c). The dispersing agents that are common for metal pastes are conceivable for said sinter pastes.

Accordingly, the sinterable mixture of a preferred embodiment of the present invention contains an additional dispersing agent (c).

In the scope of the invention, dispersing agent shall be understood to mean substances that can dissolve or disperse other substances through physical processes.

According to the invention, the dispersing agents that are common for metal pastes are conceivable. Preferably, organic compounds having at least one hetero atom and 6 - 24 carbon

atoms, more preferably 8 - 20 carbon atoms, specifically 8 to 14 carbon atoms, are used as dispersing agent.

Said organic compounds can be branched or non-branched. Dispersing agents (c) preferably
5 are cyclic compounds, in particular cyclic and unsaturated compounds.

Moreover, the organic compounds used as dispersing agent can be saturated, mono-unsaturated or multi-unsaturated compounds.

10 The at least one hetero atom contained in the organic compounds that can serve as solvent is preferably selected from the group consisting of oxygen atoms and nitrogen atoms.

The at least one hetero atom can be part of at least one functional group.

15 According to a particularly preferred embodiment, the dispersing agent used in this context is an alcohol.

Monocyclic mono-terpene alcohols, such as, for example, terpeneol, in particular α -terpeneol, are specifically preferred.

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It is particularly preferred for the boiling point of the dispersing agent to be below the temperature used for sintering the pastes. It is specifically preferred for the boiling temperature of the dispersing agent to be below 240 °C, more preferably below 230 °C, in particular below 220 °C.

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For example, α -terpeneol ((R)-(+)- α -terpeneol, (S)-(-)- α -terpeneol or racemates), β -terpeneol, γ -terpeneol, δ -terpeneol, mixtures of the preceding terpeneols, N-methyl-2-pyrrolidone, ethylene glycol, dimethylacetamide, 1-tridecanol, 2-tridecanol, 3-tridecanol, 4-tridecanol, 5-tridecanol, 6-tridecanol, isotridecanol, dibasic esters (preferably dimethylesters of glutaric, adipic or succinic acid or mixtures thereof), glycerol, diethylene glycol, triethylene glycol or mixtures
30 thereof can be used in this context.

According to a preferred embodiment, it is preferred to use aliphatic hydrocarbon compounds as dispersing agent. In this context, the aliphatic hydrocarbons can consist of saturated com-
35 pounds, mono- or multiply-unsaturated compounds, and mixtures thereof. Preferably, the aliphatic hydrocarbon compounds consist of saturated hydrocarbon compounds, whereby these can be cyclic or acyclic, such as, for example, n-alkanes, isoalkanes, cycloalkanes or

mixtures thereof. The aliphatic hydrocarbon compounds can, for example, be represented by the formulas, C_nH_{2n+2} , C_nH_{2n} , and C_nH_{2n-2} , whereby n is an integer between 5 and 32. In a particularly preferred embodiment, the aliphatic hydrocarbon compounds that can be used as dispersing agent are selected from the group consisting of hexadecane, octadecane, isohexadecanes, isooctadecanes, cyclohexadecanes, and cyclooctadecanes.

Dispersing agent (c) differs from organic compound (b), in particular dispersing agent (c) is not an organic compound included in the definition of organic compound (b).

The dispersing agent usually is present in an amount of 6 to 40 % by weight, preferably 8 to 25 % by weight, specifically 10 to 20 % by weight, each relative to the total weight of the mixture according to the invention.

The type and amount of dispersing agent can be used to adjust the flow properties of the sinter pastes. Sinter pastes are preferably applied by means of printing methods to the components to be sintered.

Polymers comprising oxygen atoms (component (d))

It has also been found, surprisingly, that the addition of organic polymers comprising oxygen atoms further increases the sinterability.

Therefore, the mixture according to the invention comprises a polymer comprising oxygen atoms in a preferred embodiment. A polymer, in which the oxygen present is bound as ether and/or hydroxide, is particularly preferred. Also preferred is a polymer that comprises alkoxy groups, in particular ethoxylate and/or methoxylate groups.

For example, polysaccharides, such as, e.g., celluloses, which are preferably chemically modified, for example which have been alkoxyated or alkylcarboxylated, are suitable polymers.

The celluloses preferably comprise a degree of substitution of 2.0 to 2.9, more preferably between 2.2 and 2.8. The degree of substitution indicates the average number of chemically modified, in particular etherified, hydroxyl groups per glucose unit. Ethyl cellulose is specifically preferred. It preferably has an ethoxy content of 43.0% to 53.0%, particularly preferably of 47.5% to 50%, in particular of 48.0% to 49.5%, each relative to the number of hydroxyl groups, whereby the ethoxy content of a fully substituted cellulose would be 54.88%. Prefer-

ably, the viscosity of the cellulose is 60 to 120 cps, more preferably 90 to 115 cps, particularly preferably 85 to 110 cps. In this context, the viscosity was determined according to ASTM D914 on a mixture consisting of 80 % by weight toluene and 20 % by weight ethanol using a Hercules Horizontal Capillary Viscosimeter at 25 °C.

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Preferably, the cellulose is selected from the group consisting of methylcellulose, ethylcellulose, ethylmethylcellulose, carboxymethylcellulose, hydroxypropylmethylcellulose, hydroxyethylcellulose, hydroxyethylmethylcellulose, or mixtures thereof. Ethylcellulose is a particularly preferred cellulose.

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The presence of ethylcellulose improves the sinterability of the paste even more through optimised conversion of the organic compound to carbon monoxide.

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Preferably, the mixture according to the invention contains 0.05 to 2.0 % by weight of the oxygen-containing polymer, in particular of the cellulose, relative to the total weight of the mixture, even more preferably 0.1 to 0.8, and particularly preferably 0.2 to 0.5 % by weight.

Further ingredients

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Moreover, the mixture according to the invention can contain further ingredients, such as customary surfactants, de-foaming agents, binding agents or viscosity-controlling agents. Preferably, the mixtures can contain wetting agents.

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The further ingredients are usually added in an amount of up to 0.01 % by weight, preferably from 0.001 to 0.01 % by weight, each relative to the total weight of the mixture according to the invention.

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Preferably, the mixture according to the invention comprises essentially no glass, in particular no glass frit. Glass-forming agents, such as lead oxide, bismuth oxide, alkali and alkaline earth oxide, tellurium oxide, and the like are typical ingredients of a glass frit.

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In this context, essential shall mean that the mixture contains less than 2 % by weight, preferably less than 1 % by weight, more preferably less than 0.5 % by weight, in particular less than 0.1 % by weight, specifically less than 0.05 % by weight, for example 0 % by weight glass and/or glass frit, whereby the specified weights each are relative to the total weight of the mixture.

In a specific embodiment, the metal particles a) of the sinterable mixture according to the invention are silver particles. It has been evident, surprisingly, that optimal sinterability can be attained if the oxygen content of the silver relative to the organic compound (b) can be perfectly matched to each other (for example by selecting partially oxidised silver and/or mix-
 5 tures of silver and silver oxide). In a preferred embodiment, the molar ratio of total oxygen present in the silver particles and organic compound (b) to silver is approx. 1.0 to approx. 3.5, preferably approx. 1.2 to approx. 3.0, and, in particular, approx. 2.0 to approx. 2.7.

Moreover, the molar ratio of total carbon present in organic compound (b) to silver is in the
 10 range of approx. 5 to approx. 20, more preferably of approx. 7 to approx. 16, and, in particular, of approx. 10 to approx. 15.

Moreover, good sinterability results can be attained, if the composition of the mixture accord-
 ing to the invention is selected appropriately such that the molar ratio of carbon present in
 15 organic compound (b) to total oxygen present in metal particles (a), in particular in the silver particles, and organic compound (b) is adjusted appropriately to be in the range of approx. 200 to approx. 600, more preferably in the range of approx. 400 to approx. 570, and, in particular, in the range of approx. 500 to approx. 550.

20 In a preferred embodiment, the mixture according to the invention contains

- (a) 75 to 90 % by weight metal particles, preferably selected from the group consisting of silver, copper, aluminium, and nickel, in particular of silver
- (b) 0.05 to 3.0 % by weight organic compound (b) that preferably is selected from the group consisting of fatty acids, fatty acid salts, and fatty acid esters, in particular fatty
 25 acids, and that further preferably is present as coating on the metal particles (a), and
- (c) 6 to 30 % by weight of a dispersing agent that preferably is selected from the group of alcohols, in particular from the terpineols, and
- (d) if applicable, 0.05 to 1.0 % by weight of a cellulose, in particular ethylcellulose,
 whereby the molar ratio of carbon contained in organic compound (b) to oxygen con-
 30 tained in metal particles (a) is in the range of 5 to 40, preferably in the range of 10 to 35, more preferably in the range of 12 to 30, and particularly preferably in the range of 15 to 25, whereby the specified weights each relate to the total weight of the sinterable mixture.

Sintering

Also a subject matter of the present invention is a method for producing the mixture according to the invention, whereby metal particles (a), organic compound (b), and, if applicable, the dispersing agent (c) are being mixed.

According to a preferred refinement of the present invention, the mixing of metal particles (a) and organic compound (b) proceeds in that organic compound (b) is being slurried in solvents and is milled together with metal particles (a) in disintegration devices, in particular in bead mills. Subsequently, the coated metal particles can be dried and dust can be removed, if applicable, in a further step.

The sinterable mixture according to the invention can be produced in mixing apparatus and stirrers that are familiar to a person skilled in the art. In a preferred refinement of the production method according to the invention, the metal particles are coated with organic compound (b) in a first step.

The coated particles are mixed with a dispersing agent (c) in a subsequent step.

According to the invention, the pastes according to the invention are used in a sintering process.

Preferably, sintering shall be understood to mean connecting two or more components through heating without producing a liquid phase. Accordingly, the sintering proceeds as a diffusion process.

According to the invention, connecting at least two components shall be understood to mean attaching a first component on a second component. In this context, "on" simply means that a surface of the first component is connected to a surface of the second component regardless of the relative disposition of the two components or of the arrangement containing the at least two components.

In the scope of the invention, the term, component, is preferred to comprise single parts. Preferably, said single parts cannot be disassembled further.

A component in the scope of the present invention can be any object regardless of its function. In this context, the terms of component, part, and substrate are considered to be synonymous in the scope of the present invention.

According to specific embodiments, a component is an object that comprises at least one metal surface.

- 5 According to specific embodiments, the term, components, refers to parts that are used in high-performance electronics.

Accordingly, components can, for example, be diodes, LEDs (light-emitting diodes, lichtemittierende Dioden), DCB (direct copper bonded) substrates, lead frames, dies, IGBTs (insulated-gate bipolar transistors, Bipolartransistoren mit isolierter Gate-Elektrode), ICs (integrated circuits, integrierte Schaltungen), sensors, heat sink elements (preferably aluminium heat sink elements or copper heat sink elements) or other passive components (such as resistors, capacitors or coils). Preferably, the components can just as well be non-metallic components.

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The components to be connected can be identical or different components.

Preferred embodiments of the invention relate to the connecting of LED to leadframe, of LED to ceramic substrate, of dies, diodes, IGBTs or ICs to leadframes, ceramic substrates or DCB substrates, of sensors to leadframe or ceramic substrate, of DCB or ceramic substrate to copper or aluminium heat sink elements, of leadframe to heat sink element or of tantalum capacitors, preferably in un-housed condition, to leadframe.

It is also preferred to connect more than two components to each other. For example, (i) LED or chip can be connected to (ii) leadframe and (iii) heat sink element, whereby the leadframe preferably is situated between (i) LED or chip and (iii) heat sink element. It is just as well to connect a diode to two heat sink elements, whereby the diode preferably is situated between two heat sink elements.

30 According to a preferred embodiment, the components can comprise at least one metal surface. Said metal surface preferably is part of the component. Preferably, said metal surface is situated on at least one surface of the component.

The metal surface can comprise pure metal. Accordingly, it can be preferred for the metal surface to comprise at least 50 % by weight, more preferably at least 70 % by weight, even more preferably at least 90 % by weight or 100 % by weight of pure metal. Preferably, the

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pure metal is selected from the group consisting of aluminium, copper, silver, gold, palladium, and platinum.

On the other hand, the metal surface can just as well comprise an alloy. The alloy of the metal surface preferably contains at least one metal selected from the group consisting of silver, gold, nickel, palladium, and platinum. It can be preferred just as well that the alloy of the metal surface contains at least two metals selected from the group consisting of silver, gold, nickel, palladium, and platinum. The fraction of the alloy accounted for by the elements selected from the group consisting of silver, gold, nickel, palladium, and platinum preferably is at least 90 % by weight, more preferably at least 95 % by weight, even more preferably at least 99 % by weight, for example 100 % by weight.

According to a preferred embodiment, the metal surface preferably contains at least 95 % by weight, more preferably at least 99 % by weight, and even more preferably 100 % by weight of said alloy. The metal surface can just as well have a multi-layer structure. Accordingly, it can be preferred that at least one surface of the components to be connected comprises a metal surface made of multiple layers that comprise the pure metals and/or alloys specified above.

According to a preferred embodiment, at least one metal surface of a component, in particular of a DCB substrate, comprises a layer made of copper onto which a layer made of nickel is applied. If applicable, yet another layer made of gold can be applied onto the layer made of nickel. In this case, the thickness of the layer made of nickel preferably is 1 - 2 μm and the thickness of the layer made of gold preferably is 0.05 - 0.3 μm . On the other hand, it can just as well be preferred to have a metal surface of a component comprise a layer made of silver or gold and, above it, a layer made of palladium or platinum.

According to a further preferred embodiment, the individual layers also contain a glass in addition to the specified pure metals or alloys. It can be preferred just as well that the layers are a mixture of (i) glass and (ii) the pure metals or alloys.

According to the invention, at least two components are being connected to each other through sintering.

For this purpose, the at least two components are first made to contact each other. The contacting is effected by means of the metal paste according to the invention in this context. For

this purpose, an arrangement is provided, in which metal paste is situated between each two of the at least two components.

5 Accordingly, if two components, i.e. component 1 and component 2, are to be connected to each other, the metal paste according to the invention is situated between component 1 and component 2 before the sintering process. On the other hand, it is conceivable to connect more than two components to each other. For example three components, i.e. component 1, component 2, and component 3, can be connected to each other in appropriate manner such that component 2 is situated between component 1 and component 3. In this case, the metal
10 paste according to the invention is situated both between component 1 and component 2 as well as between component 2 and component 3. The invention provides the individual components in a sandwich arrangement and provides them to get connected to each other.

15 According to the invention, sandwich arrangement shall be understood to mean an arrangement, in which two components are situated one above the other and in which the contact surfaces to be connected are situated essentially parallel with respect to each other.

A further aspect of the present invention is a method for connecting at least two components that comprises the following step of:

- 20
- providing a sandwich arrangement that comprises at least a first component, a second component, and a mixture according to the present invention, whereby the mixture is situated between the first and the second component, and
 - sintering said sandwich arrangement.

25 The arrangement of at least two components and metal paste, whereby the metal paste is situated between two components of said arrangement, can be produced according to any method known according to the prior art.

30 Preferably, firstly, at least one surface of a component 1 is provided with the metal paste according to the invention. Then, another component 2 is placed by one of its surfaces on the metal paste that has been applied to the surface of component 1.

35 According to a preferred embodiment of the method, at least one of the components possesses a metal surface, preferably a gold surface, palladium surface, silver surface or copper surface onto which the mixture according to the invention is being applied.

An embodiment of the method comprising the following steps is also preferred:

- a) applying a mixture according to the present invention to a component surface of a component;
- b) providing a sandwich arrangement by arranging a second component appropriately such that said mixture is situated between the first component and the second component; and
- 5 c) sintering said sandwich arrangement.

An embodiment, in which at least one of the component surfaces onto which the mixture is being applied, is a non-precious metal surface, in particular copper, is particularly preferred.

- 10 It has been evident, surprisingly, that a mixture according to the invention, in which the molar ratio of carbon contained in organic compound (b) to oxygen contained in metal particles (a) is in the range of 11 to 48, specifically 14 to 40, is advantageous, in particular if one of the component surfaces to be connected comprises a non-precious metal surface, in particular copper. It has also been evident that sintering at a low process pressure, for example 0 MPa,
- 15 is feasible in particular at this molar ratio.

- The application of the metal paste to the surface of a component can be effected through any conventional method. Preferably, the metal paste is applied by means of printing methods, for example by screen printing or stencil printing. However, the metal paste can be applied
- 20 just as well by means of dispensing technology, by means of spraying technology, by means of jet technology, by means of pin transfer or by immersion.

- It is preferable, following the application of the metal paste, to contact the surface of said component that has been provided with the metal paste to a surface of the component to be
- 25 connected thereto by means of the metal paste. Accordingly, a layer of the metal paste is situated between the components to be connected.

- Preferably, the thickness of the wet layer between the components to be connected is in the range of 15 - 200 μm . In this context, thickness of the wet layer shall be understood to mean
- 30 the distance between the opposite surfaces of the components to be connected prior to the sintering process. The preferred thickness of the wet layer depends on the method selected for applying the metal paste. If the metal paste is applied, for example, by means of a screen printing method, the thickness of the wet layer can preferably be 15 - 50 μm . If the metal paste is applied by means of stencil printing, the preferred thickness of the wet layer can be
- 35 in the range of 50 - 200 μm . According to a preferred embodiment, a drying step is performed prior to the sintering process.

Preferably, drying shall be understood to mean reducing the dispersing agent fraction in the metal paste.

5 The drying can proceed either after producing the arrangement, i.e. after contacting the components to be connected. However, the drying can just as well proceed right after application of the metal paste onto the at least one surface of the component and before contacting to the component to be connected.

10 Preferably, the drying temperature is in a range of 50 - 160 °C.

Obviously, the drying time depends on the specific composition of the metal paste and the size of the arrangement to be sintered. Common drying times are in the range of 5 - 45 minutes.

15 The arrangement consisting of the at least two components and metal paste situated between the components is finally subjected to a sintering process.

20 In this context, the dimensions of the components can preferably vary from approx. 0.5 mm² to 180 cm², whereby preferred components are rectangular or circular.

The sintering process preferably proceeds at a temperature of 180 °C or less and 250 °C or less, in particular at 200 °C or more and 240 °C or less.

25 In this context, the process pressure preferably is in the range of 30 MPa or less and 0 MPa or more, more preferably in the range of 5 MPa or more and 25 MPa or less. However, the sintering process can also be implemented without applying any process pressure, i.e. at a process pressure of 0 MPa. The sintering time depends on the process pressure and preferably is in the range of 2 - 60 minutes.

30 The sintering process can proceed in an atmosphere that is not subject to any limitations. However, preferably the sintering process is carried out in an atmosphere that contains oxygen.

35 The sintering process takes place in a conventional suitable apparatus for sintering, in which the above-mentioned process parameters can preferably be set.

The invention is illustrated through the examples specified in the following, though these may not be construed such as to limit the invention in any way or form.

Examples

5

Production of the metal pastes

Initially, metal pastes 1 - 13 were produced by mixing the ingredients at the quantitative ratios given in Table 1.

10

A mixture of stearic acid and lauric acid at a mass ratio of 75 :25 was used as the coating.

Partially-oxidised silver particles (D50:4 μm) were used as metal particles.

15

α -Terpineol or a 1:1 mixture of α -Terpineol and tridecanol was used as dispersing agent.

In examples 6, 8, and 10, additional cellulose (degree of substitution: 100) was added to the paste.

20

Application of the paste, and sintering procedure

The paste was applied by stencil printing at 20°C to 25°C, whereby the stencil was 75 μm in thickness and the printed area was 10 x 10 mm. A steel squeegee with a pitch angle of 60° was used. The printing speed was 50 mm/s.

25

The metal pastes produced were used to sinter two components that were to be connected to each other.

30

The sinterability (see Table 2) of different sinterable mixtures (Table 1) was determined by means of two sintering procedures, i.e. pressure sintering and pressure-free sintering. The sintering conditions are described in the following:

a) Pressure sintering

35

The pressure sintering proceeded after application of the sinter paste to a component that comprised a gold/nickel surface, with the sinter paste in contact with the gold side, or a copper surface. Subsequently, the sinter paste was contacted to a silicon

component bearing a TiNiAg metallisation and sintered at the respective pressure (process pressure) at 240 °C for 3 minutes.

b) Pressure-free sintering

5 The pressure-free sintering proceeded after application of the sinter paste to a component that comprised a gold/nickel surface (with the sinter paste in contact with the gold side) or a copper surface.

Subsequently, the sinter paste was contacted to a silicon component bearing a TiNi-Ag metallisation.

10 The following heating profile was used in pressure-free sintering: The contact site to be sintered was heated steadily over the course of 30 minutes from 25 °C to 160 °C and then maintained at 160 °C for 30 minutes. Subsequently, the temperature was raised steadily to a final temperature of 230 °C over the course of 5 minutes and then maintained at this level for 60 minutes. Subsequently, the temperature was de-
15 creased steadily to 30 °C over the course of 50 minutes.

The sintering process can proceed in a protective gas atmosphere (nitrogen) or exposed to air.

20 *Evaluation of sinterability*

The sinterability was determined by means of two equally-weighted evaluation criteria:

First criterion: Screen-cutting test

25

The sintered contact site had 5 parallel cut lines in horizontal and vertical direction. The distance between each of the cut lines was 1 mm.

30 A very good screen cut (grade = 1) is evident, if the sinter layer does not detach and the cuts are clean.

A moderate screen cut (grade = 3) is evident, if there is minor flaking and fracturing.

A very poor screen cut (grade = 5) is evident, if the sinter layer detaches.

A good screen cut (grade = 2) is evident, if the screen cut is between a very good and a moderate screen cut.

35 A poor screen cut (grade = 4) is evident, if the screen cut is between a moderate and a very poor screen cut.

Second criterion: Bending test

5 The substrate connected to the silicon component was attached on a roller as shown in Figures 1 and 2: In Figure 1 and 2, the silicon component (3), which is sintered to the substrate (nickel/gold component or copper component) (1) by means of the sinter layer (4), is attached on a roller (2) with a diameter of 2 cm. Said composite was bent over the roller proceeding from right to left. Figure 1 shows a bending test with a very good result (grade = 1), since the silicon component (3) remains fully adherent to the substrate.

10

Figure 2 shows a bending test with a very poor result (grade = 5), since the silicon component (3) is being peeled from the substrate. Grades 2-4 are between these extremes.

15

Subsequently, the grades from the screen-cutting test and the bending test were added and the mean was calculated. The mean is shown as "Sinterability" in Table 2 for the respective sinterable mixtures.

The sinterability results of the individual pastes are shown in Table 2.

Table 1. Sinterable mixtures

	1	2	3	4	5	6	7	8	9	10	11	12	13
Ag powder (with coating)	83	83	83	83	86	85	83	85	83	85	83	83	83
Coating content	0.00	0.3	0.4	0.82	0.82	0.82	1.60	1.60	2.10	2.10	3.00	4.00	5.00
α -Terpineol	17	17	17	17	7	7.45	17	7.45	17	7.45	17	17	17
Tridecanol	0	0	0	0	7	7.3	0	7.3	0	7.3	0	0	0
Ethylcellulose	0	0	0	0	0	0.25	0	0.25	0	0.25	0	0	0
Mole ratio C : O	0	3.6	4.8	10	10	10	19	19	25	25	36	47.5	59

The values in the line titled "Coating content" refer to % by weight of organic compound b) relative to the total weight of silver powder and organic compound b) (that is present as coating on the silver particles).

- 5 The numbers for the coated silver powder, α -terpineol, tridecanol, and ethylcellulose each referred to the total weight of the sinterable mixture.

Table 2. Sinterability

	1	2	3	4	5	6	7	8	9	10	11	12	13
Pressure sintering (240 °C, 3min)													
20 MPa, Au/Ni surface, Au on top	5	3.5	2	1	1	1	1	1.5	1.5	2	3	5	5
10 MPa, Au/Ni surface, Au on top	5	4	3.5	3	4	1	1	1.5	1.5	2	2	4	5
10 MPa, Cu surface	5	5	5	5	5	4	1	1	1.5	2.5	1	3	5
Pressure-free sintering (230 °C, 1h)													
in air, Au/Ni surface, Au on top	5	5	5	5	4	3.5	3	3	3.5	3.5	2.5	4	5
in protective gas, Au/Ni surface, Au on top	5	5	5	5	5	4	3	3	3.5	3.5	2	3.5	5
in air, Cu surface	5	5	5	5	5	5	3.5	3.5	4	4	2.5	3.5	5
in protective gas, Cu surface	5	5	5	5	5	5	2.5	2.5	3.5	3.5	1.5	3.5	5

Sinterability: 1 = very good, 2 = good, 3 = moderate, 4 = poor, 5 = very poor

5 Claims

1. Mixture containing
 - (a) metal particles and
 - (b) an organic compound represented by Formula I: R^1-COR^2 (I),
10 whereby R^1 is an aliphatic residue having 8 to 32 carbon atoms, and R^2 comprises either the -OM moiety or the $-X-R^3$ moiety, whereby M is a cation and whereby X is selected from the group consisting of O, S, N- R^4 , and whereby R^3 is a hydrogen atom or an aliphatic residue, and R^4 is a hydrogen atom or an aliphatic residue,
15 whereby the molar ratio of carbon present in organic compound (b) to oxygen present in metal particles (a) is in the range of 3 to 50.
2. Mixture according to claim 1, whereby at least one metal of metal particles (a) is selected from the group consisting of silver, copper, nickel, aluminium as well as alloys
20 and mixtures thereof.
3. Mixture according to claim 1 or 2, whereby at least one metal of metal particles (a) is selected from the group consisting of silver, copper, and mixtures of copper and silver.
25
4. Mixture according to any one or more of the preceding claims, whereby organic compound (b) is a C_8 - C_{30} fatty acid, preferably a C_8 - C_{24} fatty acid, more preferably a C_{12} - C_{18} fatty acid.
- 30 5. Mixture according to any one or more of the preceding claims, whereby organic compound (b) is selected from the group consisting of octanoic acid, stearic acid, lauric acid, palmitic acid, and any mixtures thereof.
- 35 6. Mixture according to any one or more of the preceding claims, whereby the paste contains an additional polymer that comprises oxygen atoms.

7. Mixture according to any one or more of the preceding claims whereby organic compound (b) is present in the form of a coating on particles (a).
8. Mixture according to any one of the preceding claims, whereby compound (b) is present in an amount of 0.1 to 4.0 % by weight, more preferably between 0.3 and 3.0 % by weight, even more preferably between 0.4 and 2.5 % by weight, particularly preferably between 0.5 and 2.2 % by weight, specifically between 0.8 and 2.0 % by weight, each relative to the total weight of particles (a) and compound (b).
9. Mixture according to any one or more of the preceding claims, whereby metal particles (a) have an oxygen content of 0.01 to 0.15 % by weight, preferably of 0.05 to 0.10 % by weight, each relative to the weight of metal particles (a).
10. Mixture according to any one or more of the preceding claims, whereby the molar ratio of carbon contained in organic compound (b) to oxygen contained in the metal particles is in the range of 4 to 45, preferably of 5 to 40, more preferably of 10 to 35, in particular of 12 to 30, and specifically of 15 to 25 or in the range of 12 to 45, with 15 to 14 being preferred.
11. Mixture according to any one or more of the claims 1 to 10, additionally containing (c) a dispersing agent.
12. Mixture according to claim 11, whereby dispersing agent (c) is selected from the group consisting of alpha-terpineol, beta-terpineol, gamma-terpineol, delta-terpineol, mixtures of the afore-mentioned terpineols, N-methyl-2-pyrrolidone, ethylene glycol, dimethylacetamide, 1-tridecanol, 2-tridecanol, 3-tridecanol, 4-tridecanol, 5-tridecanol, 6-tridecanol, isotridecanol, dibasic esters, preferably dimethylesters of glutaric, adipinic or succinic acid or mixtures thereof, glycerol, diethylene glycol, triethylene glycol, and mixture thereof.
13. Method for producing a mixture according to any one or more of the claims 1 to 10, characterised in that metal particles (a), organic compound (b), and, if applicable, dispersing agent (c) are being mixed.
14. Method for the connecting of at least two components, comprising

- providing a sandwich arrangement that comprises at least a first component, a second component, and a mixture according to any one or more of the claims 1 to 12, whereby the mixture is situated between the first and the second component, and
 - 5 - sintering said sandwich arrangement.
15. Method according to claim 14, whereby the sintering process is implemented at a temperature of 180 °C or higher and 250 °C or less, preferably at 200 °C or more and 240 °C or less.
- 10 16. Method according to any one of the claims 14 or 15, whereby the centering is implemented at a process pressure of 0 MPa or more and 30 MPa or less, preferably of 5 MPa or more and 25 MPa or less.
- 15 17. Method according to any one or more of the claims 14 to 16, whereby at least one of the components possesses a metal surface, preferably a gold surface, palladium surface, silver surface or copper surface onto which the mixture is being applied.
18. Method according to any one or more of the claims 14 to 17, comprising
- 20 a) applying a mixture according to any one or more of the claims 1 to 12 onto a component surface of a first component;
- b) providing a sandwich arrangement by arranging a second component appropriately such that said mixture is situated between the first component and the second component; and
- 25 c) sintering said sandwich arrangement.
19. Method according to any one or more of the claims 14 to 18, characterised in that at least one of the component surfaces onto which the mixture is being applied is a non-precious metal surface, in particular copper.