

Tin-based solder alloy powder

The invention relates to a tin-based solder alloy powder the powder particles whereof having a thin outer surface layer of stressed castor oil and a process for the manufacture thereof. The invention relates also to a solder paste comprising the tin-based solder alloy powder.

5 US 6,290,745 B1 and US 2006/0208042 A1, both disclose a process for the manufacture of solder alloy balls. During said process the metallic solder alloy is melted in a high temperature-resistant plant or animal oil, then stirred and dispersed in multiple shear treatments by rotors and stators into solder alloy balls of defined diameter in the range of 1 to 100 μm . US 6,290,745 B1 discloses a final washing step of rinsing the so-manufactured solder alloy balls with a fat-dissolving solvent like acetone.

The object of the invention is to improve the storage-stability of a tin-based solder alloy powder as can be evaluated from the solderability performance of a solder paste made from the tin-based solder alloy powder and a solder flux composition, as is conventional in the art. The solderability performance can be determined by the so-called solderability test (solder ball test) on a ceramic substrate or by a wetting test on a copper sheet. Such tests can be made with solder pastes prepared with fresh and with aged samples of a tin-based solder alloy powder. Aging means keeping a freshly prepared tin-based solder alloy powder in question under defined conditions (e.g. storage at 55°C under ambient exposure, i.e. in the presence of air and at 50% Relative Humidity) and taking samples after 16, 31 and 63 days; from those powder samples solder pastes can then be prepared.

In the course of the solderability test the solderability performance is determined and gives an indication of the effect of inorganic oxygen-containing species present on the surface of the tin-based solder alloy powder on formation of undesired solder ball clusters during a soldering process. The solder paste to be tested is printed onto ceramic substrates and then tested. To this end, the ceramic substrates are placed in a reflow oven at 250°C object temperature in a nitrogen environment until the tin-based solder alloy powder has fused; assessment is then done with regard to formation of remnant tin-based solder alloy powder (unsoldered tin-based solder alloy powder) and area percent covered with inorganic oxygen-containing species like tin oxide residue, the less of both the better the result. For details of the solderability test reference is made to the Examples below.

In the course of the wetting test the wetting performance is determined and gives an indication of the effect of inorganic oxygen-containing species present on the surface of the tin-based solder alloy powder on undesired de-wetting behavior. The solder paste to be tested is printed onto copper sheets and then tested. To this end, the copper sheets are placed in a reflow oven at 250°C object temperature in a nitrogen environment until the solder paste melts and wets the copper surface; assessment is then done with regard to de-wetted area percent of the area originally printed, the less percent the better the result. For details of the wetting test reference is made to the Examples below.

It has been found that the object of the invention can be solved by providing a tin-based solder alloy powder in the form of 2 to 38 μm , preferably 2 to 25 μm small spherical tin-based solder alloy particles having an inorganic surface and a thin outer surface layer of stressed castor oil, wherein the inorganic surface plus the thin outer surface layer of stressed castor oil together form a surface region of the spherical tin-based solder alloy particles, and wherein the surface region, when subjected to a ToF-SIMS (Time-of-Flight Secondary Ion Mass Spectrometry) analysis carried out with Ga^+ primary ions having an energy of 15 keV and with a total scan time of 5 minutes, exhibits a secondary ion mass spectrum comprising the negatively charged secondary ion fragments

- 113 amu (atomic mass units) with a relative signal intensity in the range of 0.7 to 3.1,
- 127 amu with a relative signal intensity in the range of 0.9 to 4.4,
- 136 amu with a relative signal intensity in the range of 1.4 to 6.7,
- 137 amu with a relative signal intensity in the range of 0.6 to 3.9,
- 152 amu with a relative signal intensity in the range of 1.3 to 12,
- 153 amu with a relative signal intensity in the range of 2.3 to 20,
- 183 amu with a relative signal intensity in the range of 0.6 to 16,
- 279 amu with a relative signal intensity in the range of 0.5 to 12, and
- 297 amu with a signal intensity of 1.

To the surprise of the applicant, said secondary ion mass spectrum comprising the negatively charged secondary ion fragments 113 amu with a relative signal intensity in the range of 0.7 to 3.1, 127 amu with a relative signal intensity in the range of 0.9 to 4.4, 136 amu with a relative signal intensity in the range of 1.4 to 6.7, 137 amu with a relative signal intensity in the range of 0.6 to 3.9, 152 amu with a relative signal intensity in the range of 1.3 to 12, 153 amu with a relative signal intensity in the range of 2.3 to 20, 183 amu with a relative signal intensity in the range of 0.6 to 16, 279 amu with a relative signal intensity in the range of 0.5 to 12, and 297 amu with a signal intensity of 1 has turned out to be an essential and characteristic feature. If

the signal intensity pattern deviates therefrom, a solder paste on the basis of such tin-based solder alloy particles exhibits inferior solderability and wetting performance.

It is believed that the signals of the negatively charged secondary ion fragments can be assigned as follows:

113 amu	$C_7H_{13}O^-$ and/or $C_6H_9O_2^-$	
127 amu	$C_7H_{11}O_2^-$	
136 amu	$^{120}SnO^-$	
137 amu	$^{120}SnOH^-$	
152 amu	$^{120}SnO_2^-$	
153 amu	$^{120}SnO_2H^-$	
183 amu	$C_{11}H_{19}O_2^-$	
279 amu	$C_{18}H_{31}O_2^-$	Fragment of linoleic acid
297 amu	$C_{18}H_{33}O_3^-$	Fragment of ricinoleic acid

The skilled person will understand the 2 to 38 μm , preferably 2 to 25 μm small spherical tin-based solder alloy particles as 2 to 38 μm , preferably 2 to 25 μm small tin-based solder alloy balls or as tin-based solder alloy balls with a diameter in the range of 2 to 38 μm , preferably 2 to 25 μm . The synonymous terms “spherical tin-based solder alloy particles” and “tin-based solder alloy balls” are used herein. In other words, the spherical tin-based solder alloy particles or the tin-based solder alloy balls are spherical or very close to spherical in shape (i.e. exhibiting an aspect value of 0.95 to 1.0, “aspect value” means the quotient of the largest and smallest linear dimension of particles; i.e. an aspect value of 1.0 means perfect spheres) with an absolute ball size in the range of 2 to 38 μm , preferably 2 to 25 μm . In still other words, the talk here is about solder alloy balls of the types T4 to T8 according to industry standard IPC J-STD-005A (T4, T5, T6, T7 or T8 correspond to 20 to 38 μm , 15 to 25 μm , 5 to 15 μm , 2 to 11 μm or 2 to 8 μm particle size or ball size). Said particle size or ball size or diameter and said particle shape can be determined by SEM (scanning electron microscopy) analysis of a statistically meaningful number of particles or balls, for example, a number in the range of up to 400 to even up to 2000.

The term “tin-based solder alloy” is used herein. It shall mean a tin-rich solder alloy or a solder alloy comprising at least a considerable and not negligible proportion of tin, for example, at least 42 wt.% (% by weight) of tin. Examples of tin-rich solder alloys are those having a tin content of, for example, in the range of 90 to 99.5 wt.%. Examples of alloying metals are copper, silver, indium, germanium, nickel, lead, bismuth and antimony. The tin-based solder alloys can contain lead or preferably be lead-free. Lead-free tin-based solder alloys can be selected, for example, from the group consisting of SnAg, SnBi, SnSb, SnAgCu, SnCu, SnSb, InSnCd, InBiSn, InSn,

BiSnAg or SnAgCuBiSbNi alloy types. Tin-based solder alloys containing lead can be selected, for example, from the group comprising SnPb and SnPbAg alloy types. The liquidus temperature of the tin-based solder alloy can be in the range of, for example, 140 to 230°C. Specific examples of tin-based solder alloys in the sense of the invention include common alloys like SAC305, SAC405, SnCu0.7 and SnBi.

This disclosure uses the term “stressed castor oil” to distinguish between stressed castor oil as opposed to other types of castor oil like fresh castor oil. Stressed castor oil comprises castor oil derivatives, i.e. it consists of castor oil which comprises contaminants in the form of castor oil derivatives. Examples of castor oil derivatives include oxidized, oligomerized or polymerized castor oil derivatives, wherein oligomerized or polymerized castor oil derivatives can also be oxidized (can have suffered oxidation as well). Stressed castor oil is castor oil which has undergone oxidative and typically also thermal stress (heat stress), for example, a castor oil which has suffered heat stress in the presence of air within a temperature range of 200 to 250°C and for a total period of 10 to 120 minutes. Fresh castor oil on the other side means castor oil which has not undergone oxidative and typically also not thermal stress, e.g. castor oil freshly obtained from castor beans and – in case it is not to be used immediately or soon - stored in a cool and dark place without air or oxygen having access to it. Fresh castor oil in the sense of this disclosure can have an acid number in the range of, for example, 0.14 to 1.97 mg KOH/g, whereas stressed castor oil in the sense of this disclosure has a higher acid number in the range of, for example, 3 to 4 mg KOH/g. The term “acid number” used herein refers to an acid number that can be determined in mg KOH/g (milligrams KOH per gram) according to industry standard DIN EN ISO 2114. The skilled person will understand that stressed castor oil in the sense of this disclosure can be obtained by subjecting fresh castor oil to said oxidative and typically also thermal stress until said acid number in the range of 3 to 4 mg KOH/g is reached. Needless to mention in itself, that it is possible to obtain such type of stressed castor oil by mixing fresh castor oil with a highly stressed castor oil exhibiting an acid number at the upper end of said acid number range of 3 to 4 mg KOH/g or even above.

To prevent misunderstandings, the thin outer surface layer of stressed castor oil, is an integral part of the spherical tin-based solder alloy particles of the invention. In a preferred embodiment, the stressed castor oil comprises no additives or additions of auxiliary substances like, for example, corrosion inhibitors or emulsification assistants; in other words, it is preferred that the stressed castor oil consists only of itself. The stressed castor oil can have a layer thickness in the nanosize range, for example, in a range of 0.5 to 5.2 nm; that thin outer surface layer thickness can be determined by Auger electron spectroscopy using an argon sputtering ion

beam at 1 keV. Adjacent and beneath that thin outer surface layer of stressed castor oil the inorganic surface of the spherical tin-based solder alloy particles is located; that inorganic surface comprises or consists of inorganic oxygen-containing species of tin and - as the case may be – also inorganic oxygen-containing species of alloying metals of the tin-based solder alloy. That inorganic surface can also have a thickness in the nanosize range, for example, in a range of 0.3 to 2.4 nm; that inorganic surface thickness can also be determined by Auger electron spectroscopy using an argon sputtering ion beam at 1 keV. Beneath said inorganic surface only the actual metallic tin-based solder alloy is present. The thin outer surface layer of stressed castor oil plus the inorganic surface together form the already mentioned surface region of the spherical tin-based solder alloy particles of the invention; insofar the surface region can have a thickness in the nanosize range of, for example, 0.8 to 7.6 nm as a total of said nanosize ranges of the outer surface layer thickness plus the inorganic surface thickness.

In the following below, a process for the manufacture of the tin-based solder alloy powder of the invention comprising successive process steps (1) to (4) is disclosed; process step (1) can comprise sub-steps (1a) and (1b). Castor oil which is separated (and recycled) in the course of sub-step (1b) and/or of process step (3) can represent stressed castor oil in the sense of this disclosure.

As already indicated above, the invention relates also to a process for the manufacture of the tin-based solder alloy powder of the invention, i.e. the tin-based solder alloy powder in the form of 2 to 38 μm , preferably 2 to 25 μm small spherical tin-based solder alloy particles having an inorganic surface and a thin outer surface layer of stressed castor oil, wherein the inorganic surface plus the thin outer surface layer of stressed castor oil together form the surface region of the spherical tin-based solder alloy particles, and wherein the surface region, when subjected to a ToF-SIMS analysis carried out with Ga^+ primary ions having an energy of 15 keV and with a total scan time of 5 minutes, exhibits a secondary ion mass spectrum comprising the negatively charged secondary ion fragments 113 amu with a relative signal intensity in the range of 0.7 to 3.1, 127 amu with a relative signal intensity in the range of 0.9 to 4.4, 136 amu with a relative signal intensity in the range of 1.4 to 6.7, 137 amu with a relative signal intensity in the range of 0.6 to 3.9, 152 amu with a relative signal intensity in the range of 1.3 to 12, 153 amu with a relative signal intensity in the range of 2.3 to 20, 183 amu with a relative signal intensity in the range of 0.6 to 16, 279 amu with a relative signal intensity in the range of 0.5 to 12, and 297 amu with a signal intensity of 1. The process comprises the successive steps:

(1) converting a hot mixture of a tin-based solder alloy melt and a stressed castor oil into a dispersion of molten spherical tin-based solder alloy particles within the stressed castor oil by subjecting the hot mixture to a rotor-stator process until a particle size in the range of 2 to 38 μm is obtained, wherein the ratio of the tin-based solder alloy melt to the stressed castor oil is in a range of 0.2 to 5 kilograms of the tin-based solder alloy melt per liter of the stressed castor oil,

(2) allowing the dispersed molten spherical tin-based solder alloy particles formed in step (1) to solidify within the stressed castor oil,

(3) separating the solidified spherical tin-based solder alloy particles from the stressed castor oil to obtain solid spherical tin-based solder alloy particles covered by residual stressed castor oil, and

(4) repeatedly rinsing and finally drying the solid spherical tin-based solder alloy particles until they have the surface region which, when subjected to a ToF-SIMS analysis carried out with Ga^+ primary ions having an energy of 15 keV and with a total scan time of 5 minutes, exhibits a secondary ion mass spectrum comprising the negatively charged secondary ion fragments 113 amu with a relative signal intensity in the range of 0.7 to 3.1, 127 amu with a relative signal intensity in the range of 0.9 to 4.4, 136 amu with a relative signal intensity in the range of 1.4 to 6.7, 137 amu with a relative signal intensity in the range of 0.6 to 3.9, 152 amu with a relative signal intensity in the range of 1.3 to 12, 153 amu with a relative signal intensity in the range of 2.3 to 20, 183 amu with a relative signal intensity in the range of 0.6 to 16, 279 amu with a relative signal intensity in the range of 0.5 to 12, and 297 amu with a signal intensity of 1, wherein a liquid composition consisting of 50 to 100 wt.% of at least one halogenated hydrocarbon solvent and of 0 to 50 wt.% of at least one organic solvent other than halogenated hydrocarbon solvents is used as rinsing fluid, wherein the wt.% total 100 wt.%.

In step (1) of the process of the invention a hot mixture of a tin-based solder alloy melt and a stressed castor oil is converted into a dispersion of molten spherical tin-based solder alloy particles within the stressed castor oil by subjecting the hot mixture to a rotor-stator process until a particle size of the molten spherical tin-based solder alloy particles in the range of 2 to 38 μm , preferably 2 to 25 μm is obtained, wherein the ratio of the tin-based solder alloy melt to the stressed castor oil is in a range of 0.2 to 5 kilograms of the tin-based solder alloy melt per liter of the stressed castor oil.

In a preferred embodiment, the stressed castor oil comprises no additives or additions of auxiliary substances like, for example, corrosion inhibitors or emulsification assistants; in other words, it is preferred that the stressed castor oil consists only of itself.

“Subjecting the hot mixture to a rotor-stator process” means treating the hot mixture with a colloid mill, i.e. passing it through a rotor-stator apparatus. Rotor-stator dispersion technique, apparatus and operating conditions are known to the skilled person; however, the skilled person is encouraged to look for useful information and details about rotor-stator apparatus and operating conditions in the afore mentioned US patent documents; insofar reference to both US patent documents, US 6,290,745 B1 and US 2006/0208042 A1 is expressly made here.

“Hot mixture” means a mixture having a temperature 20 to 30°C higher than the liquidus temperature of the tin-based solder alloy.

The hot mixture of tin-based solder alloy melt and stressed castor oil is distinguished by a ratio of 0.2 to 5 kilograms of the tin-based solder alloy melt per liter of the stressed castor oil. This hot mixture can be directly prepared by adding the tin-based solder alloy and melting it within the already sufficiently heated stressed castor oil (the stressed castor oil having a temperature which is for example 20 to 30°C higher than the liquidus temperature of the tin-based solder alloy).

The hot mixture can be prepared in a two-step approach, wherein in a first sub-step (1a) the tin-based solder alloy is melted within fresh or stressed castor oil within a first container and further wherein in a subsequent sub-step (1b) only or essentially only the solder alloy melt so produced is then transferred into a second container. That second container contains already sufficiently heated stressed castor oil so as to obtain said hot mixture of tin-based solder alloy melt and stressed castor oil which is distinguished by a ratio of 0.2 to 5 kilograms of the tin-based solder alloy melt per liter of stressed castor oil. This hot mixture of tin-based solder alloy melt and stressed castor oil is converted into a dispersion of molten spherical tin-based solder alloy particles within the stressed castor oil by passing the hot mixture through a rotor-stator apparatus until a particle size of the molten spherical tin-based solder alloy particles in the range of 2 to 38 µm, preferably 2 to 25 µm is obtained.

In step (2) of the process of the invention the dispersed molten spherical tin-based solder alloy particles formed in step (1) (i.e. the liquid spherical tin-based solder alloy droplets) are allowed to solidify within the stressed castor oil. To this end, the dispersion is allowed to cool down to a temperature below the liquidus temperature of the tin-based solder alloy. Taking measures for active cooling is possible but not necessary; i.e. it is sufficient to simply wait for the temperature to fall below the liquidus temperature. It is expedient to keep the dispersion moved until the temperature has fallen below the liquidus temperature, for example, by stirring.

The solidified spherical tin-based solder alloy particles settle under the influence of gravity and impurities remain essentially in the liquid stressed castor oil phase.

In step (3) of the process of the invention the solidified spherical tin-based solder alloy particles are separated from the stressed castor oil to obtain solid spherical tin-based solder alloy particles covered by residual stressed castor oil. Examples of separation techniques include centrifugation, filtration and preferably sieving.

The residual stressed castor oil covering the solid spherical tin-based solder alloy particles is in excess and an appropriate proportion thereof is rinsed off in subsequent step (4). In said step (4) of the process of the invention the solid spherical tin-based solder alloy particles are repeatedly rinsed and finally dried until they have said surface region which, when subjected to a ToF-SIMS analysis carried out with Ga^+ primary ions having an energy of 15 keV and with a total scan time of 5 minutes, exhibits a secondary ion mass spectrum comprising the negatively charged secondary ion fragments 113 amu with a relative signal intensity in the range of 0.7 to 3.1, 127 amu with a relative signal intensity in the range of 0.9 to 4.4, 136 amu with a relative signal intensity in the range of 1.4 to 6.7, 137 amu with a relative signal intensity in the range of 0.6 to 3.9, 152 amu with a relative signal intensity in the range of 1.3 to 12, 153 amu with a relative signal intensity in the range of 2.3 to 20, 183 amu with a relative signal intensity in the range of 0.6 to 16, 279 amu with a relative signal intensity in the range of 0.5 to 12, and 297 amu with a signal intensity of 1. In said step (4) a liquid composition consisting of 50 to 100 wt.% of at least one halogenated hydrocarbon solvent and of 0 to 50 wt.% of at least one organic solvent other than halogenated hydrocarbon solvents is used as rinsing fluid, wherein the wt.% total 100 wt.%.

It is important that a liquid composition consisting of 50 to 100 wt.% of at least one halogenated hydrocarbon solvent and of 0 to 50 wt.% of at least one organic solvent other than halogenated hydrocarbon solvents is used as rinsing fluid, wherein the wt.% total 100 wt.%. The liquid composition is homogeneous, i.e. if it comprises two or more solvents, all solvents are fully miscible with each other without a miscibility gap. All solvents are volatile organic solvents having a boiling point less than (in particular much less than) the liquidus temperature, but typically higher than 40°C. It is preferred that the liquid composition consists of at least one halogenated hydrocarbon solvent, in particular of only one halogenated hydrocarbon solvent. Chlorinated hydrocarbon solvents are preferred as halogenated hydrocarbon solvents.

Examples of useful chlorinated hydrocarbon solvents include carbon tetrachloride (CCl_4), chloroform (CHCl_3), 1,1,1-trichloroethane (CCl_3CH_3), trichloroethylene (C_2HCl_3) and tetrachloroethylene (C_2Cl_4).

- 5 Examples of organic solvents other than halogenated hydrocarbon solvents include acetone, toluene, benzene, dimethyl sulfoxide, petroleum ether and ethanol.

The repeatedly performed rinsing comprises a number of, for example, 8 to 15 or preferably 10 to 15 successive rinsing steps. Typically, after such number of successive rinsing steps said
 10 surface region of the spherical tin-based solder alloy particles is formed, in particular its thin outer surface layer of stressed castor oil, so that the surface region, when subjected to a ToF-SIMS analysis carried out with Ga^+ primary ions having an energy of 15 keV and with a total scan time of 5 minutes, exhibits a secondary ion mass spectrum comprising the negatively charged secondary ion fragments 113 amu with a relative signal intensity in the range of 0.7 to
 15 3.1, 127 amu with a relative signal intensity in the range of 0.9 to 4.4, 136 amu with a relative signal intensity in the range of 1.4 to 6.7, 137 amu with a relative signal intensity in the range of 0.6 to 3.9, 152 amu with a relative signal intensity in the range of 1.3 to 12, 153 amu with a relative signal intensity in the range of 2.3 to 20, 183 amu with a relative signal intensity in the range of 0.6 to 16, 279 amu with a relative signal intensity in the range of 0.5 to 12, and 297
 20 amu with a signal intensity of 1.

Each of said successive rinsing steps can be performed at a ratio of, for example, 2 to 5 liters of the rinsing fluid per kilogram of the spherical tin-based solder alloy particles. Each of said successive rinsing steps can be performed by stirring the mixture of the rinsing fluid and the
 25 spherical tin-based solder alloy particles for a period in the range of, for example, 20 to 60 minutes and thereafter allowing the mixture to stand for the spherical tin-based solder alloy particles to sink within the rinsing fluid. Thereafter the rinsing fluid can be drained. Each of said successive rinsing steps can be performed under ambient conditions, for example, at a temperature in the range of 20 to 40°C; there is no need to raise the temperature or to apply
 30 heat.

After the final rinsing step, the rinsed spherical tin-based solder alloy particles are dried. To this end, they can be transferred into a drying oven and they can be kept there at a temperature in the range of, for example, 40 to 80°C. This oven drying can take 8 to 10 hours, for example. The oven drying can be supported by application of reduced pressure or vacuum.

If desired, any of steps (1) to (4) can be carried out in the absence of air or oxygen, i.e. taking measures like working in an inert atmosphere. However, it is preferred that all steps (1) to (4) are performed in the presence of air, i.e. air or oxygen may have access to all materials employed within the process of the invention.

- 5 After conclusion of step (4) the so-obtained 2 to 38 μm , preferably 2 to 25 μm small spherical tin-based solder alloy particles have said surface region which, when subjected to a ToF-SIMS analysis carried out with Ga^+ primary ions having an energy of 15 keV and with a total scan time of 5 minutes, exhibits a secondary ion mass spectrum comprising the negatively charged secondary ion fragments 113 amu with a relative signal intensity in the range of 0.7 to 3.1, 127
10 amu with a relative signal intensity in the range of 0.9 to 4.4, 136 amu with a relative signal intensity in the range of 1.4 to 6.7, 137 amu with a relative signal intensity in the range of 0.6 to 3.9, 152 amu with a relative signal intensity in the range of 1.3 to 12, 153 amu with a relative signal intensity in the range of 2.3 to 20, 183 amu with a relative signal intensity in the range of 0.6 to 16, 279 amu with a relative signal intensity in the range of 0.5 to 12, and 297 amu with a
15 signal intensity of 1. They can directly be used in the preparation of a solder paste or they can be stored in an air-tight package first.

- As already indicated, the tin-based solder alloy powder of the invention or the spherical tin-based solder alloy particles of the invention can be used in the preparation of a solder paste.
20 Insofar the invention relates also to a solder paste comprising the spherical tin-based solder alloy particles of the invention. Such solder paste can comprise or consist of, for example, 82 to 92 wt.% of the spherical tin-based solder alloy particles of the invention and 8 to 18 wt.% of a flux. Such solder paste can be produced by mixing the constituents of the flux and adding a tin-based solder alloy powder in the form of spherical tin-based solder alloy particles of the
25 invention. The tin-based solder alloy powder is preferably added in multiple portions, while stirring, to an already provided mixture of the flux constituents, generally without heating. The flux is not subject to any particular restrictions in terms of its composition, and it is therefore possible to use a conventional flux known to a person skilled in the art. Typically, fluxes can comprise one or more base resins (for example rosin, acrylic resin), activator (for example
30 hydrogen halide salt of amines, organic carboxylic acids), thixotropic agent (for example hydrogenated castor oil, beeswax, carnauba wax), and often an organic solvent.

The tin-based solder alloy powder in the form of spherical tin-based solder alloy particles of the invention is distinguished by a considerable storage stability which can be determined as

mentioned above. That storage stability finds its expression in superior results of the afore mentioned solderability and wetting tests.

Examples

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Preparation of stressed castor oil from fresh castor oil:

Fresh castor oil having an acid number of 1.8 mg KOH/g was poured into a container and it was heated to 240°C and subjected to a rotor-stator process for 60 minutes, until the acid number of the castor oil had increased to 3.0 mg KOH/g.

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Preparation of spherical tin-based solder alloy powder:

2 kg of SnAg3Cu0.5 alloy was added to 1 L of fresh castor oil in a container #1 and the mixture was heated to 240°C. The solder melt was transferred to a container #2 filled with 5L of stressed castor oil having an acid number of 3.0 mg KOH/g. The hot mixture was then passed through a rotor-stator apparatus for 15 minutes, resulting in a particle size of the molten SnAg3Cu0.5 alloy particles between 2 and 11 µm. The hot dispersion was then allowed to cool down to below 217°C, and the solidified spherical SnAg3Cu0.5 alloy particles so formed settled under the influence of gravity. The solidified spherical SnAg3Cu0.5 alloy particles were separated from the liquid stressed castor oil by sieving.

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Example 1 (according to the invention): 8 L of chloroform were added to the separated SnAg3Cu0.5 alloy particles and the mixture was stirred for 40 minutes. Thereafter, the mixture was allowed to stand for 10 hours before the chloroform was drained. The rinsing cycle was repeated for a further 10 times with fresh chloroform each time. After draining the chloroform in the final rinsing cycle (11th rinsing cycle) the SnAg3Cu0.5 alloy particles were dried in a drying oven at 60°C under vacuum for 10 hours. Thereafter, the SnAg3Cu0.5 alloy particles were used to make a solder paste as described below.

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Example 2 (according to the invention): It was worked like in Example 1; however, with 6 L of chloroform instead of 8 L of chloroform and with a total of 15 rinsing cycles.

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Example 3 (according to the invention): It was worked like in Example 1; however, thereafter, the SnAg3Cu0.5 alloy particles were aged by storing at 55°C in the presence of air of 50% Relative Humidity for 16 days (equals storage at room temperature of 25°C in the presence of air of 50% Relative Humidity for 3 months).

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Example 4 (according to the invention): It was worked like in Example 1; however, thereafter, the SnAg₃Cu_{0.5} alloy particles were aged by storing at 55°C in the presence of air of 50% Relative Humidity for 31 days (equals storage at room temperature of 25°C in the presence of air of 50% Relative Humidity for 6 months).

Comparative Example 5: It was worked like in Example 1; however, thereafter, the SnAg₃Cu_{0.5} alloy particles were aged by storing at 55°C in the presence of air of 50% Relative Humidity for 63 days (equals storage at room temperature of 25°C in the presence of air of 50% Relative Humidity for 12 months).

Comparative Example 6: It was worked like in Example 1; however, with 2 L of chloroform instead of 8 L of chloroform and with only one rinsing cycle.

Comparative Example 7: It was worked like in Example 1; however, with 2 L of chloroform instead of 8 L of chloroform and with two rinsing cycles.

Comparative Example 8: It was worked like in Example 1; however, with a castor oil having an acid number of 4.5 mg KOH/g.

Comparative Example 9: It was worked like in Example 1; however, with a total of 30 rinsing cycles.

ToF-SIMS analyses of the surface regions of the spherical tin-based solder alloy powders of Examples 1 to 9 were performed as described above, i.e. a commercial instrument (PHI TRIFT II ToF-SIMS) was used employing a 15 keV Ga⁺ primary ion beam to acquire the secondary ion fragment signals over a scan area of 100 µm x 100 µm with a total scan time of 5 minutes. The relative signal intensity of the characteristic signals was calculated with reference to the signal of 297 amu.

Preparation of solder pastes:

A flux was formed by melting 45 pbw (parts by weight) of a hydrogenated rosin (hydrogenated colophonium resin) having an acid value of 240 mg KOH/g at 170°C, followed by addition of 28 pbw of ethylene glycol dimethyl ether, 12 pbw of a polyamide thickener, 5 pbw of succinic acid, 8 pbw of surfactant and 2 pbw of antioxidant at 140°C.

Nine solder pastes were prepared by mixing 15 pbw of the so prepared flux with 85 pbw of the SnAg3Cu0.5 alloy solder particles of Examples 1 to 9.

5 Solderability tests (solder ball tests):

The nine solder pastes were each printed onto 5 cm x 5 cm ceramic sheets. The printed pastes were soldered by heating in a reflow oven at an object temperature of 250°C in a nitrogen environment. After the solder pastes had melted, the ceramic substrates were removed and cooled.

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After the ceramic sheets had cooled down, an assessment of the solderability performance of each solder paste was made. To this end, the ceramic sheets were visually inspected under an optical microscope for any solder beads formed around the soldered paste.

15 Wetting tests:

The nine solder pastes were each printed onto 2.5 cm x 2.5 cm copper sheets. The printed pastes were soldered by heating in a reflow oven at an object temperature of 250°C in a nitrogen environment. After the solder paste had melted, the copper sheets were removed and cooled.

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After the copper sheets had cooled down, an assessment of the wetting performance of each solder paste was made. To this end, the copper sheets were visually inspected under an optical microscope for any de-wetting from the area originally printed.

25 The relative signal intensity of the characteristic negatively charged secondary ion fragments of the surface regions of the spherical tin-based solder alloy powders of Examples 1 to 9 as well as solderability and wetting performance of the nine solder pastes prepared therewith are listed in the following table. The signal of 297 amu serves as reference signal with an intensity of 1. Signals representing a deviation from a secondary ion mass spectrum comprising negatively
30 charged secondary ion fragments 113 amu with a relative signal intensity in the range of 0.7 to 3.1, 127 amu with a relative signal intensity in the range of 0.9 to 4.4, 136 amu with a relative signal intensity in the range of 1.4 to 6.7, 137 amu with a relative signal intensity in the range of 0.6 to 3.9, 152 amu with a relative signal intensity in the range of 1.3 to 12, 153 amu with a relative signal intensity in the range of 2.3 to 20,

183 amu with a relative signal intensity in the range of 0.6 to 16, 279 amu with a relative signal intensity in the range of 0.5 to 12, and 297 amu with a signal intensity of 1 are high-lighted in bold.

Examples	ToF-SIMS results									Solderability performance	Wetting performance
	Negatively charged secondary ion fragments (amu)										
	113	127	136	137	152	153	183	279	297		
1	0.8	1.7	1.7	0.6	1.3	2.5	1.0	1.1	1	++++	++++
2	0.7	0.9	1.4	1.2	1.4	2.3	0.6	0.6	1	++++	++++
3	0.9	1.5	2.9	1.5	3.1	5.1	0.9	0.9	1	++++	++++
4	1.0	1.6	4.4	3.8	4.3	6.9	1.0	1.0	1	+++	+
5	1.1	1.9	13	4.6	13	22	1.0	1.0	1	---	--
6	0.8	1.2	0.03	0.03	0.03	0.06	0.9	0.9	1	---	---
7	0.8	1.2	0.1	0.1	0.1	0.3	0.9	0.9	1	---	---
8	3.6	5.5	9.0	4.7	18	27	26	15	1	---	---
9	2.8	4.2	21	14	65	95	1.4	0.9	1	---	---

5 Definition of ratings:

Solderability performance:

'++++': 0 to <2 solder balls observed

'+++': 2 to 4 solder balls

'+' : Cluster of 5 to 8 solder balls

10 '--': Cluster of >8 to 20 solder balls

'---': Cluster of >20 solder balls, or remained unsoldered

Wetting performance:

'++++': No de-wetting observed

'+++': >0 to <5% de-wetting from originally printed area

15 '+' : 5 to 10% de-wetting from originally printed area

'--': >10 to 40% de-wetting from originally printed area

'---': >40% de-wetting from originally printed area

Claims

1. A tin-based solder alloy powder in the form of 2 to 38 μm small spherical tin-based solder alloy particles having an inorganic surface and a thin outer surface layer of stressed
5 castor oil,
wherein the inorganic surface plus the thin outer surface layer of stressed castor oil together form a surface region of the spherical tin-based solder alloy particles, and
wherein the surface region, when subjected to a ToF-SIMS analysis carried out with Ga^+ primary ions having an energy of 15 keV and with a total scan time of 5 minutes, exhibits a
10 secondary ion mass spectrum comprising the negatively charged secondary ion fragments 113 amu with a relative signal intensity in the range of 0.7 to 3.1,
127 amu with a relative signal intensity in the range of 0.9 to 4.4,
136 amu with a relative signal intensity in the range of 1.4 to 6.7,
137 amu with a relative signal intensity in the range of 0.6 to 3.9,
15 152 amu with a relative signal intensity in the range of 1.3 to 12,
153 amu with a relative signal intensity in the range of 2.3 to 20,
183 amu with a relative signal intensity in the range of 0.6 to 16,
279 amu with a relative signal intensity in the range of 0.5 to 12, and
297 amu with a signal intensity of 1.
- 20 2. The tin-based solder alloy powder of claim 1, wherein the tin-based solder alloy is a solder alloy comprising at least 42 wt.% of tin or a tin-rich solder alloy having a tin content of 90 to 99.5 wt.%.
3. The tin-based solder alloy powder of claim 1 or 2, wherein the stressed castor oil has an acid number in the range of 3 to 4 mg KOH/g.
- 25 4. The tin-based solder alloy powder of any one of the preceding claims, wherein the thin outer surface layer of stressed castor oil has a layer thickness in the range of 0.5 to 5.2 nm.
5. A process for the manufacture of a tin-based solder alloy powder in the form of 2 to 38 μm small spherical tin-based solder alloy particles having an inorganic surface and a thin outer surface layer of stressed castor oil, wherein the inorganic surface plus the thin outer surface
30 layer of stressed castor oil together form a surface region of the spherical tin-based solder alloy particles, the process comprising the successive steps:

(1) converting a hot mixture of a tin-based solder alloy melt and a stressed castor oil into a dispersion of molten spherical tin-based solder alloy particles within the stressed castor oil by subjecting the hot mixture to a rotor-stator process until a particle size in the range of 2 to 38 μm is obtained, wherein the ratio of the tin-based solder alloy melt to the stressed castor oil is in a range of 0.2 to 5 kilograms of the tin-based solder alloy melt per liter of the stressed castor oil,

(2) allowing the dispersed molten spherical tin-based solder alloy particles formed in step (1) to solidify within the stressed castor oil,

(3) separating the solidified spherical tin-based solder alloy particles from the stressed castor oil to obtain solid spherical tin-based solder alloy particles covered by residual stressed castor oil, and

(4) repeatedly rinsing and finally drying the solid spherical tin-based solder alloy particles until they have the surface region which, when subjected to a ToF-SIMS analysis carried out with Ga^+ primary ions having an energy of 15 keV and with a total scan time of 5 minutes, exhibits a secondary ion mass spectrum comprising the negatively charged secondary ion fragments 113 amu with a relative signal intensity in the range of 0.7 to 3.1, 127 amu with a relative signal intensity in the range of 0.9 to 4.4, 136 amu with a relative signal intensity in the range of 1.4 to 6.7, 137 amu with a relative signal intensity in the range of 0.6 to 3.9, 152 amu with a relative signal intensity in the range of 1.3 to 12, 153 amu with a relative signal intensity in the range of 2.3 to 20, 183 amu with a relative signal intensity in the range of 0.6 to 16, 279 amu with a relative signal intensity in the range of 0.5 to 12, and 297 amu with a signal intensity of 1, wherein a liquid composition consisting of 50 to 100 wt.% of at least one halogenated hydrocarbon solvent and of 0 to 50 wt.% of at least one organic solvent other than halogenated hydrocarbon solvents is used as rinsing fluid, wherein the wt.% total 100 wt.%.

6. The process of claim 5, wherein the tin-based solder alloy is a solder alloy comprising at least 42 wt.% of tin or a tin-rich solder alloy having a tin content of 90 to 99.5 wt.%.

7. The process of claim 5 or 6, wherein the stressed castor oil has an acid number in the range of 3 to 4 mg KOH/g.

8. The process of any one of claims 5 to 7, wherein the thin outer surface layer of stressed castor oil has a layer thickness in the range of 0.5 to 5.2 nm.

9. The process of any one of claims 5 to 8, wherein the liquid composition consists of at least one halogenated hydrocarbon solvent.

10. The process of any one of claims 5 to 9, wherein the repeatedly performed rinsing comprises 8 to 15 successive rinsing steps.
11. The process of any one of claims 5 to 10, wherein each of said successive rinsing steps
5 is performed by stirring the mixture of the rinsing fluid and the spherical tin-based solder alloy particles for a period in the range of 20 to 60 minutes and thereafter allowing the mixture to stand for the spherical tin-based solder alloy particles to sink within the rinsing fluid.
12. A solder paste comprising the tin-based solder alloy powder of any one of claims 1 to 4
10 or manufactured by the process of any one of claims 5 to 11.