

DESCRIPTION

SOLDER COMPOSITION, CONNECTING PROCESS WITH
SOLDERING, AND CONNECTION STRUCTURE WITH
5 SOLDERING

Technical Field

The present invention relates to a solder composition,
and particularly a solder composition in the form of a paste,
10 that is, a solder paste which is used, for example, for
solder-connecting an electronic part onto a substrate. In
addition, the present invention relates to a connecting
process as well as a connection structure with soldering
with using such solder composition, and particularly such
15 solder paste.

Background Art

A connecting process using soldering (that is, a
connecting process with soldering) is widely used as a
20 process for mounting an electronic part onto a substrate.
Such electronic part is mounted with a fine pitch. Thus,
when an amount of a solder material of a solder connection
portion is small, or when a sufficient bonding strength of
the solder connection portion is hardly ensured due to an
25 insufficient strength of a solder material itself, a solder-

connecting process is employed wherein the solder connection is reinforced by means of a reinforcing resin portion.

In order to form such reinforcing resin portion, a thermosetting resin such as an epoxy resin is often used, wherein a curing step is required so as to cure the thermosetting resin. When such curing is able to be carried out simultaneously in a reflow step wherein a solder connection portion is formed, it would be convenient since a connecting process with soldering becomes simpler. Therefore, in mounting the electronic part onto the substrate, a so-called "resin pre-application" may be employed wherein a connection material containing a thermosetting resin which is to form the resin reinforcing portion is applied to a portion where the electronic part is to be mounted before mounting the electronic part.

As a connection material which is used for the above "resin pre-application", a thermosetting flux has been proposed which comprises a thermosetting resin, and also a solder paste has been proposed wherein solder particles (or solder powder) is contained in the thermosetting flux (see, for example, Patent Reference 1 indicated below). It is said that using such solder paste is advantageous in that the solder connection portion and also the reinforcing resin portion are both formed simultaneously between electrodes

in a single step without supplying a solder material separately.

Patent Reference 1: Japanese Patent Kokai Publication No. 2001-219294

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Disclosure of the Invention

The present inventors have found that even the connecting process with soldering, wherein the above solder paste which contains the solder particles in the thermosetting flux is used, does not readily provide a desired connection structure with soldering. Particularly, it is difficult to achieve a connection structure with soldering having a sufficient bonding strength. Thus, objects of the present invention are to provide a novel solder composition, and particularly such composition in the form of a paste which is able to provide a connection structure with soldering having a sufficient bonding strength, also to provide a connecting process with soldering wherein such solder composition is used, and further to provide a connection structure with soldering which is formed by using such solder composition.

After intensive studies by the present inventors as to the above objects, the following have been found:

When the solder paste wherein the solder particles are mixed in the known thermosetting flux as described above

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is used, it is difficult in a reflow step to fluidize (or move) molten solder particles as desired, which makes it difficult to form a connection structure with soldering having a sufficient bonding strength. In detail, the solder particles are melted by means of heating for the formation of the connection structure with soldering in the reflow step, but on the other hand, such heating have a curing reaction of the thermosetting resin proceed simultaneously. The thermosetting resin which is under such curing reaction prevents the movement (or flowing) of the molten solder particles, and as a result, it becomes difficult for the molten solder particles to contact with and to be integrated with other molten solder particles.

Particularly, when the curing of the thermosetting resin proceeds prior to the melting initiation of the solder particles, movement of the molten solder particles is prevented by the thermosetting resin which has already started to gel, which interferes the self-alignment effect of the molten solder particles, so that the molten solder material may not spread over surfaces of an electrode which is an object to be connected. As a result, the solder material solidifies without sufficiently connecting the electrode, which means that no normal connecting is carried out (that is, no appropriate solder connection portion is formed), which causes defects such as an electric

conduction fault.

The present inventors have further intensively studied the formation of the appropriate solder connection portion by integrating the molten solder particles which move to
5 gather together even when the curing reaction of the thermosetting resin is proceeding, and have concluded that coexistence of other material in the solder paste is effective which material is able to suppress the prevention of moving of the molten solder particles by the
10 thermosetting resin which is under curing. Further additional studies thereafter have found that, as said other material, a solid resin, particularly a thermoplastic resin is suitable which is characterized in that it changes to be in a liquid-like state when heated for the purpose of connecting
15 with soldering, and that such change precedes the initiation of curing of the thermosetting resin, that is, a temperature at which the solid resin changes to be in the liquid-like state is lower the curing initiation temperature of the thermosetting resin with a proviso that such solid resin
20 excludes a thermosetting resin, according to which the present invention has been completed.

Said other material as described above provides an effect in that said material suppresses the prevention of the movement of the molten solder particles regardless of the
25 presence of the thermosetting resin which is under curing,

and such effect may be likened to the provision of plasticity to the thermosetting resin which is under curing while it is losing its fluidity or flowability, and therefore in the sense of the above provision, said other material which provides
5 with such effect may be said to be a kind of a plasticizer.

The present invention, therefore, provides a solder composition which comprises:

- (1) a metal material comprising solder particles, and
- (2) a thermosetting flux material comprising a
10 thermosetting resin and a solid resin which changes (or transforms) to be in a liquid-like state when heated with a proviso that the thermosetting resin is excluded from the solid resin,

wherein a temperature at which the solid resin
15 changes to be in the liquid-like state is lower than a temperature at which the thermosetting resin starts to cure.

The solder composition according to the present invention is preferably in the form of a paste at normal temperature, and such preferable composition may be said
20 to be a solder paste. Thus, the solder composition according to the present invention may optionally further comprise, in addition to the metal material and the thermosetting flux material, a component which is required to have the solder composition be in the paste form, for
25 example a solvent (such as butyl carbitol, hexyl carbitol,

methylecarbitol, and diethylecarbitol). The solder paste is advantageous in that its application to an object to be connected (such as an electrode) is easy, and another object to be connected (such as an electronic part) may be tentatively bonded to the applied solder paste using tackiness of the solder paste.

The solder composition such as a solder paste according to the present invention comprises the metal material and the thermosetting resin material. The metal material comprises at least the solder particles and it may further comprise other metal component. The thermosetting resin material comprises the thermosetting resin and the solid resin (excluding the thermosetting resin), and it may further comprise other component(s) as described below if necessary. The solid resin is in its solid state at normal temperature (which corresponds a temperature at which the solder composition is applied to the object, and usually in the range between 10 °C and 40°C), and has a property that it becomes in its liquid-like state when it is heated so as to melt the solder particles.

The solder composition according to the present invention may be produced by mixing the metal material and the thermosetting flux material, and each material may be produced by mixing components which constitute each material. Such mixing may be carried out in any

appropriate manner, and it is desirable as to the thermosetting flux material that the curing of the thermosetting resin does not start during mixing. It is noted that said other metal component or said other
5 component as described above may be mixed to be contained by the metal material or the thermosetting flux material respectively, or said other metal component or said other component may be contained together by a mixture of the metal material and the thermosetting flux
10 material upon mixing them to form such mixture. As said other component, the following may be exemplified: a component which makes the solder composition to be in the paste form (e.g. a solvent), a curing accelerator, and said other metal component.

15 The solder particles used for the solder composition according to the present invention may be any appropriate particles as far as they form the solder composition according to the present invention as described in the present specification. For example, they may be particles
20 of a metal, usually an alloy which is readily melted such as a so-called solder material, and a so-called lead-free solder material which does not contain a lead component. Concretely, the following solder materials may be exemplified: Sn-Ag-Cu, Sn-Ag, Sn-Cu, Sn-Bi, Sn-Zn, Sn-
25 Ag-Bi-In, Sn-Ag-Cu-Bi and so on. It is noted that the size

and the form of the solder particles are not particularly limited. For example, solder particles or solder powder which are commercially available, and particularly those which are commercially available for the electrically
5 conductive adhesives or the solder pastes may be used as the solder particles for the solder composition according to the present invention.

The thermosetting resin used in the solder composition according to the present invention may be any appropriate
10 one as far as it forms the solder composition according to the present invention as described in the present specification. Known thermosetting resins which are generally known to be used for the electrically conductive adhesives, the solder pastes or the like may be used. For
15 example, the following resins may be exemplified: an epoxy resin, an acrylic resin, a urethane resin, a phenol resin, a urea resin, a melamine resin, an unsaturated polyester resin, an amine resin, a silicone resin and the like. The thermosetting resin used for the solder
20 composition according to the present invention preferably comprises a main agent (or main ingredient) and a curing agent, and optionally, the thermosetting resin may further comprises a curing accelerator, and it is usually preferable that it comprises the curing accelerator.

25 The solid resin used in the solder composition

according to the present invention may be any appropriate one as far as it forms the solder composition according to the present invention as described in the present specification, and it preferably comprises a thermoplastic resin. For example, the following resins may be exemplified: a terpene resin, a xylene resin, an amorphous rosin, an olefin resin, an acrylic resin, an amide resin, a polyester resin, a styrene resin, a polyimide resin, a fatty acid derivative wax, a highly polymerized rosin, a fatty acid amide and the like.

The above mentioned "(the solid resin) is characterized in that it changes to be in a liquid-like state when heated" means that the solid resin in its solid state is changed (or transformed) to be in its liquid-like state through heating which melts the solder particles contained in the solder composition according to the present invention for the purpose of forming a connection structure with soldering. Such change may occur simultaneously with melting of the solder particles, and it is preferable that the change of the solid resin from its solid state to the liquid-like state is prior to the melting of the solder particles. In other embodiment, the melting of the solder particles may occur earlier than the change. It is noted that the present invention determines that the melting of the solder particles occurs when the solder particles are heated to a liquidus

curve temperature of a solder material of which the solder particles are made (or a eutectic temperature in the case of a eutectic solder material).

With the solder composition according to the present invention, the change of the solid resin from its solid state to its liquid-like state occurs prior to the initiation of curing of the thermosetting resin, that is, the temperature at which the state of the solid resin changes to its liquid-like state is lower than the temperature at which the thermosetting resin starts to cure. In the present specification, the temperature at which the thermosetting resin starts to cure means a so-called cure initiation temperature. Such temperature is obtained by subjecting the thermosetting resin (including a curing agent and a curing accelerator if any) to the DSC measurement. Particulars as to the measurement can be seen from JIS K7121, which is incorporated by reference in their entity. Particularly, a temperature vs. calorie curve is obtained by the DSC measurement while a sample is heated, and the curing initiation temperature is defined as a temperature at which the curve starts to get away from a baseline of the curve. Such curing initiation temperature may be set variously by changing kinds of the main agent, the curing agent and the curing accelerator if any and/or a composition of them, and thus set curing initiation temperature may be determined by the method according to

the above mentioned JIS.

In the present specification, the term "liquid-like" state is used to include not only the true liquid state but also a state which can be regarded as the liquid state. As far as
5 the solder composition according to the present invention is constituted, a viscosity of the solid resin which is in the liquid-like state (i.e. the liquid state solid resin) may be high. Thus, the term "liquid-like" state is used so as to include a state which is very flowable like water, an organic
10 solvent or the like as well as a state which is so viscous that it is generally not included within a concept of a usual liquid.

In a preferable embodiment, whether or not the solid resin is changed to be in the "liquid-like" state is
15 determined by a softening temperature (or softening point) of the solid resin as a measure which is measured by the softening temperature testing method (a ring-and-ball method as defined in JIS K2207, which is incorporated by reference in their entity). That is, it has been found
20 preferable to determine that, in the case wherein the solid resin heated, when the temperature of the solid resin is equal to or above the softening temperature of the solid resin, the solid resin is in the liquid-like state, and on the other hand, when the temperature of the heated solid resin
25 is below the softening temperature of the solid resin, the

solid resin is still in the solid state. In this embodiment, when the solid resin is heated, the softening temperature of the solid resin can be regarded to be a transition temperature from the solid state to the liquid-like state of the solid resin.

Thus, in a particularly preferable embodiment of the present invention, which of the melting of the solder particles and the change of the solid resin from the solid state to the liquid-like state occurs first is determined based on which of the liquidus curve temperature of the solder material forming the solder particles (or the eutectic temperature in the case of a eutectic solder material) and the softening temperature of the solid resin is lower. In one preferable embodiment according to the present invention, the liquidus curve temperature of the solder material of which the solder particles are made (or the eutectic temperature in the case of a eutectic solder material) is preferably equal to or higher the softening temperature of the solid resin, and the former temperature is higher than the latter temperature more preferably by at least 10°C, and particularly preferably by at least 20°C. In these preferable embodiments, the change of the solid resin to be in the liquid-like state occurs prior to the melting of the solder particles.

In the present invention, similarly to the above, which

of the initiation of the curing of the thermosetting resin and the change of the solid resin from the solid state to the liquid-like state occurs first is preferably determined based on which of the curing initiation temperature of the thermosetting resin and the softening temperature of the solid resin is lower. As described above, it is preferable that the change of the solid resin from the solid state to the liquid-like state occurs earlier than the initiation of the curing of the thermosetting resin, so that the curing initiation temperature of the thermosetting resin is higher than the softening temperature of the solid resin. For example, the curing initiation temperature of the thermosetting resin is higher than the softening temperature of the solid resin preferably by at least 10°C, more preferably by at least 20°C, and particularly preferably by at least 30°C. It is noted that the curing initiation temperature is measured according to JIS K7121 as described above.

When the curing initiation temperature of the thermosetting resin is higher than the softening temperature of the solid resin, an extent to which the flowability of the molten solder particles is prevented in the reflow step by means of the thermosetting resin contained in the solder composition which is under curing is lowered, so that good connection with soldering becomes possible.

In this embodiment, it is preferable that the liquidus curve temperature of the solder material for the solder particles is equal to or above the softening temperature of the solid resin.

5 It is noted that the solid resin is preferably compatible with thermosetting resin, particularly with the main agent thereof, wherein it is possible to form the solder paste having a sufficient flowability without using any volatile solvent when the solid resin is mixed into the thermosetting
10 resin, particularly the main agent thereof. As a result, a problem(s) due to using the solvent such as deposition of its gas onto a reflow apparatus which gas is formed from the solvent, contamination of an apparatus atmosphere by means of such gas, and the like may be alleviated or
15 deleted.

 In the solder composition according to the present invention, it is preferable that the thermosetting flux material has an activity which removes an solder oxide film. In this embodiment, the thermosetting resin and/or the solid
20 resin may have such activity. As the thermosetting resin having such activity, for example the epoxy resin, the acrylic resin, the phenol resin, and the amine resin may be exemplified. As the solid resin having such activity, for example the xylene resin and the amorphous rosin may be
25 exemplified. In other embodiment, the thermosetting flux

material may comprise a component having such activity (i.e. an activator) separately from the thermosetting resin and the solid resin. As such separate component, for example m-hydroxybenzoic acid, measaconic acid, o-hydroxycinnamic acid, usnic acid, 3, 4-dihydroxybenzoic acid, hippuric acid, and succinic acid may be exemplified. Such activator may not be added to the thermosetting flux material, but may be added into the solder composition separately.

10 The solder composition according to the present invention contains, based on the total weight of the solder composition,

preferably 70 to 92 % by weight, more preferably 75 to 90 % by weight, and particularly 80 to 85 % by weight of the metal material, and

preferably 8 to 30 % by weight, more preferably 10 to 25 % by weight, and particularly 15 to 20 % by weight of the thermosetting flux material.

20 The thermosetting flux material contains, based on the total weight of the thermosetting flux material,

preferably 30 to 50 % by weight, more preferably 35 to 50 % by weight, and particularly 40 to 50 % by weight of the main agent,

25 preferably 30 to 50 % by weight, more preferably 35 to 50 % by weight, and particularly 40 to 50 % by weight of

the curing agent, and

preferably 2 to 20 % by weight, more preferably 2 to 15 % by weight, and particularly 5 to 15 % by weight of the solid resin.

5 In addition, the thermosetting flux material may further contain the curing accelerator, in which preferably 1 to 3 % by weight, more preferably 1 to 2.5 % by weight, and particularly 1 to 1.5 % by weight of the curing accelerator is contained based on based on the total weight of the
10 thermosetting flux material. Further, the thermosetting flux material may contain the solvent, in which not larger than 5 % by weight, more preferably 0.5 to 3 % by weight, and particularly 0.5 to 1 % by weight of the curing accelerator is contained based on based on the total weight of the
15 thermosetting flux material. Also, the thermosetting flux material may further contain the activator, in which preferably 3 to 10 % by weight, more preferably 4 to 9 % by weight, and particularly 5 to 7 % by weight of the activator is contained based on the total weight of the thermosetting
20 flux material.

The present invention also provides a connecting process with soldering wherein a first electrode such as a connection electrode of an electronic part (hereinafter, a term "connection electrode" is used generically for the
25 purpose of simplicity) is connected with soldering to a

second electrode such as a circuit electrode of a substrate (hereinafter, a term "circuit electrode" is used generically for the purpose of simplicity).

Such connecting process with soldering comprises the
5 steps of:

locating the solder composition, preferably the solder paste according to the present invention as described above or below between the connection electrode and the circuit electrode;

10 heating to melt the solder particles (for example, by heating the substrate) wherein the solid resin is changed into its liquid-like state while the curing reaction of the thermosetting resin is made proceed; and

solidifying thus changed solid resin and the molten
15 solder material (for example, by cooling the substrate, which may be done by returning the substrate temperature to normal temperature wherein the already cured thermosetting resin is also cooled).

When the solder particles are melted as described
20 above, the molten solder particles gather together while moving to be integrated, so that they form a solder connection portion which electrically connects the connection electrode and the circuit electrode. Therefore, the present invention provides a process for producing the
25 substrate onto which the electronic part is mounted wherein

the electronic part is connected to the substrate with using the solder composition according to the present invention.

Further, the present invention provides a connection structure with soldering which electrically connects the first
5 electrode and the second electrode (for example, the connection electrode and the circuit electrode, respectively), which structure is formed by the above described connecting process with soldering. Such connection structure with soldering is formed by locating
10 the solder composition, preferably the solder paste according to the present invention as described above or below between the first electrode and the second electrode; changing the solid resin into its liquid-like state while the curing reaction of the thermosetting resin is made proceed
15 upon melting the solder particles (for example, by heating the substrate); and then solidifying the solid resin in the liquid-like state and the molten solder material (for example, by cooling the substrate). The connection structure with soldering comprises a solder connection portion which is
20 formed between the first electrode and the second electrode and a reinforcing resin portion made of the cured thermosetting resin and the solidified solid resin wherein the reinforcing resin portion covers at least a portion of a surface of the solder connection portion.

Effect of the Invention

The solder composition or the connecting process with soldering according to the present invention suppresses the prevention, due to the thermosetting resin which is under gelling, of the flowability of the solder particles in their molten states in the reflow step, which prevention in turn interferes the self-alignment effect of the solder material, so that the flowability of the solder particles is more sufficiently ensured, whereby the solder connection portion which is in a more appropriate form and which has a sufficient bonding strength may be formed. As a result, the connection structure with soldering which is formed by such solder composition and such connecting process with soldering has the appropriate solder connection portion.

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Brief Description of Drawings

Fig. 1 shows steps of a process of mounting an electronic part onto a substrate which process is one embodiment of the connecting process with soldering according to the present invention.

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Fig. 2 shows a cross-sectional view of a connection structure with soldering of one embodiment according to the present invention.

Fig. 3 shows an example of a defect which is caused when using the conventional solder paste.

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In the drawings, numerals indicate the following elements:

- 1 ... substrate, 2 ... electrode, 3 ... solder paste,
- 4 ... electronic part,
- 5 5 ... connection structure with soldering,
- 5a ... solder connection portion,
- 5b ... reinforcing resin portion

Embodiments for Carrying Out the Invention

10 In the solder composition according to the present invention, an amount of the metal material is preferably 70 to 92 % by weight based on the total weight of the solder composition, and the balance may be the thermosetting flux material. Substantially all of the metal material may be the
15 solder particles, and in other embodiment, a portion of the metal material may be other metal component, particularly powder of said other metal component as described below.

Upon carrying out a connection process with soldering while using the solder composition according to the present
20 invention, when heating to a rather higher temperature is allowable, for example particles of a solder material based on Sn (tin)-Ag (silver)-Cu (copper) (of which liquidus curve temperature is about 220 °C) may be used for the solder composition according to the present invention. On the
25 other hand, when the heating temperature is required to be

as low as possible, for example, particles of a solder material based on Sn (tin)-Bi (bismuth) (of which liquidus curve temperature is about 139 °C) may be used for the solder composition according to the present invention.

5 It is noted that the metal material may include, in addition to the solder particles, metal powder of for example Ag (silver), Pd (palladium) and/or Au (gold). Such metal powder may preferably be in the form of flakes or particles, and the metal powder may be particularly in the
10 form of fine foil elements (or fine flake elements). Such metal powder may be contained in an amount of 0.5 to 10 % by weight, and preferably 0.5 to 5 % by weight based on the total weight of the metal material of the solder composition so that connecting with soldering is improved. The above
15 mentioned metals for such metal powder have a melting point which is higher than the used solder material, are unlikely to form an oxide film in the atmosphere, and help the molten solder material in its flowable state flow over the metal powder, so that the metal powder provides nuclei
20 around which molten solder particles gather, whereby the wetting property of the solder material is improved. When using the Sn-Bi solder material, 1 to 3 % by weight of Ag (silver) (which is preferably in the form of particles) may be included by the metal material based on the total weight of
25 the metal material, and such inclusion of silver is able to

improve the bonding strength of the solder connection portion.

The thermosetting resin which forms the solder composition according to the present invention may be any appropriate one as described above. Thus, those skilled in the art are able to select an appropriate thermosetting resin based on the disclosure of the present specification, and no additional explanation is required. In one example wherein an epoxy resin is used as the main agent, the following main agent, curing agent and curing accelerator may be used to obtain a thermosetting flux material. It is noted that the unit "% by weight" is based on the total weight of the thermosetting flux material.

· Main Agent (for example 30 to 40 % by weight):

hydrogenated bisphenol A epoxy resin

(3, 4-epoxycyclohexyl)methyl 3', 4'-epoxycyclohexyl-carboxylate (commercially available as CELLOXIDE 2021P from Daicel Chemical Industries, Ltd.)

bisphenol F epoxy resin

bisphenol A epoxy resin

· Curing Agent (for example 30 to 40 % by weight):

methyl cyclohexene-dicarboxylic anhydride

(tetrahydromethylphthalic anhydride)

methylhexahydrophthalic anhydride

· Curing Accelerator (for example 1 to 2 % by weight):

2-phenyl-4-methyl-5-hydroxymethyl imidazole

2-phenyl-4, 5-dihydroxymethyl imidazole

In addition to the above three components, the thermosetting resin or the thermosetting flux material may contain the activator (for example 3 to 10 % by weight), the solvent (for example up to 5 % by weight) or the like.

Thus, those skilled in the art are able to prepare an appropriate thermosetting flux material which forms the solder composition according to the present invention based on the disclosure of the present specification, and no additional explanation is required. In one example wherein the epoxy resin is used, the following formulation may be used for the thermosetting flux material. It is noted that the unit "% by weight" is based on the total weight of the thermosetting flux material.

- Main Agent (for example 30 to 40 % by weight):

hydrogenated bisphenol A epoxy resin

- Curing Agent (for example 30 to 40 % by weight):

tetrahydromethylphthalic anhydride

- Curing Accelerator (for example 1 to 2 % by weight):

2-phenyl-4-methyl-5-hydroxymethyl imidazole

- Activator (for example 3 to 10 % by weight):

m-hydroxybenzoic acid

- Solvent (for example up to 5 % by weight)

butyl carbitol

· Solid Resin (for example 3 to 20 % by weight):

alkylphenol modified xylene resin

The above thermosetting resin has a curing initiation temperature above 70°C when blended according to the
5 above formulation. Therefore, when an alkylphenol modified xylene resin having a softening temperature of 70°C is used as the solid resin, the softening temperature of the solid resin is lower than the curing initiation temperature.

10 The following are to be noted:

In place of the hydrogenated bisphenol A epoxy resin, (3, 4-epoxycyclohexyl)methyl 3', 4'-epoxycyclohexyl-carboxylate, a bisphenol F epoxy resin or a bisphenol A epoxy resin may be used as the main agent.

15 In place of tetrahydromethylphthalic anhydride, methylhexahydrophthalic anhydride may be used as the curing agent.

In place of 2-phenyl-4-methyl-5-hydroxymethyl imidazole, 2-phenyl-4, 5-dihydroxymethyl imidazole may be
20 used as the curing agent.

In place of m-hydroxybenzoic acid, measaconic acid may be used as the activator.

In place of the alkylphenol modified xylene resin, a fatty acid amide or a highly polymerized rosin may be used
25 as the solid resin.

In place of butyl carbitol, methyl carbitol may be used as the solvent.

Amounts of the above alternatively usable components may be the same as those of the components to be replaced.

5 When an acid anhydride is used as the curing agent, the addition of the activator may be omitted since the acid anhydride has an activity to remove a solder oxide film.

When the solder composition according to the present invention contains the particles of a lead-free solder
10 material, the following formulations are recommendable as one examples of the thermosetting flux material:

In the case wherein the Sn-Ag-Cu solder material (liquidus curve temperature: 220°C) is used,

15 Weight Ratio of metal material (whole of which may be the solder particles) to thermosetting flux material = 8: 1

Main Agent: hydrogenated bisphenol A epoxy resin (38 % by weight)

Curing Agent: tetrahydromethylphthalic anhydride
20 (38 % by weight)

Curing Accelerator: 2-phenyl-4-methyl-5-hydroxymethyl imidazole (1 % by weight)

Curing Initiation Temperature of Thermosetting Resin:
151°C

25 Activator: m-hydroxybenzoic acid (10 % by weight)

Solid Resin: highly polymerized rosin (softening temperature: 140°C) (13 % by weight)

Note: The unit "% by weight" is based on the total weight of the thermosetting flux material.

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In the case wherein the Sn-Bi solder material (liquidus curve temperature: 139°C) is used,

Weight Ratio of metal material (whole of which may be the solder particles) to thermosetting flux material = 8: 1

10 Main Agent: hydrogenated bisphenol A epoxy resin (38 % by weight)

Curing Agent: tetrahydromethylphthalic anhydride (38 % by weight)

15 Curing Accelerator: 2-phenyl-4-methyl-5-hydroxymethyl imidazole (1 % by weight)

Curing Initiation Temperature of Thermosetting Resin: 151°C

Activator: m-hydroxybenzoic acid (10 % by weight)

20 Solid Resin: alkylphenol modified xylene resin (softening temperature: 120°C) (13 % by weight)

Note: The unit "% by weight" is based on the total weight of the thermosetting flux material.

25 Next, the present invention will be explained with reference to the drawings by means of one example wherein

an electronic part is connected to a circuit substrate, and particularly the electronic part is mounted onto the circuit substrate by connecting a connection electrode of the electronic part to a circuit electrode of the substrate.

5 Fig. 1 schematically shows the steps of a process of mounting an electronic part by means of the connecting process with soldering according to the present invention when viewing from a side of the electronic part. It is noted that in Fig. 1(d), only a connection structure with soldering
10 is shown in its cross-sectional view. Fig. 2 schematically shows, in a cross-sectional view, a connection structure with soldering as one embodiment according to the present invention. Fig. 3 shows an example of a defect which is caused through a connecting process with soldering
15 wherein the conventional solder paste is used.

 First, with referring to Fig. 1, the process of mounting the electronic part is explained which process is one embodiment of the connecting process with soldering according to the present invention. The mounting process
20 uses the solder composition according to the present invention as described above and below is used as a solder paste, and mounts the electronic part onto the substrate by solder-connecting the connection electrode of the electronic part to the circuit electrode which is formed on the
25 substrate.

Referring to Fig. 1(a), the circuit electrode 2 (hereinafter, referred to as merely "electrode 2") is formed on the substrate 1. The connection electrodes 4 of the electronic part 4 which is to be mounted onto the substrate 1 are solder-connected to the electrodes 2 respectively. Prior to placing the electronic part 4 on the substrate, the solder paste 3 is applied to surfaces of the electrodes 2 as shown in Fig. 1(b). For the application of the solder paste 3, any known appropriate application manner such as screen printing, application with using a dispenser or the like may be used.

Then, the electronic part 4 in the form of a chip is placed on the substrate 1. That is, leads 4a as the connection electrodes which are present at the both ends of the electronic part 4 are aligned with the electrodes 2, and the leads 4a are placed down on the solder paste 3 on the electrodes 2 as shown in Fig. 1(c). By such placing down, the electronic part 4 is tentatively bonded due to the tackiness of the solder paste 3. Thereafter, the substrate 1 onto which the electronic part 4 has been mounted is passed to a reflow apparatus, in which the substrate is heated to a temperature which is equal to or above the liquidus curve temperature of the solder material forming the solder particles in the solder paste 3. By means of such heating, the solder particles in the solder paste 3 are

melted and moved so as to gather together and thereby a solder connection portion is formed as shown in Fig. 1(d) while the solid resin is changed to be in the liquid-like state followed by the curing of the thermosetting resin, whereby a reinforcing resin portion is formed.

Thereafter, the substrate 1 is removed out from the reflow apparatus so as to return it to be in normal temperature, and thereby the solid resin which has been changed into its liquid-like state and the molten solder material which has been made from the solder particles are cooled to be solidified. In this way, the solder connection portion 5a is formed in the form of an appropriate fillet which connects the electrode 2 and the lead 4a (see Fig. 2). Thus, using the solder paste 3, the connection structure with soldering 5 is formed wherein the lead 4a as the connection electrode of the electronic part 4 and the electrode 2 of the substrate 1 are connected with soldering.

Since the solid resin of the thermosetting flux material contained in the solder composition 3 changes to its liquid-like state when the solder particles are melted as described above, the thermosetting flux material prevents the flowability of the molten solder particles not so severely even though it is heated to such a temperature that the solder particles are melted. As a result, the prevention of the self-alignment effect of the molten solder material is

suppressed, so that an appropriate solder connection portion is formed. After the completion of such connecting with soldering, by means of the completion of curing of the thermosetting resin and the solidification of the solid resin
5 by being cooled to normal temperature which resin has once been in the liquid-like state in the thermosetting flux material, the cured thermosetting resin and thus solidified solid resin become in a sufficiently rigid state, which functions as the reinforcing resin portion 5b which covers
10 at least a portion of a surface of the solder connection portion 5a and reinforces the solder connection portion 5a.

Such connection structure with soldering 5 is formed by placing the solder paste 3 between the electrode 2 and the lead 4a followed by heating the substrate 1 so as to
15 melt the solder particles, and then cooling the substrate. The structure includes as shown in Fig. 2 the solder connection portion 5a which is formed between the electrode 2 and the lead 4a, and the reinforcing resin portion 5b which is formed of the thermosetting resin cured
20 by being heated and the solid resin solidified by being cooled. The reinforcing resin portion 5b covers at least a portion of, preferably most of, and more preferably substantially all of the surface of the solder connection portion.

25 The connecting process with soldering as described

above comprises the step of placing the solder paste 3 having the above described composition between the electrode 2 and the terminal 4a, the step of heating the substrate 1 so as to melt the solder particles wherein the curing reaction of the thermosetting resin is made proceed while the solid resin is changed into its liquid-like state, and the step of solidifying thus changed solid resin and the molten solder material by cooling the substrate 1 to normal temperature. In the above heating step, it is particularly preferable that the change of the solid resin into its liquid-like state occurs prior to the melting of the solder particles and the curing initiation of the thermosetting resin. In this particularly preferable embodiment, it is more preferable that the melting of the solder particles precedes the curing initiation of the thermosetting resin. That is, it is most preferable that the change of the solid resin into its liquid-like state occurs first, the melting of the solder particles occurs second, and the curing initiation of the thermosetting resin occurs last.

It is noted that the present invention, in its broadest sense, resides in that, not only the presence of the solid resin in the solder composition, but also the occurrence of its change to be in its liquid-like state at a temperature which is lower than the curing initiation temperature of the thermosetting resin provides the appropriate solder

connection portion covered with the reinforcing resin portion in the connection structure with soldering.

Using the above described connecting process with soldering according to the present invention suppresses the occurrence of the insufficient connection which is likely to be formed when using the conventional solder paste for mounting a similar electronic part 14. For example, Fig. 3 schematically shows, in a cross-sectional view, an example of the electric conduction fault in the connection structures with soldering formed when a lead 14a of the electronic part 14 is connected to an electrode 12 by using the conventional solder paste wherein solder particles of an Sn-Bi lead-free solder material are contained while no solid resin as described above is contained therein and the curing of the thermosetting resin tends to start excessively earlier than the melting of the solder particles.

Referring to Fig. 3(a), the conventional solder paste 13 is supplied onto the electrode 12 on the substrate 11, and a lead 14a of the electronic part 14 to be mounted is placed on such solder paste 13. In the reflow step, the solder particles contained in the solder paste 13 are melted by being heated while the curing of the thermosetting resin proceeds. When the curing initiation of the thermosetting resin is excessively earlier than the melting of the solder particles, the solder particles are melted in the

thermosetting resin which has already started its gelation and is under gelling.

Thus, the free movement of the molten solder particles is prevented, so that the molten solder particles do not
5 gather and grow sufficiently to wet surfaces of both of the electrode 12 and the lead 14a. As a result, although a portion of the molten solder particles 13a gather and spread over the surface of the electrode 12, the remaining portion of the molten solder particles are kept dispersed in
10 the flux material 13b in the form of small solder balls 13a or in the form of agglomerates 13a of some small solder balls as shown in Fig. 3(b). In such situation, since the lead 14a is supported by the flux material 13b which is gelling, there is no going down of thus supported lead 14a
15 toward the electrode 12 which is required for the formation of a normal connection with soldering. Thereafter, when such reflow step is continued, no normal connection with soldering which encloses the lead 14a is formed although a portion of the molten solder particles gather to form a
20 solder material portion 13a over a surface of the electrode 12, so that there may occur the electric conduction fault in which the electrode 12 and the lead 14a are not connected at all.

Contrary to the above, using the solder composition in
25 which the solid resin is contained in the thermosetting flux

material and the softening temperature of the solid resin is lower than the curing initiation temperature of the thermosetting resin according to the present invention provides the following effects: In the reflow step, even
5 when the liquidus curve temperature of the solder material for the solder particles is higher than the curing initiation temperature of the thermosetting resin, the effect of the thermosetting resin which has already started its curing and is under curing may be alleviated by the solid resin which
10 was already in the liquid-like state since the softening (and thus the change into the liquid-like state) of the solid resin occurs before the curing initiation of the thermosetting resin,

Therefore, when the liquidus curve temperature of the
15 solder material for the solder particles is lower than the curing initiation temperature, no solder particles of such solder material are not melted in the thermosetting resin which has started its curing and is in under gelling, or when the liquidus curve temperature of the solder material for the
20 solder particles is higher than the curing initiation temperature, the degradation of the self-alignment effect due to the prevention of the movement of the molten solder particles by means of the gelling thermosetting resin is suppressed. Thus, the occurrence of the defects such as
25 the electric conductive fault may be prevented which is

caused by the molten solder material which has not sufficiently extended between the electrodes so that the objects to be connected have not been electrically connected followed by the solidification of such solder material.

Further, after the reflow step, the solder connection portion is covered by the reinforcing resin portion which is formed by solidifying the changed solid resin through cooling which solid resin remains compatibilized with the cured thermosetting resin, so that a brittle solder connection portion having a less bonding strength is reinforced which portion is formed by using a lead-free solder material having a lower melting point, whereby connection reliability of the solder connection portion is able to be ensured.

According to the connecting process with soldering of the present invention, in the connecting process so-called "resin pre-application" which beforehand applies, to an object to be connected, a connection material containing a thermosetting resin for the formation of the reinforcing resin portion, the solder composition is used as described above which comprises the metal material containing the solder particles and the thermosetting flux material containing the solid resin having a temperature at which it changes to be in the liquid-like state (preferably the

softening temperature of the solid resin) is lower than the curing initiation temperature of the thermosetting resin. Thus, the occurrence of the defects such as the electric conductive fault may be prevented. Such fault occurs when
5 the thermosetting resin has started to cure excessively earlier than the melting of the solder particles and such molten solder material has not sufficiently extended between the electrodes as the objects to be connected, followed by the solidification of such solder material while
10 they have remained electrically unconnected.

Examples

Production of Solder Paste

Various solder compositions as the solder pastes were
15 prepared by mixing components in various formulations as shown in Table 1 below. It is noted that each component of the formulations is indicated in a unit of "parts by weight" in Table 1. The following are to be noted:

As the main agent, a hydrogenated bisphenol A epoxy
20 resin was used.

As the curing agent, tetrahydromethylphthalic anhydride was used.

As the curing accelerator, 2-phenyl-4-methyl-5-hydroxymethyl imidazole was used.

25 As the activator, m-hydroxybenzoic acid was used.

As the solid resin, an alkylphenol modified xylene resin (commercially available from Fudow Co., Ltd., trade name: Nikanol HP-70, softening temperature: 70°C) in Examples 1 to 3, while an alkylphenol modified xylene resin
5 (commercially available from Fudow Co., Ltd., trade name: Nikanol HP-150, softening temperature: 150°C) in Comparative Examples 1 to 3

First, the solid resin and the epoxy resin as the main agent were heated and mixed at a temperature above the
10 softening temperature of the solid resin.

To thus resulted mixture, the acid anhydride as the curing agent, the curing accelerator, the activator and the solvent were blended and kneaded together at a room temperature to obtain the thermosetting flux material. A
15 planetary mixer or rolls were used for such kneading. The curing initiation temperature of the thermosetting resin was measured by a differential scanning calorimetry (commercially available from Seiko Instruments Inc., trade name: DSC6220) with a temperature elevation rate of
20 10°C/min. The curing initiation temperature of the thermosetting resin was defined as a temperature at which a curve starts to get away from a baseline of the curve wherein the curve is a temperature vs. calorie curve obtained by the DSC measurement while a sample is heated
25 according to the JIS as described above.

The 42Sn-58Bi solder particles (commercially available from Mitsui Kinzoku, trade name: solder powder, average diameter: 0.03 mm, melting point: 139°C) were blended with thus obtained thermosetting flux material at a room temperature with a planetary mixer to obtain the solder paste. A weight ratio of the solder particles to the thermosetting flux material was 83:17.

Table 1

component	Example 1	Example 2	Example 3	Comparative Example 1	Comparative Example 2	Comparative Example 3
main agent	40	40	40	40	40	40
curing agent	40	40	40	40	40	40
curing accelerator	1.5	2	2.5	1.5	2	3
activator	7	7	7	7	7	7
solid resin	11.5	11	10.5	11.5	11	10
total	100	100	100	100	100	100
DSC curing initiation temperature	144°C	100°C	86°C	141°C	99°C	61°C
number of solder balls	not more than 2 O	not more than 2 O	not more than 2 O	not less than 5 X	not less than 5 X	not less than 5 X
bonding strength test	O	O	O	O	O	O
overall estimation*)	O	O	O	X	X	X

10 O: success in test, X: rejection in test

*) The overall estimation considers the number of the solder balls and the bonding strength test. When the

both tests are passed, "O" is indicated. On the other hand, when at least one of the both tests is not passed, "X" is indicated.

5 Connecting with Solder Paste

Using a metal mask having a thickness of 100 μm and openings (size: 0.4 mm x 0.5 mm), thus obtained solder paste was applied on electrodes formed on a substrate (FR4 substrate having a thickness of 0.6 mm) with a printer.
10 Electronic parts (1005 chip) were placed on the printed solder paste layers on the electrodes with a chip mounter.

Then, the substrate was heated on a hot plate heated to 200°C for three minutes so as to melt the solder particles, followed by cooling the substrate to a room
15 temperature, so that the electronic parts were mounted onto the substrate.

Estimation of Connection Structure with Soldering (Bonding Strength Test of Connection Structure)

20 Using a tool having a wedge form edge, a force was applied to the electronic part so as to separate the part, and a shear force when the part was separated (a so-called shear strength) was measured. The tool had an edge angle of 60°, and it was moved at a speed of 100 mm/min. For

the measurement, a tensile testing machine (commercially available from Aiko Engineering Co., Ltd., trade name: 1605HTP) equipped with a load cell of 50 N was used.

As a Comparative Example, using a solder paste
5 (commercially available from Tamura Corporation, trade name: LFSOLDER401-11, including Sn-Bi eutectic solder material) in place of the solder paste according to the present invention, the electronic parts were similarly mounted and the shear strength was similarly measured.

10 The shear strength of the Comparative Example was 29 N. Based on such strength, it was determined that when the connection structure with soldering has a shear strength which is as at least 1.5 times as that of the Comparative Example, such structure passes this bonding
15 strength test.

The shear strengths of the connection structures with soldering formed by using the solder compositions according to the present invention were measured, and all of the structures passed the bonding strength test as shown
20 in above Table 1. That is, the shear strength was not smaller than 44 N in each of the Examples. Thus, it has been found that the connection structure with soldering obtained by using the solder paste according to the present invention has a sufficient bonding strength.

(Solder Ball Number Test)

Using a microscope, the balls of the formed connection structure with soldering around the electronic part connected as described above were counted. It was
5 determined that when the number is not larger than two, the connection structure passes the solder ball number test. The results are shown in above Table 1.

Industrial Applicability of the Invention

10 The solder composition and the connecting process with soldering according to the present invention ensure the sufficient bonding strength while suppressing the occurrence of the defects such as electric conduction fault, and therefore, they and also the connection structure with
15 soldering according to the present invention can be used for the applications wherein an electronic part is mounted onto a substrate with soldering.

Particularly, by using, in the present invention, a lead-free solder material having a lower melting point, especially
20 an Sn-Bi solder material as the solder material for the solder particles, the following advantages may be provided.

Recently, according to the requests as to the environmental protection, the lead-free solder material has mainly been used in the electronic industrial fields. An Sn-
25 Ag-Cu solder material which is generally used has a

liquidus curve temperature of 220°C, which is rather higher when compared with that of the conventional Sn-Pb eutectic solder material. Therefore, it is difficult to apply such lead-free solder material to a substrate or an electronic
5 part of which allowable temperature limit is low.

To the contrary, an Sn-Bi solder material has a liquidus curve temperature of 139°C, and thus it is expected that such solder material is applicable to an electronic part of which allowable temperature limit is low
10 (such as a CCD, an aluminum electrolytic capacitor or the like). On the other hand, the Sn-Bi solder material is relatively mechanically brittle, and also it is difficult for such solder material to form a solder connection portion having an appropriate form through the reflow step when
15 using with the conventional solder paste as described above, so that the connection reliability is not sufficient and therefore the field to which the Sn-Bi solder material is applicable has been limited.

When such Sn-Bi solder material having the above
20 mentioned features is used in the form of the solder paste in which the thermosetting flux material including the solid resin is mixed according to the present invention, the field to which the Sn-Bi solder material is applicable is greatly broadened. With the solder composition, for example the
25 solder paste according to the present invention, the

reduction of the flowability of the thermosetting flux material due to the curing of the thermosetting resin in the reflow step can be compensated by the solid resin which has been changed to its liquid-like state and functions as a plasticizer. Particularly, by appropriately setting the relative relationship between the curing initiation temperature of the thermosetting resin and the softening temperature of the solid resin as the plasticizer, the flowability of the molten solder particles is ensured in the reflow step, so that the good connection structure with soldering is able to be foremd.

Therefore, an extent to which the gathering of the molten solder particles is prevented by the thermosetting flux material is lowered, so that the solder connection portion having a more appropriate form is able to be provided. In addition, the formed solder connection portion is covered and reinforced by the reinforcing resin portion which is made of the cured thermosetting resin and the solidified solid resin, which compensates the insufficient bonding strength of the Sn-Bi solder material, so that the connection reliability is improved.

The present invention thus provides a connecting process in which the Sn-Bi solder material as a low melting point solder material is industrially applied, so that such process expands its applicable field to the substrates, the

electronic parts and the like of which allowable temperature is low as described above. Simultaneously, an additional advantage is expected in that the heating temperature of the reflow step can be set at a lower temperature so that
5 for example the number of preheating stages may be reduced, the reflow apparatus may be more compact, and/or the electric power consumption may be decreased.

Further, there is no need of a costly conventional connecting process in which connecting with soldering at a
10 low temperature is required due to the allowable temperature upper limit of heating, such as a process wherein an Ag paste is used which contains silver powder in a resin adhesive, or a soldering process in which locally heating by means of laser beam or Softbeam so as to
15 connect individually without heating a whole substrate, so that neither costly material nor apparatus is required, which results in the cost reduction upon connecting with soldering.

In addition, since the liquidus curve temperature of the low melting point lead-free solder material is considerably
20 lower than that of the Sn-Pb eutectic solder material (189°C), it is possible to use a material having a low allowable temperature which has been considered to be unusable (for example a less expensive material such as a paper-phenol resin material), and there is no need of a
25 costly material such as a BT (bismaleimide-triazine) resin, which results the reduction of the material cost.

CLAIMS

1. A solder composition which comprises:

(1) a metal material comprising solder particles, and

5 (2) a thermosetting flux material comprising a thermosetting resin and a solid resin which changes to be in its liquid-like state when heated with a proviso that the thermosetting resin is excluded from the solid resin,

10 wherein a temperature at which the solid resin changes to be in the liquid-like state is lower than a temperature at which the thermosetting resin starts to cure.

2. The solder composition according to claim 1 wherein a temperature at which the solid resin changes to be in the liquid-like state is a softening temperature of the solid resin.

3. The solder composition according to claim 2 wherein the softening temperature of the solid resin is lower than the temperature at which the thermosetting resin starts to cure by at least 10°C.

4. The solder composition according to any one of claims 1 to 3 wherein the temperature at which the solid resin changes to be in the liquid-like state is not higher

than a liquidus curve temperature of a solder material of the solder particles.

5 5. The solder composition according to any one of claims 1 to 4 wherein a solder material which forms the solder particles contains tin and bismuth.

6. The solder composition according to any one of claims 1 to 5 wherein it is in the form of a paste.

10

7. The solder composition according to any one of claims 1 to 6 wherein the thermosetting resin comprises:

15 at least one as a main agent selected from the group consisting of an epoxy resin, an acrylic resin, a urethane resin, a phenol resin, a urea resin, a melamine resin, an unsaturated polyester resin, an amine resin and a silicone resin; and

at least one curing agent which cures the main agent.

20 8. The solder composition according to any one of claims 1 to 7 wherein the solid resin comprises at least one selected from the group consisting of a terpene resin, a xylene resin, an amorphous rosin, an olefin resin, an acrylic resin, an amide resin, a polyester resin, a styrene
25 resin, a polyimide resin, a fatty acid derivative wax, a

highly polymerized rosin and a fatty acid amide.

9. The solder composition according to claim 7 or 8 wherein the solid resin is compatible with the main agent.

5

10. A connecting process with soldering in which an electrode as a first electrode is connected to other electrode as a second electrode, comprising the steps of:

10 locating the solder composition according to any one of claims 1 to 9 between the first electrode and the second electrode;

15 heating these electrodes and the solder composition so as to melt the solder particles wherein the solid resin is changed into its liquid-like state while a curing reaction of the thermosetting resin is made proceed; and

solidifying said solid resin and molten solder material.

11. The connecting process according to claim 10 wherein the first electrode is a connection electrode of an electronic part, and the second electrode is a circuit electrode formed on a substrate.

12. A production process of a substrate which has an electronic part thereon, comprising the step of connecting the electronic part to the substrate using the connecting

25

process with soldering according to claim 11

13. A connection structure with soldering between an electrode and other electrode which structure is formed by using the connecting process with soldering according to claim 10 or 11, comprising

a solder connection portion connecting those electrodes, and

a reinforcing resin portion which is made of the solidified solid resin and the cured thermosetting resin.

14. The connection structure with soldering according to claim 13 wherein the reinforcing resin portion covers at least partly a surface of the solder connection portion.