

Joining to Aluminium

The invention relates to an improved solder flux, in particular a solder flux for use in soldering to aluminium. The invention also relates to a process for making
5 aluminium surfaces solderable using the flux and conventional solders.

Soldering processes are typically facilitated by the use of a flux. One of the obstacles to a successful solder joint is an impurity at the site of the joint, for example, dirt, oil or oxidation. The impurities can be removed by mechanical
10 cleaning or by chemical means, but the elevated temperatures required to melt the filler metal (the solder) encourages the work piece (and the solder) to re-oxidize. This effect is accelerated as the soldering temperatures increase and can completely prevent the solder from joining to the work piece.

15 There is a strong desire on the part of industry participants in a wide range of industries and end-use applications to lower the weight and cost of assemblies, such as electronic circuits and wire harnesses including those used in automotive, LED assemblies and PV modules. Specifically there is a desire to eliminate the currently used copper layer in printed circuit boards and replace it
20 with aluminium. Further, it would be advantageous to replace typical solder coated copper ribbon with solder coated aluminium in order to achieve weight and cost savings.

However, soldering directly to aluminium poses significant technical challenges.
25 Specifically it is extremely difficult to break down the oxide layer on the surface in order to create a direct connection to the aluminium metal. Aluminium is very prone to oxidation creating a very tenacious oxide layer, which tends to reform immediately after exposure to air.

30 Soldering to aluminium can be accomplished by depositing/plating onto the aluminium or by creating an intermediate layer that results in a solderable surface. Other approaches include use of very aggressive fluxes to remove the

oxide layer combined with highly reactive solders such as SnZnAl. Joining directly to aluminium can also involve use of brazing alloys which is implemented at high temperatures. This process is not compatible with electronic assemblies. Recent attempts to develop a solder pastes to solder directly to aluminium
5 involve reflow process at very high temperatures ($>280^{\circ}\text{C}$), which again cannot be tolerated by electronic components and substrates. Accordingly, there is a need for a solder flux which enables simple soldering to aluminium without the need for an intermediate layer or an aggressive solder, and which can be used in a soldering process that is compatible with electronic assemblies.

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The present invention seeks to tackle at least some of the problems associated with the prior art or at least to provide a commercially acceptable alternative solution thereto.

15 The present invention provides a flux comprising one or more amines.

Each aspect or embodiment as defined herein may be combined with any other aspect(s) or embodiment(s) unless clearly indicated to the contrary. In particular, any features indicated as being preferred or advantageous may be combined
20 with any other feature indicated as being preferred or advantageous.

The term “flux” used herein encompasses a species for removing impurities, for example, dirt, oil or oxides, from a work piece prior to soldering.

25 The term “aluminium work piece” used herein encompasses a work piece having aluminium and/or aluminium alloy at a surface thereof.

The inventors have surprisingly found that the flux of the present invention is capable of enabling soldering to an aluminium work piece.

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In use, the flux is contacted with the surface of an aluminium work piece to be soldered. The flux may be contacted with the surface prior to soldering, typically

by immersing the work piece in the flux. Alternatively, the flux may be contacted with the surface together with solder. For example, the surface may be contacted with a paste comprising the flux and solder particles. In this case, the flux will remove aluminium oxide from the surface of the work piece before a subsequent heating step causes the solder particles to form a solder joint.

Without being bound by theory, it is considered that the presence of one or more amines may serve to dissolve aluminium oxide from the aluminium work piece. Accordingly, a subsequent soldering step may result in the formation of a strong solder joint.

As well as removing aluminium oxide from the surface of an aluminium work piece, the flux may also inhibit subsequent re-oxidation of the surface. This may be particularly advantageous when the soldering step is carried out some time after the flux is contacted with the surface of the aluminium work piece. In addition, this may enable the use of solder pastes containing species that may otherwise cause re-oxidation or corrosion of the aluminium. The one or more amines may also advantageously function as a surfactant in the flux.

The one or more amines may advantageously exhibit high thermal stability. Accordingly, the flux may be used at high temperatures with a wide range of solders.

The flux is advantageously water soluble, meaning that any residue formed on the aluminium surface after it has been contacted with the flux may be removed by washing. Such a step eliminates any potential concerns regarding corrosion and reliability.

The amines preferably comprise an ethanolamine and/or an ethoxylated amine. Such amines (e.g. ethoxylated tallow amines and ethoxylated polyamine) may be particularly effective at activating the surface of the aluminium substrate, i.e. they may be particularly effective at dissolving aluminium oxide, and may also exhibit

particularly high thermal stability. Such amines may also function as particularly effective surfactants.

The one or more amines is preferably selected from: monoethanol amine,
5 diethanol amine, triethanol amine, aminoethylethanol amine, ethoxylated tallow amines, and etholoxated polyamine. Such amines are particularly effective at dissolving aluminium oxide from the surface of an aluminium work piece.

In a particularly preferred embodiment, the flux comprises:

- 10 from 10 to 45 % by weight monoethanol amine, and/or
 from 15 to 30 % by weight triethanol amine, and/or
 from 10 to 35 % by weight aminoethylethanol amine, and/or
 from 5 to 36 % by weight ethoxylated tallow amines, and/or
 from 1 to 10 % by weight etholoxated polyamine.

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Such a combination of amines in the recited ranges may result in a flux which exhibits particularly high thermal stability and aluminium oxide dissolution. The flux may also be particularly effective at inhibiting subsequent re-oxidation and/or corrosion of the treated surface.

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In a particularly preferred embodiment, the flux comprises:

- from 10 to 40 wt.% monoethanol amine;
 from 15 to 30 wt.% triethanol amine;
 from 10 to 35 wt.% aminoethylethanol amine;
25 from 5 to 20 wt.% ethoxylated tallow amine; and
 optionally from 1 to 10 wt.% ethoxylated polyamine.

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Such a combination of amines in the recited ranges may result in a flux which exhibits particularly high thermal stability and aluminium oxide dissolution. The
30 flux may also be particularly effective at inhibiting subsequent re-oxidation and/or corrosion of the treated surface.

The flux preferably further comprises an activator. The activator may serve to help dissolution of aluminium oxide from the surface of an aluminium work piece.

The activator is preferably selected from one or more of zinc chloride, aluminium chloride and fluoroboric acid. Such species are particularly effective at removing aluminium oxide.

In a preferred embodiment, the flux comprises:

- from 1 to 5 % by weight aluminium chloride and/or
- 10 from 5 to 15 % by weight zinc chloride, and/or
- from 5 to 15 % by weight fluoroboric acid.

The flux may advantageously further comprise a surfactant, preferably selected from octyl phenol ethoxylates and nonyl phenol ethoxylates.

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In a preferred embodiment, the flux comprises:

- from 10 to 40 wt.% monoethanol amine;
- from 15 to 30 wt.% triethanol amine;
- from 10 to 35 wt.% aminoethylethanol amine;
- 20 from 5 to 20 wt.% ethoxylated tallow amine;
- from 1 to 5 wt.% water;
- from 1 to 5 wt.% ammonium chloride;
- from 5 to 15 wt.% zinc chloride;
- from 5 to 15 wt.% fluoroboric acid, 50%;
- 25 from 1 to 5 wt.% tin fluoroborate; and
- from 1 to 5 wt.% nonyl and/or octyl phenoethyloxate (total amount of).

In a preferred embodiment, the flux comprises

- from 10 to 40 wt.% monoethanol amine;
- 30 from 15 to 30 wt.% triethanol amine;
- from 10 to 35 wt.% aminoethylethanol amine;
- from 5 to 20 wt.% ethoxylated tallow amine;

- from 1 to 5 wt.% water;
- from 1 to 5 wt.% ammonium chloride;
- from 5 to 15 wt.% zinc chloride;
- from 5 to 15 wt.% fluoroboric acid, 50%;
- 5 from 1 to 5 wt.% tin fluoroborate; and
- from 1 to 10 wt.% ethoxylated polyamine.

The fluxes of these preferred embodiments exhibit particularly favourable aluminium dissolution and high temperature stability, and are particularly suitable
10 for rendering an aluminium work piece in a condition for subsequent soldering using a tin-based solder.

The flux may be for use in the manufacture of a printed circuit board, an LED or a photovoltaic module.

15 In a further aspect, the present invention provides a solder paste comprising the flux described herein. The solder paste typically also comprises solder particles. Any conventional tin-based solder may be used, for example lead-based solders (e.g. Sn63Pb37, Sn62, Pb36Ag2) or lead-free solders (e.g. SnBi, SnBiAg, SAC305, Low Ag SAC, Innot, SnAg and Sn100). The solder particles preferably
20 comprise one or more of tin, tin-silver alloy, tin-silver-copper alloy, tin-bismuth alloy and tin-silver-bismuth alloy. Particularly suitable solder particles may comprise one or more of: SnBi, SnBiAg, SAC305, Low Ag SAC, Innot (see, for example, WO2004096484, the contents of which is hereby incorporated by
25 reference), SnAg and Sn100. Such solder particles may form a particularly strong solder joint with an aluminium work piece. In addition, such solders are advantageously lead-free, which avoids problems with toxicity.

The amounts of solder particles and flux contained in the solder paste are not
30 limited. The amount of solder particles contained in the solder paste may be, for example, from 10 to 99 % by weight, or from 25 to 90 % by weight, or from 50 to 85 % by weight, or from 65 to 80 % by weight. The solder paste may alternatively

contain lower or higher amounts of solder particles. The flux may make up, for example, the substantial remainder of the solder paste. The solder paste may contain, for example, from 1 to 90 % by weight flux, or from 10 to 75 % by weight flux, or from 15 to 50 % by weight flux, or from 20 to 35 % by weight flux. The
5 solder paste may alternatively contain lower or higher amounts of solder flux. The solder paste may contain species other than solder particles and flux.

The solder paste is typically stable in air at ambient conditions for at least three hours, preferably at least five hours. This may enable easy handling and storage
10 of the paste.

In a further aspect, the present invention provides a soldered joint manufactured using the flux or the paste described herein. Such a soldered joint may exhibit high strength and/or thermal stability.
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In a further aspect, the present invention provides a method of processing an aluminium surface comprising:

providing an aluminium surface;
contacting the aluminium surface with a flux as described herein followed
20 by contacting the aluminium surface with a molten liquid comprising tin or tin alloy.

The term "aluminium surface" encompasses a surface at which is provided aluminium and/or aluminium alloy. Once contacted with the flux, the aluminium
25 surface may be substantially devoid of aluminium oxide. The subsequent step of contacting the aluminium surface with a molten liquid comprising tin or tin alloy may result in the formation of an aluminium-tin eutectic. Such an aluminium-tin eutectic may enable effective soldering onto the aluminium surface using, for example, a conventional surface mount technology (SMT) process using
30 conventional alloys.

The method may be effectively carried out in air or nitrogen atmospheres. The method is preferably carried out in a nitrogen atmosphere in order to minimise re-oxidation of the aluminium surface once it has been contacted with the flux.

- 5 The aluminium surface is contacted with the flux for a sufficient time to substantially remove aluminium oxide therefrom. The aluminium surface may be contacted with the flux for at least two seconds, preferably from 3 to 30 seconds, more preferably from 5 to 15 seconds.
- 10 The aluminium surface is preferably heated prior to being contacted with the flux, preferably to a temperature of at least 80 °C, more preferably to from 90 to 150 °C, even more preferably to about 100 °C or about 130 °C. This may serve to increase the amount of aluminium oxide removed by the flux.
- 15 The method preferably further comprises washing the aluminium surface after contacting the aluminium substrate with the molten liquid. This may ensure that the aluminium surface is substantially free of impurities, thereby increasing the strength of a subsequent soldered joint formed on the aluminium-tin eutectic.
- 20 The step of contacting the aluminium surface with a flux may comprise spraying and/or dipping and/or brushing.

- The step of contacting the aluminium surface with a molten liquid comprising tin or tin alloy may comprise hot air solder levelling and/or wave soldering. Such
- 25 techniques are known in the art.

- The method typically further comprises applying solder to the aluminium surface. The solder may be applied using any conventional soldering method. Preferably, the solder is applied using surface mount technology (SMT) reflow soldering.
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In a further aspect, the present invention provides an aluminium substrate having an aluminium surface processed according to the method described herein.

In a further aspect, the present invention provides an aluminium substrate having a surface portion comprising an aluminium-tin eutectic layer.

- 5 In a further aspect, the present invention provides a solder-coated aluminium ribbon, preferably a photovoltaic solder-coated aluminium ribbon, wherein the aluminium ribbon comprises the substrate described herein.

- 10 In a further aspect, the present invention provides a printed circuit board or LED comprising the aluminium substrate described herein.

- In a further aspect, the present invention provides use of the flux as described herein or the solder paste described herein in the manufacture of a device selected from: a printed circuit board, an LED and a photovoltaic module.

- 15 In a further aspect, the present invention provides a method for making aluminium surfaces solderable, preferably solderable with a tin-based solder, the method using the flux as described herein or the paste as described herein.

- 20 Aspects of the present invention are further described as follows:

Concept:

- 25 Current invention involves soldering - Sn or Sn based alloys to Al surfaces. This can be achieved through the use of specially designed fluxes and/or pastes.

Process:

Process 1:

- 30 - Process involves application of a specially developed/formulated flux to Al surface. The Al surface may comprise or consist of aluminium and/or aluminium alloy.

- Fluxed Al surface is exposed to liquid metal, e.g., a traditional HASL (refer Schematic 1a) or wave solder equipment (refer Schematic 1b) for a very short time.
- 5 - During this short exposure of fluxed surface to liquid metal, surface oxides are removed and Al and Sn form an AlSn eutectic at the interface.
- After this tinning step, any residue is thoroughly cleaned. This eliminates the risk for corrosion and related reliability concerns.
- 10 - The end result of this process is an Al surface with a metal plating that can be soldered using standard electronic materials and processes.

Process 2:

- Alternate process uses a specially designed solder paste which uses common lead-free solder alloys with the specially formulated flux.
- 15 - Flux is water soluble and any residue on the joint can be cleaned easily. This step eliminates any potential concerns of corrosion and reliability as an inherent nature of the highly active fluxes used.
- Process is same as standard SMT (surface mount technology) reflow soldering.

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Material Sets:

Fluxes:

- 25 - Fluxes used to remove Al oxides to promote adhesion of Solders to Al surfaces. These fluxes are corrosive in nature and use a combination of amines to provide activity.
- E.g., for liquid flux formulation 1, weight percentage - Monoethanol amine ranging from (10% -40%), Triethanol Amine ranging from (15%-30%), Aminoethylethanol Amine (10%-35%), Ethoxylated Tallow
- 30 Amines (5% - 20%), Water (1% - 5%), Ammonium Chloride (1% - 5%),

Zinc Chloride (5 % - 15%), Fluoroboric Acid, 50% (5% - 15%), Tin Fluoroborate (1% - 5%), Nonyl / OctylPhenolEthoxates (1% - 5%)

- 5 - E.g., for liquid flux formulation 2 - weight percentage - Monoethanol amine ranging from (10% - 40%), Triethanol Amine ranging from (15% - 30%), Aminoethylethanol Amine (10% - 35%), Ethoxylated Tallow Amines (5% - 20%), Water (1% - 5%), Ammonium Chloride (1% - 5%), Zinc Chloride (5 % - 15%), Fluoroboric Acid, 50% (5% - 15%), Tin Floroborate (1% - 5%) and Etholoxated Polyamine (1% - 10%).
- 10 - E.g., for liquid flux formulation 3 - weight percentage - Monoethanol amine (30% - 45%), Triethanol Amine (18% - 22%), Ethoxylated Tallow Amine (10% - 17%), Water (2% - 5%), Ammonium Chloride (1% - 3%), Zinc Chloride (10 % - 13%), Fluoboric Acid, 50% (10% - 15%), Tin
- 15 Floroborate (2% - 4%).
- 20 - E.g., for paste flux formulation 4 - weight percentage - Monoethanol amine (10% - 40%), Triethanol Amine ranging from (15% - 30%), Aminoethylethanol Amine (10% - 35%) Ethoxylated Tallow Amine (10% - 36%), Water (1% - 5%), Ammonium Chloride (1% - 5%), Zinc Chloride (5 % - 15%), Fluoboric Acid, 50% (5% - 15%), Tin Floroborate (1% - 5%) and Etholoxated Polyamine (1% - 10%).
- 25 - E.g., for paste flux formulation 5 - weight percentage - Monoethanol amine ranging from (12% - 20%), Triethanol Amine (15% - 20%), Ethoxylated Tallow Amine (30% - 35%), Water (1% - 5%), Ammonium Chloride (1% - 4%), Zinc Chloride (10% - 13%), Fluoboric Acid, 50% (10% - 15%), Tin Floroborate (2% - 4%).
- 30 Amines that may be used for corrosion inhibitors include, for example: ethoxylated amines such as, for example, ethoxylated tallow amine and ethoxylated polyamine. Ethoxylated amines have multiple functions such as:

activators, surfactants, corrosion inhibition and to provide thermal stability to withstand soldering temperatures/time and assist in removal of flux residues with water after soldering operations.

- 5 Activators that may be used include, for example: ammonium chloride, zinc chloride, tin fluoroborate, fluoroboric acid, aminoethyl ethanol amine, alkanolamines e.g. monoethanol amine, triethanol amine, diethanolamine, ethoxylated amines e.g. ethoxylated tallow amine and ethoxylated polyamines.
- 10 Surfactants that may be used include, for example: ethoxylated molecules such as, for example, ethoxylated tallow amine, ethoxylated polyamine, octyl phenol ethoxylates and nonyl phenol ethoxylates.

Solder

- 15 - The flux described herein may be used in combination with solder particles.
- Any common Sn based solder can be used for soldering to Al.
- Soldering can be lead-based (for e.g., Sn63Pb37, Sn62, Pb36Ag2) or
- 20 lead-free (SnBi, SnBiAg, SAC305, Low Ag SAC alloys, Innotot, SnAg, Sn100, etc.)
- There is no need for highly reactive solders such as Zn based, which are currently been recommended.

25 *Applications:*

- Standard Electronic PCBs,
- Electronic PCBs for Automotive applications,
- LEDs (e.g., Die attach, package attach and optically reflective
- 30 surfaces),
- PV modules (assembly using Sn coated Al ribbons),
- Others (e.g., highly thermal conductive preforms)

Advantages:

5 The amines may serve to remove the aluminium oxide layer present on the surface of aluminium substrates. The amines are also stable at high temperatures.

The invention will now be described in relation to the following non-limiting drawings, in which:

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Figure 1 shows a schematic of a method of processing an aluminium surface according to the present invention.

15 Figure 2 shows a schematic of a method of processing an aluminium surface according to the present invention.

Referring to Figure 1, process schematic 1a is a schematic of a method of the present invention. The steps include, from left to right, (a) flux application to an aluminium work piece by spraying or dipping, (b) immersion of the aluminium
20 work piece into a bath containing metal or metal alloy to plate or coat the aluminium substrate, (c) cleaning the aluminium work piece, and (d) soldering using a conventional/standard SMT process with standard alloys. Process schematic 1b includes, from left to right, (a) flux application to an aluminium work piece by wave flow, dipping, or brushing, (b) pre-heating the aluminium work
25 piece, (c) wave soldering, (d) cleaning and (e) soldering using a conventional/standard SMT process with standard alloys.

Referring to Figure 2, process schematic 2 is a schematic of a method of the present invention. The steps include, from left to right, (a) formation of a specially
30 developed solder paste using standard alloys, (b) printing/dispensing of the solder paste onto an aluminium work piece, (c) picking and placing components onto the paste, (d) carrying out solder reflow, and (e) cleaning of the assembly.

The invention will now be described in relation to the following non-limiting examples.

5 Example 1

A flux according to the present invention was prepared comprising, in weight percentage - Monoethanol amine ranging from (10% -40%), Triethanol Amine ranging from (15%-30%), Aminoethylethanol Amine (10%-35%), Ethoxylated
 10 Tallow Amines (5% - 20%), Water (1% - 5%), Ammonium Chloride (1% - 5%), Zinc Chloride (5 % - 15%), Fluoboric Acid, 50% (5% - 15%), Tin Floroborate (1% - 5%), Nonyl / OctylPhenolEthylloxates (1% - 5%).

Aluminium boards were immersed in the flux under varying conditions prior to
 15 soldering. The conditions are shown in Table 1:

Contact time	Atmosphere	Pre-heating of board	Solder pot temperature
3 seconds	air	none	285 °C
10 second	air	130 °C	285 °C
10 second	N ₂	130 °C	285 °C
8 second	N ₂	130 °C	285 °C

Table 1. Immersion conditions.

20 While all conditions gave reasonable results, the most uniform, icicle-free soldered aluminium boards were prepared under nitrogen with a pre-heating step and a contact time of 8 seconds or more.

Example 2

The soldered joints formed in Example 1 were investigated using an electron microscope. A nice uniform interface was observed, indicating a good bond between the solder and the aluminium substrate. EDS analysis shows that the aluminium/solder interface contains mostly Al and Sn atoms. CuSn IMC is
5 observed in the bulk.

The foregoing detailed description has been provided by way of explanation and illustration, and is not intended to limit the scope of the appended claims. Many variations in the presently preferred embodiments illustrated herein will be
10 apparent to one of ordinary skill in the art and remain within the scope of the appended claims and their equivalents.

Claims:

1. A flux comprising one or more amines, wherein the flux comprises:
from 10 to 40 % by weight monoethanol amine,
5 from 15 to 30 % by weight triethanol amine,
from 10 to 35 % by weight aminoethylethanol amine,
from 5 to 20 % by weight ethoxylated tallow amines, and
from 1 to 10 % by weight ethoxylated polyamine.
- 10 2. The flux of claim 1 comprising an activator, wherein the activator is selected from one or more of zinc chloride, aluminium chloride and fluoroboric acid.
3. The flux of claim 2 comprising:
15 from 1 to 5 % by weight aluminium chloride and/or
from 5 to 15 % by weight zinc chloride, and/or
from 5 to 15 % by weight fluoroboric acid.
4. The flux of any preceding claim further comprising a surfactant, preferably
20 selected from octyl phenol ethoxylates and nonyl phenol ethoxylates.
5. The flux of any preceding claim comprising:
from 1 to 5 wt.% water;
from 1 to 5 wt.% ammonium chloride;
25 from 5 to 15 wt.% zinc chloride;
from 5 to 15 wt.% fluoroboric acid, 50%;
from 1 to 5 wt.% tin fluoroborate; and
from 1 to 5 wt.% nonyl and/or octyl phenoethyloxate.
- 30 6. The flux of any preceding claim comprising:
from 1 to 5 wt.% water;
from 1 to 5 wt.% ammonium chloride;

from 5 to 15 wt.% zinc chloride;
from 5 to 15 wt.% fluoroboric acid, 50%; and
from 1 to 5 wt.% tin fluoroborate.

- 5 7. A solder paste comprising the flux of any preceding claim, wherein the
solder paste comprises solder particles selected from one or more of: tin, tin-
silver alloy, tin-silver-copper alloy, tin-bismuth alloy and tin-silver-bismuth alloy.
8. A soldered joint manufactured using the flux of any of claims 1 to 6 or the
10 paste of claim 7.
9. A method of processing an aluminium surface comprising:
providing an aluminium surface;
contacting the aluminium surface with a flux as described in any of claims
15 1 to 6 followed by contacting the aluminium surface with a molten liquid
comprising tin or tin alloy.
10. The method of claim 9 further comprising washing the aluminium surface
after contacting the aluminium substrate with the molten liquid.
- 20 11. The method of claim 9 or claim 10, wherein the step of contacting the
aluminium surface with a flux comprises spraying and/or dipping and/or brushing.
12. The method of any of claims 9 to 11, wherein the step of contacting the
25 aluminium surface with a molten liquid comprising tin or tin alloy comprises hot air
solder levelling and/or wave soldering.
13. The method of any of claims 9 to 12 further comprising applying solder to
the aluminium surface.

14. Use of the flux of any of claims 1 to 6 or the solder paste of claim 7 in the manufacture of a device selected from: a printed circuit board, an LED and a photovoltaic module.