

Fundamentals of solder paste technology

Solder pastes are key materials in surface mount technology (SMT) for assembly of printed circuit boards (PCBs). Introduction of lead-free has placed new demands on materials and processes in SMT, requiring materials and process engineers to adopt to lead free whilst ensuring process yields stay at the highest possible levels. Key is the solder paste, a material of great complexity involving engineering sciences, metallurgy, chemistry and physics. This article helps those working with solder pastes improve their understanding of this key material.

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Keywords: Printed Circuit Board, Surface Mount Technology, Lead-Free Solder Paste, Soldering

Background

Almost all electronics equipment contains printed circuit boards (PCBs), which are critically important for satisfactory functioning of the equipment. PCBs have patterns of electrically conducting copper tracks to which electronic components are joined. The joints between the tracks and the components are made by soldering the components to the copper tracks, generally by using a material known as solder paste.

Solder pastes are made by mixing a metal alloy powder (around 90% by weight) with a cream-like material made of organic chemicals (around 10% by weight). The organic chemicals cream is referred to as 'flux' and is generally a trade secret and/or covered by patents. The purpose of flux is to give the solder paste its cream-like texture and to enable formation of metal joints by ensuring that the metal surfaces are 'clean' of oxides at the time the metal joint are formed.

To achieve satisfactory process yields, it is important to understand the design and engineering of the solder paste in order to select the right materials and use correct process conditions.

Metal surfaces need 'cleaning' because they undergo oxidation on exposure to the environment and form compounds with oxygen, nitrogen, water and pollutants, such as oxides of sulphur, in the air. The degree of oxidation and the nature of the chemical bond between the metal surface and the oxidising chemical species determines the affinity between the metal atoms and the oxidising chemical species. For example, copper surfaces form copper(I) and copper(II) oxides. The copper oxides interact with carbon dioxide and moisture in air to form carbonates or hydroxyl carbonates. Iron behaves like copper, whereas nickel produces a continuous thin film of oxide. Silver reacts with traces of hydrogen sulphide to form silver sulphide. Once a layer of these kinds of compounds forms on the surface of the metal, it causes passivity of the metal surface. The metal surface then becomes solder-repellent, which leads to poor wettability and poor soldering of joints on the PCB. Furthermore, solder alloys also undergo surface oxidation, forming compounds on the surface with oxygen,

water and nitrogen that also interfere with soldering.

So, effective soldering requires that metal surfaces are clean of passivating surface chemical layers through the use of a technique called fluxing, which involves the application of a chemical cream to the metal surface. The flux must have the right chemistry to destroy surface passivation layers. Fluxes for soldering electronic PCBs require several features:

1. To remove the passivation layers and make the metal surfaces active and wettable by the solder alloy.
2. To protect cleaned surfaces with a layer of some substance, usually rosin, which prevents contact with air prior to application of the molten solder.
3. To promote wetting of the surfaces to be joined by controlling the surface forces that determine the wetting process.
4. To provide the right rheology for excellent paste printability, tack and slump characteristics.

Although the first function is the main one, good results can not be obtained for the PCB manufacturer if the flux does not perform the other functions satisfactorily. To be commercially viable, a flux must have all the properties that allow it to be used in common PCB manufacturing operations, such as SMT. The properties that control requirements (1) to (4) above include chemical activity, activation temperature or window, thermal stability, surface tension, wetting power, rheology, print performance (for SMT), toxicity and nature/amount of residues.

Rosin is the base material for many flux systems. It is a natural resin that has been known for many years. Basically, it is colophony (named after Colophon, an Ancient City in Asia Minor or the Greek pitch that was used as an incendiary weapon by the Ancient Greeks). It is a natural organic compound extruded by trees of the genus *Pinus* and in particular *Pinus Palustris*. It is a solid product that is sometimes vitreous and sometimes crumbly, with colour ranging from light yellow to brown. Rosins are a complex mixture of organic compounds, most of which are terpenoids and hydrocarbons. Although the exact composition depends on the source, the

most important compound is abietic – or sylvic – acid (C₂₀H₃₀O₂). Also present in rosins are d- and l-pimaric acids.

Rosin is not soluble in water, but it is soluble in organic solvents such as alcohols, hydrocarbons, ethers and halocarbons. A typical high grade water white rosin is comprised of the following:

| | |
|--------------|-----|
| Abietic Acid | 85% |
| Pimaric Acid | 12% |
| Others | 2% |

Rosin is widely used in fluxes because it offers many advantages:

- It attacks the passivation layer of several metals, especially that of copper-producing copper abietate
- It does not attack bulk copper, even after prolonged contact
- It can be dissolved in suitable solvents and applied to surface to be joined. After solvent evaporation, for example as in SMT reflow, it forms a thin coating that protects the fluxed surface and promotes wetting by the molten solder.
- It forms a good vehicle for more active fluxing compounds, such as amine hydrobromides.
- Rosin solder pastes generally have good tack and rheological performance with respect to printability, slump and shelf-life, relative to non-rosin pastes.

Rosin fluxes can be divided into two main classes: activated and non-activated. Activated fluxes can be further divided into rosin mildly activated (RMA) and rosin strongly activated (RSA). Non-activated fluxes (MIL-F-14256) are used by manufactures of avionics equipment because the residues can be safely left on the soldered boards without any risk of corrosive attack. Activated fluxes are similar to non-activated fluxes except that they contain an additional activating agent (activator) that is much more reactive towards the passivation layer of metals than rosin. The degree of flux activation depends on the nature and quantity of the activator. Classically, types of activators used include bromine salts of amino compounds and carboxylic acids^[1,2].

Solder paste is a mixture containing (a)solder in powder form, (b) resins (e.g. rosins), (c) activator(s), (d) solvent, (e) thickening agents and rheology aids, and (f) antioxidants. Upon heating, the solvent evaporates and the activators attack the metal surfaces, resulting in cleaning. On further heating, the solder powder particles melt and form a liquid mass, which makes the joint.

The important properties of solder powder, from a solder paste performance objective, include the following:

- Consistency of chemical composition.
- Level of impurities.
- Particle size and shape.
- Particle size distribution.
- Surface chemistry.

These properties have a number of important effects on paste performance^[9, 10,11,13]. For example, as users move to finer pitch applications, smaller particle size powders are required for acceptable print performance. This includes Type 5 to Type 7 solder powders made by BizEsp. The surface area of the powder, of course, increases with decreasing particle, and special manufacturing techniques are required to achieve acceptable quality when manufacturing Type 5 -7 powders. Particle size, shape and distribution have important implications in paste rheology and affect print and syringe dispensing performance^[9,10].

General flux formulations

Typical flux systems have been described in several studies.

Solvents

The solvents is much more than just a vehicle for holding the flux components in solution without precipitation. It is of fundamental importance and determines the following:

- (i) ease of application, such as syringe dispensing and printing;
- (ii) drying and formation of a protective film;
- (iii) absence of sputtering and wettability promotion when the boards contact the molten solder.

If the solvent dries too quickly, the protective rosin film hardens and is not displaced correctly by the solder^[1,2]. If it dries too slowly, the protective film will contain some solvent, which evaporates abruptly in contact with the molten solder and causes sputtering. The evaporation process itself is a complex phenomenon and is affected by the nature of the solvent (chemical structure, hydrogen bonding

and Lewis acid/base characteristics), the number of solvents in the mixture, chemical interactions with other components in the mixture temperature, vapour pressure, surface/volume ratio, and convection. Further complications arise from the presence and pick-up of moisture.

The solvent also affects tack and the viscoelastic properties of the solder paste. The most important factor to consider here is Lewis acid: base type interactions between the solvent and other paste components that lead to molecular or solder particle structuring in the paste. Solvents include butyl carbitol, dibutyl carbitol, glycols and polyhydroxy aliphatic and aryl alcohols.

Rosins

Classically, fluxes contain gum rosin, wood rosin or tall oil rosin, having a minimum acid value of 130, dissolved in a solvent. The approximate acid values of typical rosins are shown in *Table 1*. These values can usually be determined using a simple KOH titration. Derivatives of rosins are also used, such as dimerized resin, saponified resin or rosin-derived ester resin (also know as ‘ester gums’). DymereX is a modified resin and is sold by manufactures as a particularly suitable resin for soldering flux due to its outstanding characteristics: high softening point, non-crystalline nature, resistance to oxidation and excellent solvent release properties. DymereX has also been recommended in several texts, for example Yost et al. Foral AX-E is an acidic resin that is produced by hydrogenating rosin to an exceptionally high degree. It is recommended by a major supplier (Hercules) as a replacement for tall oil rosin due to its exceptionally pale colour, excellent heat stability, post-reflow colour retention, resistance to oxidation and low odour. These characteristics mean that post-reflow residue is exceptionally light in colour.

Activators

Alkyl and aryl carboxylic acids are widely used as activators in ‘no-clean’ and water washable electronic fluxes for wave

Table 1. Acid values of rosins

| Sample | Acid Number (KOH mg equivalent) |
|-------------|---------------------------------|
| Tall oil | 60 |
| Portuguese | 162 |
| Unirez 7104 | 251 |
| DymereX | 147 |
| Rosin H | 154 |
| American WW | 158 |

soldering and SMT reflow soldering. Examples include adipic, succinic and glutaric acids in no-clean and water washable fluxes^[1,2]. Malic acid is used as a component in activation systems of no-clean and water washable fluxes^[7]. Numerous activators have been reported in the open literature and also stated in current and lapsed patents of several US and Japanese paste manufacturers. Other types of activators that are known to be used in RMA, RSA and water washable fluxes include the following:

- Organic halogen acid adducts
- Halogenated organics
- Ammonium halides
- Halopyridines

Rheology aids

The rheological performance of a paste (i.e. its flow behaviour when subjected to a stress) is arguably the most important determinant of the quality of a solder paste. Rheology affects shelf-life (where rheological stability of around several months is required), paste printing performance, cold slump and hot slump^[10,11,17]. Solder paste printing is a complex process with numerous parameters that can affect the final outcome. Furthermore, typical of a dense suspension soft solid, the rheological behaviour of solder pastes is highly complex. In simplistic terms, a solder paste exhibits non-Newtonian and thixotropic behaviour when subjected to a shearing stress. The viscosity of a material can be defined as the ratio of shear force to shear rate. For Newtonian liquids, this ratio has a constant value and plot of shear force versus shear rate is a straight line through the origin. Materials made up of complex organic molecules with a range of organic functional groups are capable of intermolecular interactions that lead to an inherent steady state structure in the material. This phenomenon can also occur as a result of interactions between particles, such as solder spheres. For such materials, the thixotropic nature can be shown by a shear rate sweep experiment (for example, in a parallel plate geometry) in which the material is subjected to a shear rate cycle of 0 to 100 per seconds and then 100 to 0 per second (called a rheogram). The thixotropy is then equal to the area between the ascending and descending shear rate curves. It is indicative of the degree of molecular and solder particle structure in the paste. Other notable features of the rheogram are the initial increase in viscosity, as the shear stress increases without significant

shear rate increase, followed by the paste 'yielding' and then undergoing shear thinning, i.e. decrease in viscosity with increasing shear rate.

The above behaviour is desirable and necessary for satisfactory printing and anti-slump properties. A paste is subjected to a wide range of shear rates during various phases of the printing process. These phases are classified as mixing, rolling and screening.

The mixing phase refers to the process of transferring the paste from its container to the screen surface. This process involves relatively low shear rates. During the printing process, the paste in front of the squeegee tends to form a cylindrical shape and appears to 'roll' as it is pushed back and forth by the squeegee. As the squeegee moves, the paste shear thins and this is necessary for the formation of a satisfactory 'roll.' Finally, the paste is subjected to considerable shear as it is forced through the stencil apertures and onto metal pads on the PCB. At the instant, the paste is forced through the apertures, the viscosity reaches a minimum and the shear rate is at a maximum. At this instant the paste has lost all of its inherent internal structure. Once the squeegee has passed over the apertures, the stencil and PCB are separated mechanically. The shear rate drops instantaneously and the paste must very rapidly re-build its internal structure to avoid cold slump. This is particularly important with current levels of fine pitch assembly where the small gap between pads may be bridged if the paste deposits slump and touch. The ability of the paste to resist slump is also important in reflow where hot slump can also lead to bridging. Here, the inherent 'yield' of the solder paste resulting from its internal molecular and solder particle structure is important in resisting hot slump.

The chemicals present in a typical flux system have the ability to attain a structure at steady state that results from molecular and particle interactions. However, the above discussed rheological properties of the paste can only be fully attained through the use of rheological aids (thixotropes and thickeners). Thixotropes and thickening agents such as castor oil derivatives, cellulose derivatives, starch, ethoxylated amines have been reported.

Anti-oxidants

It has been reported that anti-oxidants such as benzotriazoles are effective oxidation inhibitors for various metals including copper and its alloy^[13,14]. In soft

soldering the function of the flux is to remove the passivating layers and then form a protecting blanket (e.g. the rosin melt in SMT reflow) to prevent further oxidation during the joining process. The ability to protect the metal surfaces just prior to and during solder reflow is important as it allows for more effective wetting. This in turn allows the solder paste formulator to use lower amounts of activators thereby enhancing the no-clean feature of the solder paste. In the electronics industry, it has been common practice to use thin films of benzotriazole for the protection of copper surface from oxidation. Paste manufacturers have extended these concepts to solder paste formulations by incorporating anti-oxidants.

Some considerations for paste manufacture

Although, the idea of mixing metal powder in a thick emollient appears simple, a large number of variables are involved in paste manufacture^[1,3]. The steps in paste manufacture are:

- Formulating the flux vehicle
- Producing, sizing and storing solder powder

- Flux vehicle
- Basic flux vehicle (e. g. rosin and solvent).
- Polymer additives
- Activation level
- Type(s) of activator(s)
- Thickening agents
- Secondary solvent
- Solder powder
- Oxide layer thickness
- Particle size distribution
- Particle shape and uniformity
- Source alloy compositional uniformity
- Source alloy compositional control
- Particle alloy uniformity
- Mixing process
- Insufficient material properties specified as product controls
- Process procedure sequence
- Mixing rates, times and temperatures
- Post-formulation property adjustment procedures (e. g. viscosity control, % metal control)
- Absence of mixing atmosphere control (e. g. humidity)

Figure 1. Variables involved in paste manufacture

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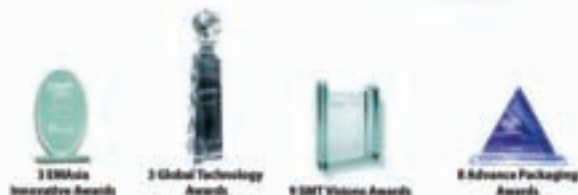
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9. Shelf life-crusting
10. Shelf life-separation
11. Component hold before and during reflow
12. Reflow quality-detail
13. Reflow quality-spatter
14. Reflow quality-joints

Figure 2. Most commonly encountered defects encountered when using solder pastes

- Blending flux and powder to form the solder paste and packaging. The variables involved in each of these steps can have a direct effect on product quality. Additionally, there are interactions between the variables that also have important effects on product quality. For example, it has been show that the thickness of the oxide film on powder spheres, which is critically dependent on the conditions and method of solder atomisation, interacts strongly with variables in blending such as blending sequence and atmosphere. The result is a marked effect on the rate of ‘crusting’ and the length of storage life-time.

All the defects in Figure 2 can be traced to the three steps involved in solder paste manufacture, including blending and packaging.

A consideration is air introduced during the mixing process that can encourage solder balling. The mechanism for this involves the reaction at room temperature during storage of activator and surface oxide that produces a metal salt (typically a halide or a carboxylate). This in turn reacts with carbon dioxide and water trapped in the mix to yield metal carbonate. Further reaction with carbon dioxide and water produces insoluble basic carbonate. Further reaction with carbon dioxide and water produces insoluble basic carbonate deposits. These deposits both precipitate in the body of the solder pate drying storage and also coat metal particles. When this effect occurs to a significant degree, it causes a ‘crust’ to form on the surface of the paste in a jar. At the same time, crusting throughout the body of the solder paste encourages solder balling

during reflow. Additionally, it could lead to a catastrophic increase in the viscosity of the product, making dispensing or printing very difficult or even impossible.

Another issue is the type of the residue formed after reflow and its cleanability. The volume of flux in a paste is large (up to 45%) and combined with the trend towards finer pitch assemblies makes cleanability or ‘no clean’ a serous issue. A reported solution is to use a two component activation system, one part of which is specific to the powder and the other selected to flux the substrates and leads. It has been reported that the two component activation system could be present at a lower level than the broad-action single activator systems. This would lead to lower residues and may obviate the need for cleaning.

Testing

The quality assurance tests for solder pastes are well known and are documented in several standards. All BizEsp products, for example, are tested according to industry standard test methods.

Recommendations for formulation of solder pastes

A survey of patents and papers suggests that similar or identical compounds are cited in most of the publications. Furthermore, the quantity ranges cited for formulation components are similar. The types of materials and ranges are shown in Table 2. These materials are blended and used to make solder paste by using a ‘one-stock’ or ‘two-stock’ approach. The flux product is then mixed with solder powder (88-91% by weight). Suppliers specify the temperature ranges and shear rates for the incorporation of the various rheology aids.

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Biographies

Dosten Baluch, BSc. Chemistry, Ph.D. Materials Science and MBA was educated in UK and has 10 years ‘hands-on’ experience of solder powder production, solder flux and paste formulation and testing gained in USA and UK with international companies. He was involved with lead-free research at inception and has worked with clients such as Motorola, AC Delco and AVX in USA and Celestica Europe.

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| Material | % Weight |
|---------------|----------|
| Solvent | 32-40 |
| Rosin | 49-52 |
| Activators | 0-4 |
| Rheology | 8-15 |
| Hydroxyamines | 0-2 |
| Anti-oxidants | 0-2 |