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An Introduction to Electrically Conductive Adhesives and their Current Applications

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SUMMARY

Conducting adhesives have been adopted in niche markets that require high levels of interconnection density. Typically conducting adhesives have been used in hybrid technology, die-attach and display assemblies. These materials offer a more environmentally acceptable processing route than lead based solders. This feature has helped to raise their profile within the industry as a result of increased environmental concern over lead containing alloys particularly within Europe. This is particularly attractive since these materials can be processed at lower temperatures than lead free metal alloys, an important consideration when manufacturing boards that contain thermally sensitive packages.

In this document we discuss the types of adhesive that are currently available, current applications and their advantages and disadvantages. The requirements for developing or agreeing on appropriate test methods for assessing the performance of these materials during both manufacture and service are particularly highlighted.

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1 INTRODUCTION

The demand for manufacturers to produce low cost lightweight items such as laptop computers and digital cameras with excellent performance capabilities is a major driver in the conducting adhesives market. This coupled with increasing environmental concern over lead containing alloys particularly within Europe is pushing conducting adhesive technology to new limits.

Conducting adhesives are not new materials: epoxy based materials loaded with silver particles have been available for several decades. Over this period the technology has evolved although the basic principle remains the same; an organic resin base filled with conductive particles is used to surface mount a component to a board. Conducting paths are established through contact between the metallic particles suspended in the adhesive which also provides a means of mechanical attachment. Typically, conducting adhesives have been used in limited areas of the electronics packaging industry in hybrid, die-attach and display assemblies. However the market for these materials is rapidly expanding to encompass flip-chip applications such as smart cards.

This brief document provides an introduction to conductive adhesives describing the types of materials available, suitable applications, limitations of the current technology and is aimed at electronics engineers.

2 OVERVIEW OF CONDUCTIVE ADHESIVE TECHNOLOGY

Conducting adhesives are broadly classified into two groups, one of which conducts isotropically (in any direction) and the other anisotropically (in one direction only).

2.1 ISOTROPIC CONDUCTIVE ADHESIVES (ICAS)

Isotropic conductive adhesives conduct in three dimensions analogous to conventional solder materials. They are usually formulated as pastes consisting of conductive particles randomly dispersed in an organic resin. The most popular systems are based on epoxy resins heavily loaded with silver filler particles. Conducting paths are established by point-to-point contact between the filler particles and the component/substrate terminations. Generally these adhesives are applied to circuit boards by either screen printing or pneumatic dispensing, depending upon the rheology of the formulation. They are currently used mainly for die attach and hybrid circuit manufacture. ICAs are processed at lower temperatures than solder pastes. Some adhesive systems used as carriers for the conducting particles are prone to moisture uptake. This can lead to degradation of electrical properties. Furthermore the impact strength of ICAs is comparatively low which can lead to failures when used in applications such as mobile phones.

2.2 ANISOTROPIC CONDUCTIVE ADHESIVES (ACAS)

Anisotropic conductive adhesives have been specifically designed to conduct in one direction only i.e. that perpendicular to the board whilst providing insulation in the plane of the adhesive layer. This property is achieved by having a much lower volume of filler particles than is used in ICAs such that adjacent particles in the resin do not touch. The electrical connection is achieved by mechanical entrapment of the particles between the component and substrate pads during the cure stage as shown in fig 1.

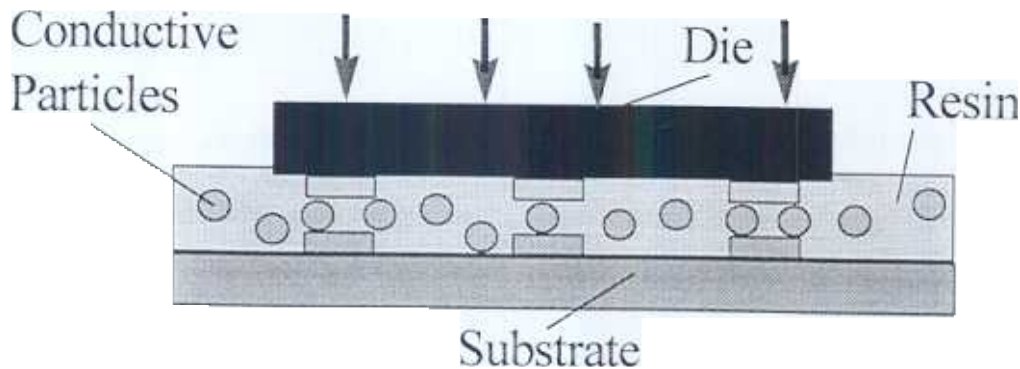


Fig. 1 Schematic of anisotropic conductive adhesive for flip-chip attach

The filler particles are metal spheres or polymer spheres coated with noble metals. The latter are preferred as they provide a degree of 'springiness' in the electrical contact to improve thermo-mechanical reliability. They are most often used to attach fine pitch/area array devices to glass substrates such as LCD displays. They may also be attractive for chip-scale package (CSP) attach applications (e.g. smart cards) since they remove the necessity to clean and underfill after conventional soldering.

Anisotropic conductive adhesives can be grouped into two categories: those that conduct prior to processing and those where conduction occurs after processing. Pre-processing ACAs are supplied as sheets or tapes that can be preformed to match the footprint of the package. Such films are complicated to produce and rely on conducting material filling cavities in the film that are created by either laser drilling or etching. Post processing ACAs consist of a homogenous dispersion of conducting particles suspended in a paste or occasionally in a film. The conducting pathways are usually established through a combination of pressure and heat applied during processing. This requires specialised equipment.

3 THE BENEFITS AND LIMITATIONS OF USING CONDUCTING ADHESIVES

The benefits that conducting adhesives can offer over traditional solders include:

- ultra-fine pitch interconnections.
- compatibility with a wide range of different surfaces.
- low temperature processing - limiting thermal stressing of components.
- low or zero emission of volatile organic compounds.
- potentially clean application - no flux residues.
- reduced pre- and post-cleaning.
- lead and heavy metal free materials.
- wide range of materials available for tailoring to meet specific requirements.

However they do suffer from limitations in the following areas:

- reduced impact resistance (compared with solder).
- no self alignment of components.
- increased thermal resistance - can affect ability to conduct heat away from components.
- increased electrical resistance.
- more difficult to rework.

- reliability may be more sensitive to terminations and board finish.

4 SURFACE PREPARATION AND OTHER REQUIREMENTS

Two factors affect the strength of adhesive bonds: the adhesion between the adhesive and the substrate and cohesion within the adhesive itself. The strength at the interface between a chip or substrate and the adhesive can be influenced by surface preparation. Surfaces to be bonded must be clean and dry and free from, for example, flux residues¹. These can be removed by vapour phase degreasing followed by vacuum baking². Plasma etching has also been used to clean surfaces but this can lead to adhesive bleeding i.e. flow of adhesive over the surface of the substrate².

Not surprisingly the strength of the adhesive bond reflects the interaction between the adherend and the adhesive. Bond strengths of epoxy based adhesives are excellent with ceramics and aluminium but less substantial with plastics and tin. Gold, silver and silver-palladium give excellent results and are the preferred metal surfaces for adhesive bonding.

The thickness of the adhesive layer must be carefully chosen so that the gap between the substrate and the package is completely filled. Incomplete filling is responsible for forming voids and poor conduction or failed joints.

Softening of FR-4 substrate can occur at the temperatures required for, for example, curing epoxies due to the high bonding force applied to the assembly and the time required to establish the bond. This can result in the surface connection pads sinking into the substrate resulting in a loss or reduction in conduction. To some extent this deformation is recoverable after curing as the epoxy recovers although the extent to which it recovers will depend on how much plastic deformation has occurred within the substrate.

5 ADHESIVE MATRICES AND CURING CYCLES

Both thermoplastics and thermosets are used as adhesives. Thermoplastics have an advantage over thermosets in that they will soften if reheated which greatly simplifies reworking. In contrast thermosets are difficult to rework once cured. However due to their greater range of thermal stability they can be used in more demanding applications e.g. under bonnet or in aircraft manufacture. Reworking thermoset based conducting adhesives usually requires mechanical removal of the component from the board followed by chemical cleaning. This often causing damage in epoxy based boards e.g. FR-4.

Thermoplastic adhesives are usually styrenic copolymers e.g. SBS (styrene-butadiene-styrene) or SEBS (styrene-ethylene-butylene-styrene) although polyimides and poly(vinyl butyral) have also been used. Polyimide in particular has to be processed at higher temperatures than the styrene compounds due to its higher softening point (glass transition temperature (T_g)). However the higher T_g of this material does enable it to be used in higher temperature applications. Although attractive from a rework viewpoint pure thermoplastic adhesives do not in general provide sufficient adhesion strength at elevated temperatures.

Cure of thermosetting materials is usually achieved by heat although UV cured systems are available. Most thermosets are based on epoxy although polyurethane, silicone and acrylics

can also be used. The epoxy resin is either a pure thermoset or blended with a thermoplastic polymer. Epoxy based ICAs are usually supplied as one-part systems. These require refrigerated storage and shipping at -40°C which raises transportation costs and can generate significant logistical issues. Thermoplastics have an advantage over thermosets in that they do not have to be cured, just heated above the softening point.

6 ISOTROPIC CONDUCTIVE ADHESIVES

6.1 CURRENT ICA TECHNOLOGY

This class of adhesives is the most promising in terms of direct replacement for solder technology, although there are still some technical hurdles that need to be addressed. Most of the current state-of-the-art ICA materials are based upon epoxy resins with flakes of silver as the filler material. Silver is the preferred filler because the silver oxide formed during oxidation remains electrically conductive. The electrical properties of the cured material are therefore preserved provided that the particles remain in contact. Nickel, copper and gold/palladium are also used as conductors although the build up of copper oxide will lead to reduced electrical conductivity.

The adhesive carrier is highly loaded in ICAs with metal contents³ of 80 - 90 wt% (25-30 vol %). The high loading of metal is required to give good conduction although the mechanical performance of the adhesive suffers with increasing filler content. Flakes are used in preference to spheres in order to maximise the inter-particle contact surface area: a smooth sphere has the smallest surface area to volume ratio of any particle geometry.

6.2 PROCESSING ICAS

A typical ICA assembly process consists of three stages;

- (i) dispense ICA paste
- (ii) place components
- (iii) cure

Generally these materials can be dispensed by stencil printing or pneumatic dispensing in a similar manner to solder pastes. One of the attractive processing properties of ICAs is that it is possible to screen print at very fine pitches. This is possible because the filler particles can be much smaller than those found in solder paste formulations and the incidence of bridging defects is significantly reduced. The accuracy of placement with fine-pitch components is critical since there is very little 'self-alignment' of components during the cure stage as can occur during soldering. This is due to the wetting forces being much lower than those encountered in a typical soldering process.

One of the advantages of ICAs over solder is that the processing and performance temperatures can be 'tuned' to a particular application. This may be particularly attractive in the drive to remove lead from solders since ICAs offer a low temperature alternative to the high melting point lead-free solders. Cure schedules can vary enormously depending upon the resin formulation, process conditions and the ultimate desired properties of the cured joints. Snap-cure formulations are available which cure in 2-3 minutes at typical temperatures of around 150°C although the best joint properties are usually attained in a medium length (~1 hour) offline cure. In the latter case the materials are often given a short 'gelation' cure in-line and then transferred to batch ovens for the full cure.

6.3 ICA PERFORMANCE

A major obstacle to the widespread use of ICAs as a solder replacement is the in-service performance of the cured joints. The most critical of the performance issues is the degradation of electrical properties of ICA joints during ageing. Most of the current generation of ICAs show a significant degradation in electrical conductivity during ageing when the component/board termination's are eutectic SnPb alloy, Ni or Cu. However this is not the case where the component/board terminations are noble metals eg. Au, Ag and Pd. This could be due to the build-up of oxide layers on the component termination's increasing the contact electrical resistance between the Ag particles in the adhesive and the termination surface. This can be reduced to some extent by adding small conductive interpenetrating particles to the formulation to break through the non-conducting oxide layer and maintain good electrical contact. Some improvements over conventional ICA technology have been obtained using this approach although the time dependent degradation of electrical properties remains a significant issue. An alternative explanation offered for the degradation mechanism is that an electrochemical corrosion cell is present between the filler particles and the component/board terminations due to the difference in electrochemical potential between Ag (+0.79V) and SnPb (+0.13V) alloy. The corrosion cell requires moisture and oxygen to be present for corrosion to take place, and hence the degradation of electrical properties is most evident in damp heat (85°C/85%RH). This effect has been demonstrated with metal wires and is much less severe with noble metal finishes since Ag, Au, Pd and Pt all have similar electrochemical potentials. Two different strategies have been employed to reduce the corrosion cell effects; the addition of oxygen scavengers and the addition of corrosion inhibitors to the resin formulation. The oxygen scavengers work by reacting with free oxygen in the resin matrix, whereas the corrosion inhibitors bind to the component/board termination to reduce the corrosive effect. Initial trials of prototype ICA formulations have shown that both approaches have demonstrable beneficial effects upon the degradation of electrical properties at 85°C/85%RH.

The impact strength of current ICAs as measured by a drop test is relatively poor. This is a critical parameter in applications where mechanical impact is likely, such as mobile phones, portable computing and automotive/rail/aerospace applications. The impact strength of an ICA is dominated by two factors;

- adhesion strength (shear) of the ICA to substrate/component.
- dissipation of impact force by the ICA.

The first factor is largely dominated by the filler/resin ratio and is not easy to adjust as previously discussed. The second factor is an intrinsic material property that may be engineered into the resin system. Typical ICA epoxy systems are glassy materials at the temperatures typically encountered in service due to their relatively high glass transition temperature (T_g). This property limits their ability to absorb mechanical shocks in comparison with rubbers. This has been recently demonstrated in trials with experimental ICA resin systems that have T_g 's below room temperature. These rubbery materials showed significant improvements in drop-test performance compared with glassy epoxies and could offer a significant breakthrough in the impact strength of ICAs.

Flip chip on board (FCOB) circuits can be susceptible to joint cracking between the bumps and the substrate as a result of mismatched thermal expansion coefficients. This can be improved by using an epoxy adhesive as an underfill to mechanically couple the spaces between the bumps of flip chips to limit the cyclical shearing and fatigue of the joints themselves⁴. The impact resistance of ICAs can also be improved by conformally coating

boards⁵

Both the mechanical and electrical properties of ICAs can be increased by using a low melting point solder as the filler material. These filler particles are designed to melt as the supporting matrix is cured forming metallurgical connections between the component/board termination's and the filler particles. This greatly improves the electrical properties of the ICA joint and may also increase mechanical strength. Currently there appears to be little published information about the efficacy and reliability of such materials.

6.4 APPLICATIONS FOR ICAS

The current commercially available ICAs do not offer a practical replacement for solder in mainstream electronics assembly. This is partly due to the technology limitations discussed previously. Furthermore there is also reluctance by industry to embrace an unproven and potentially expensive technology. Areas where ICAs are currently used with routine success include die-attach in packages and bare boards, non-safety critical hybrid circuit manufacture and in some consumer/automotive electronics. Generally ICAs can be used with a high degree of success where;

- the assembly is protected from moisture ingress.
- component and substrate termination's are either Au, Ag or Pd.
- the assembly is not subject to violent mechanical shock.

With the increasing drive to remove lead from electronics assembly it is expected that ICAs will offer attractive alternatives to SnPb solders in applications where higher soldering temperatures cannot be tolerated. Therefore the scope of applications for ICAs is expected to increase, particularly if the 'next generation' of ICA materials discussed in section 6.3 overcome some of the technological barriers highlighted.

7 ANISOTROPIC CONDUCTIVE ADHESIVES

Anisotropic conductive adhesives have been developed primarily for the attachment of microelectronics onto glass substrates in the manufacture of flat panel LCD displays. Almost all of the worlds LCD display manufacture takes place in Japan and South East Asia, where the use of ACA technology is widespread. Some European companies are now beginning to look at this technology. The principle behind ACA technology is that the cured adhesive only conducts electricity in the z axis i.e. in a direction perpendicular to the plane of the board. This is achieved by having a much lower volume of filler particles in the resin base than for ICAs such that adjacent particles in the resin matrix do not touch each other. Typical metal loading densities are 5-10 vol% compared with 25-30 vol% in ICAs. Electrical connection between the component termination's and the substrate is achieved by entrapment of particles under pressure during curing (Fig.1). ACAs are currently receiving a lot of attention as attachment media for fine pitch area array devices and for flip-chip assembly. This is primarily due to the fact that high-accuracy dispensing in the xy plane is not required, and indeed ACA film technology removes the need to dispense entirely. ACAs can be used in ultra small pitch (below 150 μm) flip chip technology applications beyond the limit of solders and bumps. ACAs also offer the advantage that they can be applied over wide areas with little concern for pad locations.

For low power applications, the preferred filler material is Au or Au/Ni coated polymer spheres. The polymer spheres provide a degree of springiness in the particles that improve the

reliability of the electrical connection during thermo-mechanical cycling. Recent work has shown that optimum conduction occurs when metal coated polymer spheres are compressed to a height of between 80-100% of their original diameter⁶. However care needs to be taken during processing as the polymer spheres can split if too much force is applied during the curing cycle leaving metal skins. For higher power applications metal spheres or fusible solder particles are used as the filler in order to improve the current carrying capacity of the ACA joints.

ACAs are available in both paste and film formulations where the particles are randomly distributed throughout the resin. This random distribution can lead to occasional shorts, particularly at very fine pitches where the particles form a conductive path between adjacent interconnects. A recent development is an ACA film which has pseudo-ordered particles in a single layer. This dramatically reduces the chance of shorts and opens since the inter-particle spacing is very uniform throughout the layer. A Japanese company has extended this concept and produced a film consisting of a monolayer of particles sandwiched between adhesive layers. The conducting particles are suspended in a viscous thermosetting material whilst the adhesive layers are less viscous. During application the adhesive layers form the adhesive bond while the conducting particles are constrained within the viscous core material. This restricts their movement during assembly. Such systems are supplied as films and require IC's with bump connections.

7.1 ACA TECHNOLOGY LIMITATIONS

Unfortunately ACAs require specialised equipment to provide both heat and pressure simultaneously during the curing of the adhesive. Therefore applications tend to be limited to very specific interconnection challenges rather than the assembly of large area circuits with multiple component size and shapes. Prolonged heating of the FR-4 substrate at temperatures well in excess of the glass transition temperature of the epoxy can lead to localised softening of the board⁷. This can result in some sinkage of the pads due to the pressure being applied to the whole assembly and consequent conduction problems. However this increase in resistance will at least be partially compensated for by the epoxy relaxing after the pressure has been relieved.

Conductive particles tend to flow away from the component terminations as pressure is applied during curing. This effect has been modelled for area array packages and is shown to be most critical for pads in the central region of the component edges. New developments in the manufacture of ACA film as described in section 7 seem set to eliminate problems of this nature.

Co-planarity of the substrate and component terminations is also critical to achieving a reliable connection since typical particles sizes are of the order of 5-7 μm . This can be adversely affected by pad subsidence during curing. Care must also be exercised in bumping chips to ensure that the variation in bump height⁸ is within a tolerance band of $\pm 3\mu\text{m}$.

7.2 ACA TECHNOLOGY APPLICATIONS

ACA technology is well established in the Asian LCD attach market and is now finding applications in chip-on-board and other chip attach applications. ACA joined flip-chips offer significant weight savings over equivalent surface mount packages: total material savings in excess of 10 times have been reported⁷. ACA bonded flip-chips are therefore likely to appear

in many applications such as cameras and mobile phones where weight is an important issue. An emerging application area in Europe is in the production of smart-cards. The attraction of ACA technology for this application is that it removes the need for the cleaning and underfill process steps in an ultra-low cost product. The smart card application requires a rigorous reliability testing regime, including flexing of the cards through many hundreds of cycles. The ACA technology has been proven in a pilot smart card application, although the major issue with the current technology is that the relatively long cure cycle causes a bottleneck in the production line.

8 DISPENSING ADHESIVES

The general requirements of conducting adhesives are similar to those of solder paste with respect to fillet shape and pad coverage. In fine pitch applications the adhesive has to be dispensed with high volumetric accuracy and be accurately positioned (typically within $\pm 125 \mu\text{m}$). Since most adhesives are thixotropic (i.e. become less viscous when sheared) the dispensing process usually incorporates a short dwell time to ensure that the dot adheres to the board. An additional challenge is to ensure the drop of fluid that remains attached to the board does not fall over to form a tail that could lead to shorting. Conducting adhesives can be dispensed using auger or linear pumps and time/pressure methods although linear pump technology appears to produce the most consistent results⁹.

9 THE POTENTIAL OF CONDUCTING ADHESIVES

The market for conducting adhesives seems set to rapidly increase as past technical problems are solved by new technological developments. The potential market for ACAs seems particularly bright as the trend for electronic devices that are light, compact and capable of excellent performance continues. This trend coupled with new and pending legislative laws that will outlaw the use of lead and other heavy metals makes the use of conducting adhesives an attractive proposition.

10 ASSESSMENT OF THE QUALITY AND PERFORMANCE OF ADHESIVE JOINTS

The performance of adhesive joints both during manufacture and in-service reliability is a significant issue that needs to be addressed before these materials can begin to replace the metal alloys used in mainstream electronics.

During manufacture joints can fail for the following reasons:

- Softening and subsequent subsidence of the substrate (e.g. FR-4) during the curing cycle. Noting that although curing occurs at lower temperatures than those used for soldering, the time at elevated temperature is greater.
- Voiding due to vapourization of solvents or water during the curing cycle.
- Lack of coplanarity between the attachment and the substrate can adversely affect conduction in ACA's.
- Poor adhesion to the board finish.
- Poor placement of fine pitch components.

In-service failures can be caused by:

- Uptake of moisture by the adhesive leading to corrosion.

- Poor adhesion between the adhesive and substrate at elevated temperatures.
- Loss of electrical properties during ageing.
- Lack of impact strength.
- Joints cracking due to mismatched thermal expansion coefficients of the attachment, adhesive and substrate.

Whilst some of these issues can be resolved by selecting different board finishes and systems with similar thermal expansion coefficients there is no consensus as to how to test the quality and performance of adhesive joints. Typically measures of in-service performance involve either a drop test where the board is dropped edge on from a prescribed height on to a hard surface or some combination of thermal and humidity cycling. The latter environmental conditioning relies on mismatch in thermal expansion coefficients to induce failure through shear fatigue. Drop tests rely on the inertial shear force that results from rapid deceleration to cause the attachment to delaminate noting that the magnitude of this force depends on the mass of the attachment and the area in contact with the board i.e. a mass/area ratio.

From this discussion it is clear that quality control assessment of adhesive performance both during manufacture and in service is an area that requires further study in order to generate agreed guidelines for testing these materials.

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