Conductive Adhesives: The Way Forward

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INTRODUCTION

Conductive Adhesives represent an intrinsically clean, simple and logical solution for a myriad of electrical interconnect challenges. Adhesives not only provide a "lead-free", "no clean" alternative to solder, these highly compatible materials offer viable answers to problems where solder is totally inadequate. Adhesives may also play an important role in disassembly and recycling that will certainly become a necessity in the future. But is conductive adhesive technology really the right choice for today's high density interconnects and our ever-increasing environmental problems? We will examine the basic concepts needed to understand and appreciate the wide variety of conductive adhesive materials and let you draw your own conclusions.

ADHESIVE TYPES

There are a number of polymer-based bonding agents, or conductive adhesives, employed in the electronics field. The most common materials are the die attach adhesives which are used to bond bare silicon die to lead frames, BGAs and chip carriers as part of the packaging process. Billions of IC chips are packaged this way. These materials are called isotropic conductors since electrical conductivity is equal in all directions. There is another important class of bonding agents with unidirectional conductivity, called anisotropic. These anisotropic bonding agents are experiencing significant growth since they are well suited for very fine pitch bonding and solve basic interconnect problems associated with the widely used flat panel displays. Non-conductive adhesives are also used to create electrical junctions which may seem like a paradox. The common scheme employed is to mate component conductors and circuit pads, using the non-conductive adhesive as the means of producing force on the opposing junctions. Each of these adhesive types will be covered in more detail in the following sections.

Isotropic Conductive Adhesives

Isotropic conductive adhesives produce approximately equal electrical conductivity in all directions. They are typified by the silver-filled epoxies originally used for die attach, but now modified for component assembly. Epoxies have been the work horse polymers of electronics because of their ease of use, the availability of hundreds of resin-hardener combinations, balanced properties and generally superior bonding properties. Since die attach adhesives usually have good electrical conductivity, they were the obvious starting point for component assembly conductive adhesives.

Pioneers in the Polymer Thick Film field experimented with various die attach adhesives as a substitute for solder several decades ago. But since conductive adhesives do not wick onto wires and terminations or form fillets as does solder, these materials worked poorly with feed-through component devices. The advent of Surface Mount Technology (SMT) provided an excellent form factor for adhesives. Once SMT became established, conductive adhesive were developed for this application since material did not have to wick and fillet or flow into holes as was the case for feed-through device wave soldering. Assembly adhesives only needed to be dispensed on circuits and form reasonably good electromechanical junctions with components placed in the paste. The SMT form factor, which produced the desired butt joint, was the ideal packaging change needed to boost conductive adhesive technology.

One problem with using the unmodified die attach adhesives for assembly was the long cure and high temperature processing requirements. Many materials needed more than one hour cure schedule at processing temperatures of 150°C to over 200°C. This precluded their use on low cost polyester substrate, the most obvious target for adhesives since soldering was not viable due to its higher temperature processing. The long cure schedule, even if the high temperatures could be handled, was not competitive with soldering processing. During the 1980's, new materials began to appear specifically designed as bonding agents for Polymer Thick Film circuitry. Fast cure systems were designed with cure cycles that could be achieved with IR reflow ovens set at lower temperature profiles or conveyor belts speeds set higher. This meant that the conductive adhesive could be run on a Surface Mount line without modifying or adding equipment. The increasing popularity was also a big boost for PTF bonding since there was no practical way of using conductive adhesives on wave soldering lines. The 1980's saw the successful commercialization of conductive adhesive assembly.

Another problem that appears to be resolved, was that of junction instability. Even though very good adhesives became available, the junction between the component and circuit often showed a large increase in resistance after temperature and humidity aging. The result is thought to be the formation of insulative oxide on the component leads and circuit conductors. Oxidation of the circuit conductors can be solved in various ways such as adding gold flash plating. However, since most SMT component terminations are finished with tin-lead solder, this presented a greater problem. Junction stable adhesives were eventually developed that were compatible with standard solder-finished components, although mechanisms are uncertain. One material, called Poly-Solder, is thought to be stable with oxidizing surfaces because of small conductive particles that penetrate oxide. This conductive adhesive has proven so reliable, that over 100 million SMDs have been assembled with no reports of junction failures.

Not only were new, low temperature thermosets introduced, but various thermoplastic isotropic conductive adhesives were commercialized. The thermoplastics could be applied as solvent-containing pastes, dried to solids and then melted for assembly. The thermoplastics conductive adhesives, much more akin to solders, have been referred to as "organic solders". Unlike the thermosets which change chemically during curing, the thermoplastics can be remelted for repair. Bonding is much faster with the hot melts since heating is only used to bring the material to the melting point, not to induce chemical reaction. A negative characteristics of most thermoplastics is lower strength and porosity caused by entrapped solvent. Much more work can, should and is being done in the thermoplastic adhesive area.

Bi-Directional Anisotropic Conductive Adhesives

As implied, bi-directional adhesives effectively have conductivity paths in two directions. The first bi-directional conductors were not adhesives at all, but interposer strips that required continuous external force. The products are also called elastomeric conductors or pads. One of the earliest products consisted of a stack up of silicone rubber and carbon filled elastomer sheets which was then sliced vertically through the stack to produce the familiar black and clear striped pad commonly referred to as a "zebra strip". True adhesive materials evolved with similar constructions of conductive/nonconductive stripes. These bi-directional anisotropic adhesives are available in films as rolls and strips. Most use thermoplastics and are typically used to for connections to flat panel displays, especially Liquid Crystal Displays (LCDs). One of the most popular product families is made by Nippon Graphite Co. Ltd. of Japan. The product is sold under the Elform brand.

Another version of the self-adhering interconnect cable was the now defunct Scotchlink® from 3M Co.. The product consisted of parallel conductors coated with hot melt insulator. Small conductive spheres of silver were imbedded in the dielectric but they were not in contact with the parallel conductors which, incidentally, were made of metallized silver. The product was supplied in roll of different pitch. A length was cut from the roll and heat bonded to the two interconnect sites. Two hard boards, for example, could be interconnected with ScotchLink®. The concept was innovative and appears to have been unique since the adhesive served as an insulator, unlike the zebra strip style where conductors could be shorted out. The implementation, however, produced limitations. The use of thin silver as the conductor limited current and invited silver migration. The product was finally withdrawn from the market but a re-engineered version has become available recently.

Unidirectional Anisotropic Conductive Adhesive

The next evolution of interposer bonding materials was the introduction of unidirectional products in the 1980's although the concept actually goes back several decades according to patent literature. There was a serious need for an interconnect material that did not require parallel alignment and one that would also be capable of finer pitch than the strip products. The solution is remarkably simple, perhaps so simple that it was overlooked several times. The basic idea is to disperse conductive particles in a dielectric adhesive.

The loading is kept low enough so that the material is not made conductive by contact between particles allowing it to remain an insulator in its plane. It is a little like making a conductive adhesive without enough conductor. Conductor loading levels are typically much lower than for isotropics and range from 10 - 40% by volume, but with many exceptions. When the adhesive is interposed between two sets of conductors, application of heat and pressure cause inter-plane connections (Z-Axis) to be made.

The invention and rediscovery of the anisotropic concepts is quite interesting. During the early 1980's, several companies, most notably Sheldahl in the US and Sony in Japan, were attempting to connect unsolderable materials. While the Japanese worked on the LCD interconnect problem, Sheldahl, Amp and other flexible circuit manufacturers attacked the flex interconnect issue. IBM Corporation had presented a significant challenge with their Quiet Writer® typewriter program. The printing head was made of tungsten metal but it needed to be connected to a flexible circuit made of copper. After many attempts to solve the mating problem by classical means, Sheldahl and Amp, simultaneously hit on the idea of using polymer materials. Both companies produced PTF membrane switches at that time, so it was logical to investigate this area of technology. Meanwhile Sony began offering limited samples of an interconnect film made with oriented carbon fibers. In many ways, the product was like the zebra strip since the fibers were oriented in parallel. Yet, the fibers were so short that alignment wasn't critical. The US companies quickly realized that the conductors should be spherical-shaped metal. By 1985, both Sheldahl and Amp had produced reasonably good anisotropic conductive adhesives based on silver particles. A search of patents will show that the anisotropic electrical concept was conceived in the 1950's and developed more extensively in the next several decades. Fundamental patents have expired.

Today, anisotropic adhesives are available in just about every form and type ranging from pastes to dry films and from thermosets to thermoplastics. Considerable work has gone on in a many laboratories to better exploit the fascinating concept of unidirectional conductivity. Much work has been devoted to the polymer binder and many materials have hybrid properties of thermoplastic and thermosets combined. Both thermoplastics, noted for fast processing, and thermosets for higher temperature performance, are in use today. Research today, is focused on the conductive particles and perhaps a dozen basic types are under study. Today's popular conductive particles are made of polymer micro-spheres coated with nickel, gold or both metals.

Patterned Anisotropic Conductive Adhesives

Most anisotropic conductive adhesives employ a random dispersion of conductive particles because this is easy to do. More recently, adhesive films with patterns of conductors have been introduced by several companies. All are based on a bondable dielectric continuous film, but with different types of conductors. One approach, called GAZA for Grid Array Z-Axis, employs columns of isotropic conductive adhesive arranged in a grid pattern. The conductive adhesive can be patterned by printing methods with the dielectric film cast as the last operation. Alternatively, holes made be formed in a dielectric sheet and filled with conductive adhesive. Good results have been shown but the difficulty in manufacturing such materials at low cost has limited the technology. The patterned adhesive concept would seem to have benefits in many applications and further work is warranted.

Thermoset vs. Thermoplastic

Thermoplastic-based adhesives have the important advantage of fast processing and easy rework. No chemical reactions occur during application processing. Heat is applied to cause a change in physical state, typically the transition from solid form to a flowable phase. This takes a short time, perhaps less than a second. Thermoset systems undergo true chemical reactions which require several minutes to hours. Thermosets usually have a limited shelf life or pot life for those materials which must be catalyzed before use. The thermoplastic binder remains remeltable. This means that it will soften or melt if heated to a high enough temperature. Thermoplastics are therefore somewhat limited in service temperature performance. Thermoplastics also have a tendency to flow under the application of force. This is referred to as cold flow or creep. The cross-linked thermosets, however, resist deformation and are much more mechanically stable. The thermoplastics also tend to form weaker adhesive bonds. The thermosets typically start off as low molecular weight liquids which can wet out a surface for more complete bonding.

The thermoset adhesive can also react with various surfaces to form strong chemical bonds. The thermosets generally form stronger bonds that are more durable. The superior properties of thermosets compared to thermoplastics offsets the handling inconveniences and greater control requirements.

Although room temperature cure thermosets are commercially available, they are not latent and begin to react as soon as the catalyst or hardener is added. Two-part, fast cure epoxies are a good example. A useful adhesive must have a reasonable working life, usually eight hours. Some lower temperature thermosets are already catalyzed and must be kept frozen to prevent them from hardening prematurely. There are a few latent thermoset systems with reasonably low curing schedules. Thermoplastics, especially the solid films, have nearly infinite shelf life and are stored at room temperature.

Thermoset epoxies are by far, the most common conductive adhesive binders and have found use since the early 1950's. Wolfson described epoxy-silver compositions for use as die attach and replacing solder in the early 1950's. The patent literature abounds with examples of epoxy adhesives filled with silver. In the mid-70's, NASA extensively studied conductive epoxies for use in aerospace electronics. Numerous other articles have appeared which describe the properties and performance of conductive epoxy systems as bonding agents for components, especially surface mount types, and chapters that follow will contain many references. Silver-epoxy can be considered the base line for isotropic conductive adhesives used for component assembly.

APPLICATIONS FOR CONDUCTIVE ADHESIVES

Conductive adhesives dominate only one or two niche markets at this time. Die attach adhesives quickly replaced metallurgical connections many decades ago and they are unlikely to be displaced in the foreseeable future. Anisotropic conductive adhesive films are now the dominant means for connecting flat panel displays. What other areas are practical markets for conductive adhesives?

We must first recognize that solder is the de facto joining material of the electronics industry. Adhesives are always compared to tin-lead solder in every application. Only when there are significant benefits for adhesives, do end users seriously evaluate these materials. The cost of qualifying a new material and moving it into production is considerable. There must be a significant pay off before most companies will make a change. Many companies find the favorable environmental attributes of adhesives interesting, but not enough reason to make a change at this juncture. Companies tend to test adhesives as a future alternative, should the need arise, but do not really contemplate an immediate switch. In today's market, conductive adhesives must provide a better solution, improve performance, reduce cost or increase productivity to sell. What are the advantages of conductive adhesives and what are the limitations compared to solder?

Adhesives have a significant processing advantage over solder which exposes components and circuits to harsh temperature conditions. In fact, the packaging and circuit industry have had to work much harder because of the thermal shock of soldering and their products are accordingly more costly. Adhesives process under mild conditions and allow virtually every circuit substrate and component to be bonded without harmful affects. What applications benefit from lower temperature processing? Polyester-based flexible circuitry and molded circuits are obvious applications. Heat stabilized polyester film, so common in the membrane switch and low cost flex circuit industries needs to be processed below 150^{o}C. Most isotropic conductive adhesives can be cured in reasonable times at 130 - 140^{o}C making them ideal for switches and other low cost thermoplastic-based products. The low cost flexible circuit industry has already started to enthusiastically embrace adhesives for SMT assembly and the trend will continue. However, only a small part of that large market has adopted adhesive assembly at this time. One very successful product, the Hewlett Packard Ink Jet printer, uses LEDs bonded with conductive adhesives. Nearly 20 million units have been built using adhesives, a testimony to reliability and good economics.

Another important attribute of conductive adhesives is their ability to handle very fine pitch. Both isotropic and anisotropic conductive adhesives can assemble flip chips. Flip chip on organic board is a relatively new area if we consider that the technology was developed in the 1960's. Many companies are evaluating flip chips and attempting to define the joining materials and processes as the old C4 method is discarded.

All types of adhesives, isotropic, non-conductive and the several types of anisotropics, can be used here. This is an excellent area for research and development and one that is already proven. Smart card flip chips are being assembled with anisotropic adhesives. Isotropic conductive adhesives are being used to bond flip chips for several applications in the US, Japan and other countries. The finished assemblies have passed qualifications and moved into the commercial sector.

Conductive adhesives excel at solving incompatibility problems. Highly dissimilar adherents can be bonded where solder does not work. Adhesives bond readily to glass and vacuum deposited conductors while solder either will not wet or leaches off conductors. This makes conductive adhesives the best choice for nearly all flat panel displays. Anisotropic adhesives are now in use for bonding flex circuits and TAB devices to panels, but direct component attach is also enjoying success. We need to ask what other areas of assembly have incompatibility problems that adhesives can address.

We should not ignore the circuit construction and assembly area since adhesives are moving in as layer-to-layer connections. Sometimes called interposers, films of various anisotropic conductive adhesives are being used to make superior multilayer circuits. More recently, patterned array interposers have attracted interest for circuit layer assembly. As the circuit industry moves to higher density and the cost of drilling very small holes mounts, the need for new kinds of interposer conductive adhesives will grow. This is an exciting area with huge volumes that should be seriously considered. Sheldahl’s Z-Link multilayer circuit process, for example, relies on anisotropic conductive adhesive for mating layers together. The technology has attracted many millions of dollars in government and industrial support.

Intrinsically Conductive Polymers (ICPs)

The polymer chemist has long dreamed of using electrically conducting polymers to create the electrical pathways and interconnects for electronics. Intrinsically conductive polymers could offer many advantages if only their chemical and mechanical properties were similar to those of modern plastics. A highly conductive moldable or printable material would open up so many new horizons. The molded polymer circuit would likely replace etched copper. Fine "wires' could be extrude or spun like today's polymer fibers. Ultra-fine line circuitry would be possible as conductive polymers became an enabling technology for new products. And component assembly would simply involve pressing the device to the circuit while heating. Repair and disassembly would be just as easy. Unfortunately the ideal conductive polymer has been elusive.

A large number of intrinsically conductive polymers have been produced and described over the past 20 years. Two basic types of conducting polymers exist, ionic and the more common electronically conducting variety based on extensive conjugated p-electron systems. The most common electronically conducting polymers are based on polyacetylene, polyaniline, and polypyrrole. A few of these materials, have been commercialized for such end applications as battery electrodes. Doped polyacetylene has been pushed to a conductivity level of nearly 70% of that for copper metal. This is significantly higher than any values for metal-filled PTF conductors which are still an order of magnitude higher in resistance than copper. In fact, polyacetene is more conductive than copper on a mass unit basis. Why haven't ICPs moved ahead in the electronics area?

Intrinsically Conductive Polymers lack ease of processability and chemical stability. The materials can not be injection molded, thermoformed or extruded in most cases. Processes are typically tedious and difficult such as molding powder under vacuum and very high pressures. The doped materials are relatively inflexible behaving more like inorganic materials than polymers. Some modified materials can be dissolved and cast from solvents, but conductivity is usually sacrificed. The more significant problem is instability in air. The majority of materials oxidize and lose conductivity under ambient conditions. The degradation is accelerated by heat and humidity. Until the instability problem is solved, ICPs will not find any significant use in printed circuits. Much development will be required, however, but the recent announcement by France of a functional polymer transistor, based on ICPs, is very encouraging.

FUTURE POSSIBILITIES

Conductive adhesives for component assembly, including flip chips, is truly an embryonic technology. Although this class of adhesives is not really new, dedicated efforts to tailor properties toward assembly use has only begun in earnest in recent times. All of the classes of adhesives just described can greatly be improved even without major breakthroughs. However, a breakthrough in ICPs, the unusual class of organic materials that can conduct electricity, could have major ramifications for assembly, circuitry and maybe even semiconductors. Adhesives are certainly the way forward.

Bibliography

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