Introduction to Conductive Adhesives

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BACKGROUND

Adhesives may be the oldest joining material used by civilization. Early man used mud and clay as binders for dwelling construction. Ancient Egyptians made animal hide glue for assembling furniture. Native Americans (American Indians) used amber for enhancing the strength of spears. The early and broad-ranged applications for adhesives is a testimony to their compatibility and versatility. Even now, it is the extraordinary versatility and unmatched compatibility that make adhesives so important. But today, there is a newer and even more important attribute that makes adhesives essential to modern civilization—our ability to synthesize and customize them thus improving on nature. It is no wonder, that adhesives play a major role in electronics. In fact, the electronics industry has grown so dependent on synthetic polymer-based adhesives that most of our modern electronic products would be impossible without them. This book examines one very important category of electronic adhesives—conductive. This introductory chapter is intended to give the reader the essentials of polymer-based adhesives to better understand the chapters that follow. And for the specialist already familiar with adhesive principles, we hope that some new and interesting facts are also provided.

Conductive Adhesives represent an intrinsically clean, simple and logical solution for all kinds 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. But is conductive adhesive technology really the right choice for today's high density interconnects and our ever-increasing environmental problems? This chapter will give you the basic concepts needed to understand and appreciate the wide variety of materials to be discussed, and the chapters that follow will give the detailed information to let you make their own conclusion. Authors around the world, from industry, academia, private organizations, research consortia and government laboratories have contributed to this world class book on an important emerging technology.

The writers have pointed out both strengths and weakness of the various electronic adhesives to provide a balance of information. It is our hope that potential users will adopt the technology for applications where the benefits are strong and that problem solvers among the readers will want to help improve materials. This emerging branch of science and applied technology could ultimately become the successor to metallurgical solders because of its extraordinary versatility and ability to be custom engineered. Breakthroughs in the field of intrinsically conductive polymers (ICPs), that recently brought us the polymer transistor, may yield exciting new adhesive products in the future. Adhesives alone, of all the established interconnect methods, offer the best options for product recycling and reclamation that will become essential in the not too distant future.

ADHESIVE TYPES

First, we will look at the various adhesive types and then examine the materials typically used. 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 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 duration and high temperature curing requirements. Many materials required 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. 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 stable 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. The mechanism has been studied by IVF and Chalmers University, both in Gothenburg, Sweden, and information is provided in later chapters. Oxide-reducing hardeners, such as anhydrides and carboxy acids have also shown promise for improving junction stability. Several studies have confirmed that conductive adhesives are reasonably stable under 85% rh/85^{o}C on soldered surfaces.

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 name in the US.

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 although the concept actually goes back several decades. 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 difficult 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 spherically-shaped metal. By 1985, both Sheldahl and Amp had produced reasonably good anisotropic conductive adhesives based on silver particles. The author, chose the simpler term, Z-Axis Adhesive, to describe the product, a name which caught on quickly after the product was described in the trade literature. A search of patents, however, will show that the anisotropic electrical concept was conceived in the 1950's and developed more extensively in the next several decades.

Today, anisotropic adhesives are available in just about every form and type ranging from liquids 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. Several of the chapters in this book deal with work on aniostropic adhesives with details of performance and failure mechanisms.

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.

Non-Conductive Adhesives

Although it may sound like a paradox, non-conductive adhesives can be used to provide electrical interconnects. The materials are used to create mechanical tension which creates force between opposing conductors. The adhesive, of course, must form an insulation barrier between contact interfaces. This is accomplished by selective application of adhesive or, more commonly, by applying enough force to displace adhesive from between electrical contact areas. The method has been claimed to be successful for circuit-to-circuit mating, circuit-to-LCD and bare die to circuit connections. Gold contacts are preferred because of their ability to form low ohmic contacts with minimum force.

Work by the DELTA (formerly Elektronik Centralen) and other laboratorires has shown that non-conductive adhesive film could be used to mate LCDs to circuits with reliability equal to the anisotropic conductive materials. More actual contact area is achieved with the nonconductive adhesive since the entire conductor trace makes contact instead of random particle connections created with the anisotropic materials. Work done primarily in Japan, has shown that bar ICs can be reliably connected to circuit boards with nonconductive adhesives. Japanese workers have reported a process where gold bumped die are bonded to glass circuits using UV cured nonconductive adhesive. The circuit board is coated with a layer of adhesive, the die is pressed against the circuit pads and radiation cures the adhesive from the circuit side. Pressure prior to curing squeezes adhesive out of the contact areas. The polymerization of the adhesive caused shrinkage which exerts force on the junctions to produce a mechanical compression connection. Some products have been in commercial use for several years although long term failure due to polymer relaxation has been reported.

MATERIALS

Polymer-based conductive adhesives reside in the province of the chemist and material scientist. Virtually all of the polymers used in conductive adhesives today are synthetic materials designed to provide the right characteristics for printing, stenciling and other industrial dispensing methods. The seemingly simple conductive adhesives are actually very complicated mixtures of customized ingredients. The custom-crafted polymer materials and special inorganic fillers allow adhesives to be used with standard industrial processes, effectively and efficiently. Material application and bonding for many types of conductive adhesives can be practiced on the same equipment used for soldering because the chemistry has been tailored to fit the infrastructure.

Solders are inherently conductive but polymers are not. This would seem to make them a very poor choice since all but a few structures are excellent insulators. However, one very narrow class of polymers are electrically conductive and are generally called, ICPs for Intrinsically Conductive Polymers. ICPs do not yet have the required physical and chemical properties to make them practical as adhesives, however. The great strides being made in the field of intrinsically conductive polymers, like the recent announcement of the polymer transistor, suggest the ICPs will eventually be used for adhesives. Today's conductive adhesive formulators are forced to use non-conductive polymers at this point in time.

The task of converting a very good insulator to a conductor, however, is solved rather easily. Polymers readily accept fillers which modify most of their properties. Conductive adhesives are therefore produced by adding the right fillers. All commercial conductive adhesives are made with a nonconductive binders that are loaded with fillers having the desired electrical characteristics. Conductive adhesives are actually composites of polymer binder and filler making them very different from the other common class of joining materials, metallurgical solders. The requirement of fillers to achieve electrical conductivity might seem a disadvantage since solders are naturally conductive. Actually, the use of conductive filler in a nonconductive binder results in an interesting and valuable attribute for adhesives. Electrical properties are independent of most of the other characteristics. We will see why this is a positive factor next.

Since adhesives achieve conductivity by means of fillers, electrical properties can be adjusted independently of properties provided by the binder, such as mechanical. Adhesives, unlike solders, have a electrical and mechanical properties that can be adjusted and tuned independently to a large degree. The polymer binder can be modified to achieve the required application characteristics and bond strength. The filler can be selected to provide the desired electrical attributes, including directional conductivity, a feature not available in solders . There is, of course, some interaction between filler and binder, but to a large extent, electrical and mechanical adhesive properties are independent. It is best to view conductive adhesives as a complex composite where filler, binder and additives can be selected to provide formulations having a very wide range of useful properties. Next, we will briefly examine basic polymer types used as adhesive binders.

Polymer Binders for Conductive Adhesives

Polymers are commonly classified as either thermoplastics - typically able to be melted or softened with heat, or thermosets - which resist melting and cannot be re-shaped. A few of the very high temperature thermoplastics, like polyimides, actually decompose before reaching their melting points. Adhesive binders can be of either type and each system is very different especially in terms of storage and processing. The function of the binder in an adhesive is actually several fold. First, the monomer or prepolymer binder, in the case of thermosets, must provide the right handling characteristics before hardening by polymerization. Viscosity must be in the right range for the application method employed. The addition of solvent is usually avoided for polymerizable systems and the prepolymers (unpolymerized ingredients) should be low enough in viscosity to provide a dispensability after the solid ingredients have been added. Some thermoset monomers and oligomers are solids and solvents or liquid co-reactants must be used to provide the needed viscosity. However, modern resins, hardeners and catalysts can be low viscosity fluids that allow substantial amounts of fillers to be added. All thermoplastic adhesive pastes contain solvent.

Thermoplastics

Thermoplastics are a class of polymers that are capable of being heated to a specific melting point or melting range without significantly altering their intrinsic properties. The thermoplastics are also called remeltables and hot melts. Repeated melting does not change their basic properties although changes in crystallinity can occur which affect secondary characteristics like tensile strength. Very high melting thermoplastics may oxidize or otherwise degrade when attempts are made to melt them, however. The typically linear molecular structure of thermoplastics allows these materials to melt and flow unlike thermoset materials which won't melt or only soften slightly at high temperatures. Thermoplastics for adhesives must remain solids at their maximum use temperature. Pressure sensitive materials are an exception since these products remain in a pseudo-solid form during application and use. Thermoplastic adhesives are available in film form and in solvent solution pastes. Solvents are used to convert solid thermoplastic polymers to dispensable liquid pastes. The polymer must have the appropriate solubility characteristics and solvent release properties to be commercially useful. Rheology and surface chemistry are also important factors in needle dispensing, printing and stenciling. Thermoplastic adhesives can be cast and dried by the manufacturer and supplied to the end user as film, tape or preforms. The solid form, exemplified by some of the Z-Axis adhesives, is mechanically positioned and bonded by applying heat and pressure. Thousands of thermoplastic resins are commercially available which are based on perhaps less than 20 distinct polymer types. Variations in MW, additives and alloying account for the large number of products.

Thermosets

Thermosets are crosslinked polymers and generally have an extensive three-dimensional molecular structure. Crosslinks are chemical bonds occurring between polymer chains which prevent substantial movement even at elevated temperatures. The 3-D structure result in a material that cannot melt although some degree of softening may occur at high temperatures. The softening or deformation point may be at a temperature where thermal degradation occurs. Thermoplastics do not have inter-chain crosslinks and individual polymer chains will begin to slip and flow (melting) as the temperature is increased. The unmodified thermosets are usually hard, strong polymers, making them ideal binders for many types of adhesives. Solubility is very limited so that it impractical to make a useful solution with a thermoset. However, the availability of liquid thermoset precursors; resins, catalysts, hardeners and modifiers, makes solutions unnecessary. The thermoset precursors can be single molecular unit reactive materials or low molecular weight polymers, called oligomers, that can be further polymerized to hard structures. Many of the prepolymer ingredients, which include monomers, oligomers and generally reactive components, are liquids requiring no solvents. These solventless systems are ideal from an environmental point of view since there are no emissions during application or curing. Adhesives are also improved if solvent can be avoided since the possibility of solvent bubbles and voids is eliminated.

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 describes 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.

Radiation Curable Systems

Radiation curing is essentially polymerization induced by electromagnetic, beta (electron particles) or nuclear radiation. The source used in the printed circuit industry is almost exclusively high intensity ultraviolet radiation. Energetic photons cause monomers to react with one another typically through the action of a photoinitiator. Radiation is absorbed by the photoinitiator causing it to release polymerization initiating species, such as free radicals. Some initiators rearrange to a high energy state and react directly with monomers. Once the initial reaction takes place, the reacted monomer remains active so that it goes on to react with a second monomer. The process continues until most of the monomer is utilized or the active species are consumed or deactivated.

Although radiation cured conductive adhesives have been studied as far back as the 1970's, there has been a renewed interests more recently. Adhesives that are highly filled with opaque materials, like silver, are poor candidates for radiation cure systems. The popularization of low filler and no filler adhesives, the anisotropic and nonconductive, respectively, has increased the use of radiation curing. The filler levels in most anisotropic adhesives permits photons to travel through and induce curing. The unfilled materials, of course, present no problem.

The next section will deal with the all-important filler, that determines the basic type of adhesive and contributes most of the electrical characteristics to the composite.

Conductive Fillers

Silver-Based Conductors

Silver is by far the most commonly used conductive filler for isotropic conductive adhesives. This would seem, at first, a poor choice because of cost and electrochemical activity. However, silver is totally unique among the affordable metals. Its most important feature is the high conductivity of the oxide. This means that there is almost no change in conductivity as silver particles oxidize. Copper, which would appear to be the logical choice, produces adhesives that become non-conductive after exposure to heat and humidity. The use of a non-oxidizing metal, like gold, is cost prohibitive. Actually, better conductive is achieved with silver than with gold because of the next important attribute. Silver particles are easy to form and to fabricate into ideal shapes. Silver can be precipitated into a wide range of controllable sizes and shapes. This means that just the right sizes of particles can be produced for use as is or for milling into fine flake. It is even possible to precipitate silver into particles so thin that they are translucent.

Optimum silver-based adhesives are obtained by blending he right balance of flakes and particles. Flake provides improved conductivity by allowing maximum contact. The goal is to allow the plate-like particles to overlap one another like so many flagstones. The resulting voids caused by the overlapping can be filled with the small spherical particles. More sophisticated systems have optimized particle geometries which attempt to maximize metal contact. Conductive adhesives are generally compared to tin-lead solder and par conductivity has been obtained although most adhesives are 2 to 4 times more resistive. The reason for this is that the silver particles are coated with oxide, surface agents and some amount of binder. This means than a gap between particles results to increase electrical resistance. The gap produces tunneling electrons which have a higher threshold and also produce more electrical noise.

Copper

Attempts to use copper in inks and adhesives have been underway for many decades. Some of the earliest printed circuit processes used copper powder with adhesive binder. The challenge for copper-based adhesives is that of inhibiting oxidation under heat and humidity conditions. Copper oxidizes so quickly that oxide will form unless chemical inhibitors are present. The binder cannot be expected to exclude oxygen since polymers are permeable to gases. Since copper readily forms stable complexes with nitrogen-bases, like benzotriazole and imidazole, the complexing approach has been widely used to reduce oxidation. Azole-treated copper improves the stability of copper adhesives, but not enough for many applications. Over-plating with metals, like silver, has given some improvement in stability, but once again, not enough for many applications. A third approach has been to add solder powder to the adhesive mix. While this approach has merit and improves stability, the product has many of the same drawbacks as soldering since the final structure is basically a metallurgical solder joint.

Nickel

Nickel metal oxidizes slowly and is an important ingredient in stainless steel alloys. Nickel's ability to resist oxidation allows the metal to be used to make somewhat stable conductive inks. Nickel is a hard, poorly malleable metal which limits the ability to make flake in an optimized size and shape, however. Isotropic nickel adhesives, therefore, have a much higher resistance than silver-based products, up to 2 orders of magnitude higher. But nickel has found use in anisotropic conductive adhesives where spherical particles are commonly used. Nickel can be made into spheres of virtually any size and a wide range of powders are available with narrow size distributions. Nickel can also be easily plated with electroless gold to provide even more oxidation resistance.

Carbon

Carbon is an extremely inert element occurring in several allotropic forms, including the diamond and graphite. The two forms of interest here are graphite, a gray-black platelet form and carbon black, a jet-black amorphous structure. Both are electrically conductive and are used in making electronic materials. Carbon-based adhesives are only used in special applications because of their poor conductivity—up to 3 orders of magnitude lower than for silver. Some calculators have been built that use carbon-based adhesives simultaneously used as the ink to form the circuit.

Metal-Coated Particles

A large number of metal-plated conductive particles have been described and produced. The materials can be divided into two broad categories, metal core and non-conductive core. Both types of particles are used in anisotropic conductive adhesives today. The various types of plated particles are often designed for specific characteristics and end uses although the original intent was to reduce cost.
Silver, nickel and gold-plating on non-metals is the most common type of filler product. Silver was one of the first metals used because of the simple plating processes available and the metal's ability to remain conductive in an oxidizing environment. Non-conductors, like glass spheres, can be silver-plated and have been commercially available for some time. More recently, plating on plastic spheres has become popular because of useful attributes. Plated plastic particles have lower density and therefore are less prone to settling. Some plastic spheres can deform under pressure to make better contact with bonding surfaces. The preferred metal finishes for anisotropic conductive adhesive particles are nickel, gold and gold over nickel.

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 a reason to make a change unless lead is banned. Companies will test adhesives as a future alternative, should the need arise, but not really contemplate a 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 juncture.

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.

FUTURE POSSIBILITIES

Conductive adhesives for component assembly, including flip chips, is truly an embryonic technology. Although conductive adhesives are 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 described can greatly be improved even without major breakthroughs. The authors of this book hope to provide the information that will advance interest in the field and inspire others to join in developing and expanding conductive adhesive technology. Let's now review ICPs, the unusual class of organic materials that can conduct electricity since breakthroughs here could have important ramifications for adhesives, circuitry and maybe even semiconductors.

Intrinsically Conductive Polymers (ICPs)

The polymer chemist has long sought to use 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 of a functional polymer transistor, based on ICPs, is an encouragement.

Polymers Bonding

Hopefully this brief tour through the world of polymer-based conductive adhesives has piqued the reader's interest. Perhaps you will want to play a role in developing, applying and advancing the concept of Polymer Electronics. If so, you are at the right place at the right time. The Polymer Electronics concept has been most assuredly demonstrated and many basic applications have been successfully commercialized, but the best is yet to come. Immense opportunities exist for new materials development. Successful creation of intrinsically conductive polymers, for example, will boost Polymer Electronics to a new level of performance and manufacturing simplicity. Later, fabrication of molecules that became selectively conductive in response to "light" beams will bring the era of photolithography to Polymer Electronics. A new field of circuit technology will emerge based on conversion chemistry. The advent of conversion-fabricated circuitry will represent the final step in the long march in electronic circuit making progress: subtractive to additive to conversion. So, if you are a material scientist or technologist, Electronic Polymers should represent a major challenge and opportunity for you. The information age, where electronics multiplies brain power, will continue to advance and require improved performance, greater manufacturability, materials and processes that are completely safe for the environment and its inhabitants.

On the process side of the equation, new methods will continue to evolve. It is notable that many of the most recent electronic assembly innovations are the result of developments in electronic polymer materials. Ultra-fine pitch bonding, for example, has been made practical by progress in anisotropic conductive adhesives. Today, nearly all Liquid Crystal Displays (LCDs) are interconnected to circuitry using these polymer based interconnects. Rapid progress in eliminating toxic lead-based solder is the result of "solderless" bonding processes made possible by new polymer bonding agents. A new multilayer concept where double-sided circuits are assembled into stress-free, high yield multilayer structures was recently developed based on anisotropic conductive polymer films. The versatility and the newness of electronic polymer materials opens up a wealth of opportunities for the creative process developer. So if you have the special talent for conceptualizing new manufacturing methods and processes, Polymer Electronics is an area to consider.

The ultimate goal in developing new materials and processes is for the application of new products which serve needs. Today's important challenge for conductive adhesives is to apply this technology appropriately, effectively and efficiently to present needs. Although dozens of applications in computers, telecom, medical electronics and consumer products have been successfully reduced to practice, we have only scratched the surface. There are thousands of potential applications waiting to be discovered and developed using Polymer Electronics at its present level. Many of these applications already exist in the form of traditional circuit and assembly methods. A large number of products are being manufactured in ways that are much less cost-effective than could be achieved with conductive adhesives. The challenge then, for the designer, applications engineer, new product developer or the inventor, is to match needs with the attributes of Polymer Electronics Technology. The new product innovator, has the additional challenge of pulling the technology along, by finding needs that must push the materials and the processes to new levels. So if you are an applications specialist or new product innovator, the rate of progress and the final level of advancement for Polymer Electronics rests with you. You must drive this emerging technology by winning designs today -- designs that push the state-of-the-art for tomorrow.

The last, but perhaps the most important challenge, is directed toward the environmentalist. We have for so long ignored the concerns and pleas of those who would protect the environment when there was a conflict of interest with our business goals. We have all too often written off the environmentalist as unrealistic, reactionary and out of step with progress. In the last decade we have been made sadly aware of the correctness of many views held by environmental advocates. The total electronics industry has been one of the great abusers of the earth in countless ways. Only when the likelihood of catastrophic damage to the earth was publicized, did action take place. The threat of ozone depletion and the increased risk of skin cancer brought world action against those industries responsible, particularly electronic assemblers using CFCs. But equally threatening activities, principally the use of toxic metals and chemicals, must be remedied soon. Worse yet is the incorporation of toxic materials into products. Incorporation of lead, today's most insidious poison, must be stopped as soon as practical. Polymer Electronics offers a solution.

Bibliography

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