Poly-Solder®: A New Junction-Stable Conductive Adhesive for Rigid Boards

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Abstract

The concept of producing electrical paths with conductor-filled polymers dates back to the beginning of this century. During the past 90 years, a number of novel concepts and innovative products have emerged, but very few have enjoyed success. The earlier interconnect technologists could only use the polymers manufactured by nature. Later, general purpose polymers became available. Today, chemists are providing custom-crafted polymers designed to meet the needs of specific requirements for joining electronic elements. We will first briefly survey the fascinating history of polymer-based "wires" and electrical joining materials and then accelerate into the 1990's where the final obstacles are now being conquered by exciting new developments.

The focus will be on producing stable junctions, a problem area that has hindered conductive adhesive assembly for several decades. A status review will be presented on Poly-Solder, a conductive adhesive that has solved the electrical junction stability problem. Poly-Solder, originally developed in 1989 for PTF-Flexible circuitry, has been used to manufacture 10's of millions of circuit assemblies with no instances of detrimental junction resistance increase. The novel and patented oxide-penetration mechanism, which provides junctions with characteristics akin to a metallurgical joint, has been overwhelmingly confirmed by the durability of commercial products.

A new type of Poly-Solder has been developed specifically for rigid circuit boards made with any type of conductor. The new material has been shown to be stable under severe laboratory testing conditions. Worse-case stress tests, using heat and high humidity exposure on bare copper circuits and Sn-Pb coated SMDs, show stable electrical connections. Test data will be presented. The product is just moving into beta site testing and progress will be reported.

Finally, we will look at the future of Polymer Bonding Agents (PBA). What are the remaining technical obstacles? How important are the environmentally-related issues and what is the likely impact on lead-containing solder? Now in their 90th year, are Electronic Polymers finally moving into the mainstream during the final decade of the Century of Electronics?

Introduction With Brief History of Conductive Polymers

Building electrical pathways with polymer inks and adhesives is an old dream of some of the most innovative technologists that this *Century of Electronics* produced. At the turn of this century, when telegraph, telephone and radio where embryonic "electronic" products, inventors sought to print "wires" and create connections by using polymers. Today, many of us have that same dream and we are now fulfilling it. Let's first look at some of the early work which now serves as a foundation for many present product and process concepts.

The earliest circuit and interconnect ideas involved adding carbon[1-4] and copper powder[5,6] to adhesive binders to produce electrical conductivity. The copper ink was typically electroplated to solve the problem of particle oxidation. In some cases, the component lead was covered with the polymer-metal paste, followed by copper electroplating[7]. This converted the conductive adhesive junction to a metallurgical joint which was obviously stable.

By 1940, some researches had begun to realized that silver was a superior conductive filler for making polymer-based conductive products[8,9]. The unusual electrical conductivity of silver's oxide allowed inks and conductive adhesives to be made stable using silver powders and flakes without resorting to special treatments or additives. Synthetic polymers were coming into common use as the superior properties of made-made materials were recognized[10,11]. By the mid-40's, silver-filled synthetic polymers were the preferred conductive polymer system[12], although a few conductive adhesives were made from chemically-modified natural polymers[13].

During the 1950's, a number of silver-epoxy conductive adhesives were developed and epoxies soon became the preferred binder. The high composite strength and the excellent bond-forming characteristics of epoxies helped maintain this system as the defacto standard for conductive adhesives. Although the early silver-epoxy compositions were described in patents as die attach materials, the inventors also claimed the adhesives for general purpose joining[14]. However, although the die attach application soon became significant, the component joining area only saw modest use. Silver epoxy adhesives were used to some extent to attach components to hybrid circuits, but the common etched copper boards, which emerged after WW II, used mechanical connections and solder joints instead of adhesives.

Not until 1975[15], did any serious study on the use of silver as a solder alternative take place although a few papers had suggested that conductive adhesives, "are capable of replacing more conventional techniques such as soldering"[16]. A government sponsored study looked at silver-filled epoxies for electronic joining. Test methods were developed and properties measured. These conductive adhesives were referred to as "epoxy solders" and three important advantages discussed were lower temperature assembly, joining of dissimilar surfaces and the elimination of flux[17]. The study concluded that conductive adhesives were viable candidates and further consideration was warranted. Ironically, the US government is about to again sponsor the evaluation of conductive adhesives nearly two decades later. Government labs in the Denmark and Sweden, however, have been studying conductive adhesives for several years and have compiled substantial data[18,19].

In fairness to early studies, we need to understand that there were no clear motivating factors to change away from solder 20 years ago. Circuits did not require lower assembly temperature, flux and cleaning were considered safe and responsible industrial processes and nearly any connection could be made with solder. Silver-epoxy did not really offer any significant advantages where soldering worked well. Automatic soldering process, which culminated in wave soldering, worked well and satisfied most needs. The dream of polymer circuitry with polymer connections would have to wait a few more decades.

The slow change over to surface mount, away from feed-through leaded devices, provided the right form factor for conductive adhesives. This is the primary reason why interest in conductive adhesive joining accelerated in the early 1980's. The SMT process of applying a joining agent to the circuit, placing the component on top of the material and hardening the joining agent to form a lap, or butt, joint was ideal for adhesives. Till this day, there is no cost-effective process for the general use of conductive adhesive with through-hole devices. A wave-solder process equivalent just does not exist for organic joining agents mostly because of the great differences in the surface tension of molten metal and unhardened polymer.

By the 1980's the membrane switch, made with silver-polymer ink on temperature-sensitive thin plastic film, was rapidly expanding and becoming the dominant product for computer keyboards. The availability of surface mount LEDs, resistors, diodes and logic devices made it logical that these devices would be joined to the membrane switch with conductive adhesives. The very strong motivation for adhesives was that solder absolutely could not be used on circuits made with thermoplastic conductive ink on polyester base film.

By the mid-1980's a number of companies were bonding simple SMDs to membrane switches. One of the largest manufacturers to move a product line to a full polymer-based circuit and assembly was AT&T. Their business telephone line used silver conductors and LEDs, diodes and resistors bonded with silver-epoxy. AT&T was one of the first to recognize the junction stability problem with conductive adhesives. The junction formed with the common solder-coated SMD was unstable under temperature and humidity conditions. AT&T handled the problem by using silver or gold-coated components. They also issued a specification to prospective suppliers which set junction stability requirements. Table 1 outlines some of these criteria.

TABLE 1
AT&T GUIDELINES*

TEST	VALUE
Pot Life	> 4 hrs. @ 27ºC
Volume Resistivity	< 5 x 10^{-4} ohm
Junction Resistance	< 0.5 ohm
Shear Strength	>400 PSI
Environmental	<20% increase in junction resistance @ 60ºC, 90%RH, 1000 hrs.
Electromigration	pass B25 comb test, 60ºC, 90%RH, 168 hrs.

* provided by H. Rubin, AT&T

Junction Stability

In the later 1980's, Poly-Flex Circuits, a company dedicated to using only polymer material for circuits and assemblies, began to attack the junction stability problem, which was not widely known at that time. The dozens of conductive adhesive suppliers in their numerous articles and papers did not touch on that subject as far as we have been able to determine. Poly-Flex, after evaluating many commercial conductive adhesives, realized that junction instability was a fatal flaw that would need to be solved for the company to succeed in the dream of a truly environmentally responsible factory and product[20]. Many adhesives showed several orders of magnitude increase in junction resistance. This result has also been confirmed independently by AT&T who reported that all conductive adhesives showed junction resistivity increases when solder-coated components are used[21]. Government research laboratories have also verified the junction instability problem[18,19].

A six month's effort of evaluating protective coatings over the adhesive joint convinced the researchers that no organic barrier would solve the problem, only delay it. Oxygen would penetrate these materials and component oxidation would eventually degrade the electrical integrity of the adhesive junction. The most acceptable solution would be the invent a conductive adhesive that could product stable junctions with all standard component finishes. An 18 month concerted effort did indeed solve the problem. A new type of adhesive was developed that produced extremely stable electrical junctions even with solder-plated "J"-lead packages, often considered the most difficult to join for conductive adhesives[22]. Extensive testing gave the surprising result that junction resistance actually decreased under heat and humidity. The original data is reported in Table 2.

Poly-Flex Circuits named the new adhesive Poly-Solder to reflect its polymer heritage and solder-like joining characteristics. The product has now been in commercial use for about 4 years without any problems relating to junction stability. Commercial products that are now in use that were constructed with Poly-Solder include: business telephone (66 SMDs), a portable computer indicator, blood oxygen sensor for hospital use. Testing at 85%RH/85^{o}C gave similar results. Resistance of the junction typically dropped by a greater amount than could be due to the small drop in volume resistivity that the material undergoes after prolonged heating.

Pseudo-Metallurgical Junctions

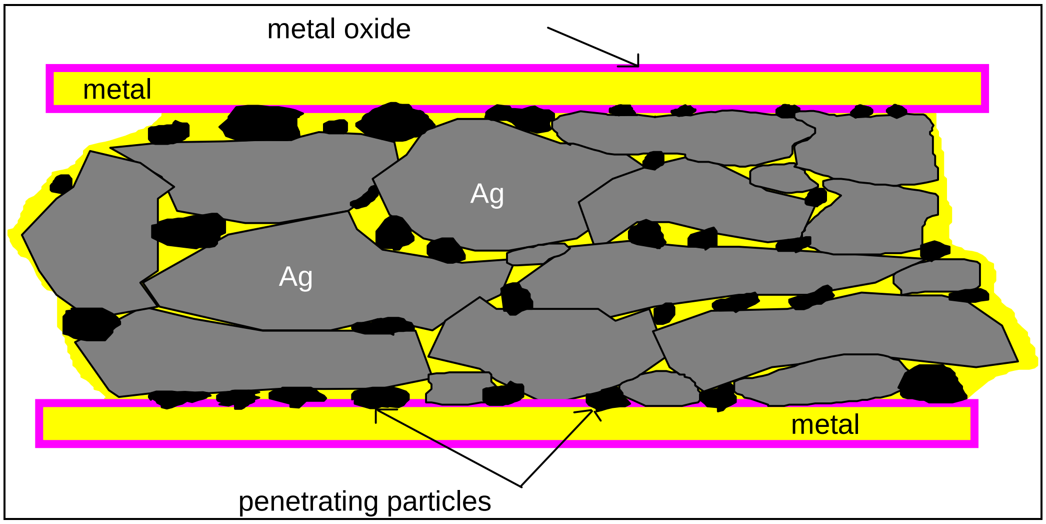
Today, we are pleased to announce that a new type of Poly-Solder, specifically designed for rigid circuit boards, has been developed. This product has the same junction stability mechanism as the product for flexible circuits. The patented composition uses conductive particles that can break and penetrate metal oxides. A special shrinkage feature of the polymer binder system creates sufficient forces so that conductive particles form connections to surfaces that behave like metallurgical junctions. Figure 1 shows the proposed mechanism for pseudo-metallurgical junction formation.

TABLE 2
POLY-SOLDER for PTF Flex

TEST	METHOD	RESULT
Mechanical		
Shear (push off):		
package: 1206, solder-plated		12-15 lb.
PLCCs, solder-plated "J" lead		0.75 lb./junction
PLCC-44; total force		30 +/- 5 lb.
Shock:		
100 G peak, 1/2 sine wave, 6ms, 18 sks.	MIL-STD-202,M213	no change
40 G peak, 1/2 sine wave, 27 ms		no change
Vibration:		
6.8 GRms, 30 min. per axis, 1.5 hrs.	MIL-STD-202,M214 test condition B	no change
Thermal/Electrical		
Shock:		
-55ºC to 85ºC, 30 min. dwell 5 min. transition, 25 cycles	MIL-STD-202,M107	-3.8% (drop in R)
Constant Humidity:		
60ºC, 90%RH, 1000 hrs.	MIL-STD-202,M103	-3.9% (drop in R)
Humidity Cycling:		
6ºC, 60ºC, 90%RH 3 cycles/day, 10 days total	MIL-STD-202,M106	-6.0% (drop in R)
Thermal Age:		
85ºC, 500 hrs.	MIL-STD-202,M10	-7.8% (drop in R)

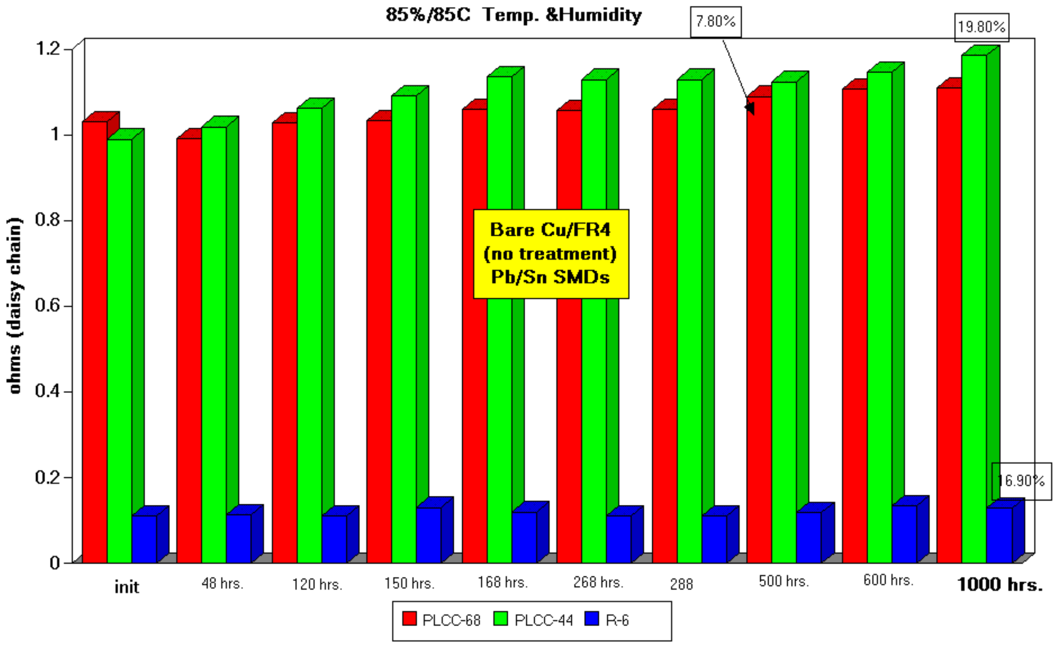
The Poly-Solder for rigid circuits was redesigned to deal with more difficult circuit substrates such as bare copper. Untreated copper is the most challenging surface for obtaining junction stability when using conductive adhesives. Alpha's goal was to develop a bonding agent that would work here since some bare copper is used for both circuits and connectors. Poly-Solder was found to be compatible with solder-coated and gold-plated printed circuit boards and they present much less difficulty than raw copper. The new Poly-Solder also generates oxide-reducing chemistry during curing to help with copper circuits that have aged to heavier oxide. The fluxing activity is canceled after the adhesive cures and the product has low ionics to qualify as a die attach product. Table 3 shows results after 1000 hours on bare, untreated copper, using tin-lead coated SMDs at 85% RH, 85°C.

FIGURE 1
PSEUDO-METALLURGICAL JUNCTIONS



Although there is a small rise in resistance because of degradation of the copper at the edges of the adhesive junctions, the total increase is under 20%, the criterion set by AT&T. Of course, moving to a gold-plated PCB reduces even the small increase. These 1000 hour tests show even better stability than the Elektronik-Centralen study[18] after 168 hours 85%RH/85°C. Chart 1 shows the humidity aging results on untreated bare copper circuit boards with Sn/Pb-coated components.

CHART 1
POLY-SOLDER ON RIGID CIRCUIT BOARDS



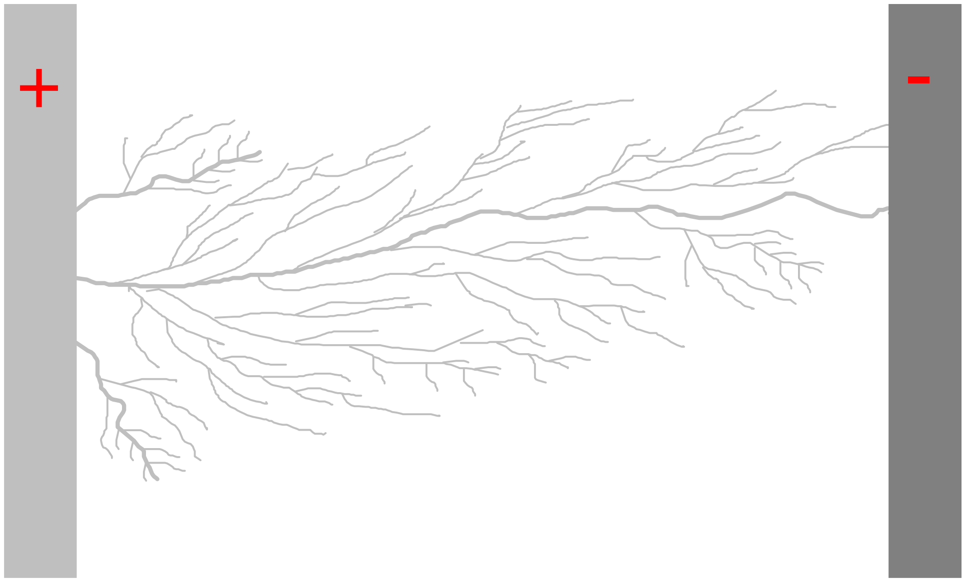
Fine Pitch

Poly-Solder for rigid boards was also optimized for fine pitch applications. We believe that conductive adhesives are inherently capable of finer pitch stenciling and printing than solder pastes because of the much finer particles that can be used on a practical basis. We have been able to consistently stencil 100 micron features without problems. Even finer resolution can be achieved with laser cut stencils and the right choice of squeegee. Although Alpha has produced solder pastes that can match this printability, these materials require special storage and inert gas reflow systems because of increased oxidation associated with the greater surface area of small particle pastes. Silver-filled conductors are not significantly effected because the conductivity of silver oxide although too fine a particle does increase electrical resistance because of the greater number of mechanical contact points per a specific junction.

Electromigration

As a final note, we would like to address the concern about electromigration associated with silver systems. Silver migration has been a well recognized problem with silver inks and the PTF circuit industry uses specific design rules to avoid the problem. Silver, at the surface of the ink, oxidizes and then hydrolyses in the presence of water molecules to form silver ions. The positive silver ions migrate to a negative electrode under the influence of a polarized current. Continuation of the process produces a tree-like dendritic growth of plated silver which shorts the circuit. But what about silver-filled conductive adhesives? Figure 2 shows the dendritic growth phenomenon.

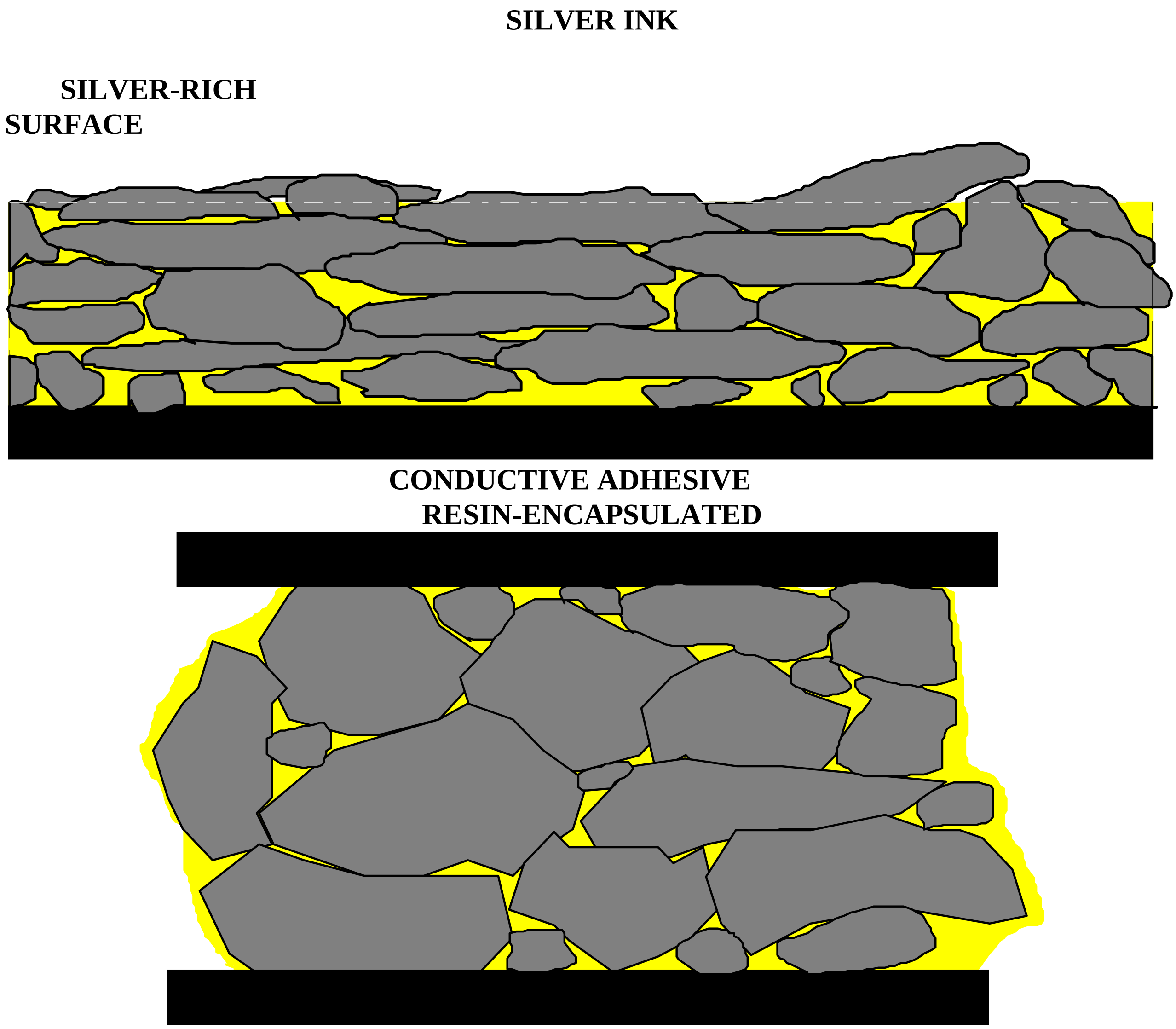
FIGURE 2
SILVER DENDRITES



The phenomenon has not been found to occur with silver-filled adhesives, however. Tests by Poly-Flex, IVF and Elektronik-Centralen have not produced migration even when conductive adhesive bars are placed close together and dc polarized under various temperature and humidity conditions. We propose the following mechanisms which are shown in Figure 2. Silver inks are specifically designed to provide a silver-rich surface. So-called "leafing" silver flakes, those treated to repel the solvent-binder system, are commonly used in silver inks. These treated silvers float to the surface during ink drying. This is a very logical design for circuit inks which are still predominantly used for membrane switches. Maximum surface conductivity is required for the switch contact and this is achieved by the silver-rich surface.

Conductive adhesives use very different silver particles. Although treatments may be used to enhance conductivity, the surfaces are not repellent and silver is not forced to the surfaces. Powders are also used in adhesives which tend to remain coated with binder at the surface regions. The net result is that conductive adhesives tend to have a resin-rich surface that encapsulates the silver. Much less silver is available to participate in migration. Thermosetting resins, because of their cross-linking, greatly reduce silver ion mobility. This phenomenon is seen in testing dielectric coatings in multilayer silver ink circuits. The thermoset epoxies out perform all others based on studies by Northern Telecom[23].

FIGURE 3
STRUCTURE DIFFERENCES IN INKS & ADHESIVES



Beta Site Program

Poly-Solder is now in beta site testing in the US, UK and Nordic facilities. The goal of Alpha Metals, the world's largest producer of electronic joining materials, is to offer a wide range of both metallurgical and polymeric materials to the electronics industry. The results of beta site testing will provide the necessary data for application notes and, perhaps, adjustments to the product. Although Poly-Solder is currently provided to companies and laboratories for evaluation, our target is to offer the material as a standard product by the end of this year.

CONCLUSION

After a long, slow trek along a meandering path of technology, polymer bonding agents now offer sufficient benefits to allow their acceptance as electronic joining materials. Key driving factors are environmental, finer pitch capabilities, lower temperature processing. Although adhesives no not provide identical test values as the soldered junction, results are now satisfactory for all but a few application areas. Conductive adhesives are now ready to move beyond the niches of PTF flexible circuits and hybrids.

Junction instability, the one remaining significant flaw that made general use and acceptance unlikely, has now been eliminated with the introduction of Poly-Solder for rigid boards. Data indicates that standard boards and SMDs can be assembled without a significant change in junction resistance after 1000 hours temperature and humidity. This break-through and the support of a world leader in electronic joining materials, is expected to help open up assembly to conductive adhesives.

FUTURE

Although solder is expected to remain the work horse in electronic assembly into the foreseeable future, polymer-based joining agents are ready to solve new problems whether they are product oriented or based on concerns over lead solders. Although no conductive adhesive exists that is even close to being a drop-in replacement, a very few of the hundreds of conductive adhesives are viable for many, but not all, component assembly needs. Now, with junction stability established, conductive adhesives will find acceptance. Although no serious obstacles now stand in the way for conductive adhesives, wider use will point out areas for improvement.

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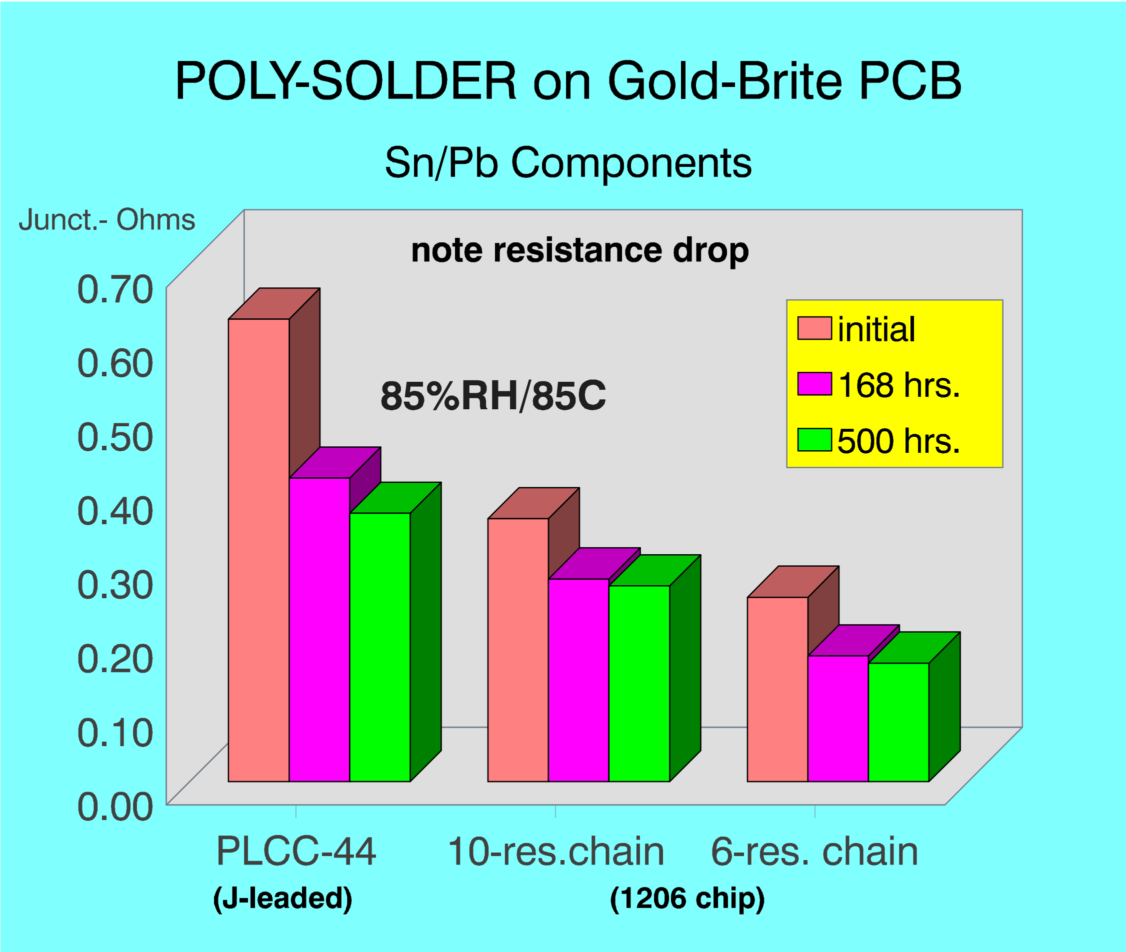
POLY-SOLDER on Gold-Brite PCB
Sn/Pb Components
Junct.- Ohms
note resistance drop
85%RH/85C
initial
168 hrs.
500 hrs.
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
PLCC-44
(J-leaded)
10-res.chain
6-res. chain
(1206 chip)

POLY-SOLDER
Volume Resistivity Stability

Init. Vol. R x E5	Temp. Cycle	Thermal Age	Temp. & Humid.
11.5 Ω	10.5 Ω (-4.3%)	8.9 Ω (-22.6%)	10 Ω (-13.0%)
Duration	500 Cycles	500 hrs.	500 hrs.
Conditions	-65 to 125C	125C	85%RH/85C

Mil-Std. 883D
75 mm x 150 mm x .025 mm strip on glass