The Effects of Temperature and Humidity Aging on the Contact Resistance of Novel Electrically Conductive Adhesives

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Abstract

Conductive Surface Mount Adhesives (CSMAs) are an alternative to traditional solders used in the electronics industry. CSMAs provide an environmentally friendly alternative to conventional Sn/Pb metal solders offering additional attractive technical advantages including low temperature processing, fine pitch capability and better resistance to thermal cycling. The two major limitations of CSMAs have been their instability on common electronic metals such as copper and Sn/Pb solder and their performance under impact testing. Recent experimental work published by National Starch Corporate Research in collaboration with Georgia Institute of Technology has shown that the unstable contact resistance of CSMAs on copper and solder is due to electrochemical corrosion of these metals under adverse conditions [1]. Based on the above fundamental understandings, Emerson & Cuming have been developing some new and unique formulas which exhibit exceptional contact resistance stability on previously unstable metal surfaces including OSP copper, Sn/Pb alloys and even 100 percent tin. Much progress has also been made in the area of mechanical performance. Recent advances in contact resistance stability have been incorporated along with the advances in impact performance to create novel materials. This paper examines the effects of thermoshock testing, high temperature aging and humidity aging on the contact resistance and the adhesion of these new formulas.

Key words : conductive adhesive, contact resistance, impact resistance, drop test, shear strength surface mount, corrosion.

1. INTRODUCTION

Traditionally CSMAs have been used in hybrid applications. These applications typically use noble metallisations such as gold and silver palladium on ceramic substrates. These materials are used to eliminate the possibility of electrochemical corrosion. Electrochemical corrosion occurs in the presence of two metals with dissimilar reduction potential and water. When silver, with a high reduction potential, is in contact with traditional electronic metals such as copper, tin and lead or other low reduction potential metals, the addition of small amounts of water completes a galvanic cell and causes the lower reduction potential metal to oxidise. This oxide is non-conductive and forms a dielectric layer at the metal interface. For this reason, it is difficult to use traditional CSMAs in applications with non-noble metals [2]. Another barrier limiting the use of CSMAs in more traditional applications involves impact resistance. Traditional CSMAs have been rigid materials which perform poorly in impact testing.

Recently, CSMAs have been re-evaluated in applications that were traditionally reserved for solders. CSMAs offer a series of attractive technical advantages over conventional Sn/Pb metal solders including low temperature processing, fine pitch capability and better resistance to thermal cycling [3,4]. The reason for this renewed interest can also be attributed to the development of adhesives with more stable contact resistance. Recent investigations within Emerson & Cuming have led to the discovery of some novel materials that provide improved performance over more traditional CSMAs. The discovery of specific corrosion inhibitors resulted in the development of CSMAs, which can now perform acceptably in such adverse conditions as 85 % relative humidity at 85°C for more than 1000 hours.

This paper shows data on the benefits of incorporating corrosion inhibitors into CSMAs. Data on the effect of eutectic tin lead and 100 % tin terminations on the new technology CSMAs will be presented. This paper also examines the effects of humidity aging, high temperature aging and thermoshock testing on the contact resistance and the adhesion of these new CSMAs.

2. ADHESIVES

A select group of adhesives was chosen for comparison. Two traditional adhesives (A1 and A2) were chosen for comparison with the new adhesives. Adhesive A1 and A2 have been commercial for a number of years and are widely used in hybrid applications. Adhesive B and C are two new commercial CSMAs using specific corrosion inhibitors. Adhesive D and E are two new experimental adhesives with improved mechanical performance. A low melting alloy has been incorporated in adhesive D and adhesive E exhibits a high glass transition temperature.

3. CONTACT RESISTANCE TEST DEVICES

3.1. Contact Resistance Stability Under 85°C / 85 % RH Testing :

A simple test device was constructed for ease of repeatability. The device consisted of a daisy chain copper pattern on an FR4 substrate. The 0,050 x 0,060 inch copper pads were separated from one another by a 0,050 inch gap. Ten such separations were included in each daisy chain or loop. This particular device was fabricated using different surface metallisations. The metals evaluated in this study included 63/37 SnPb solder and Sn plating. It has already been reported that these metals are easily oxidised in the presence of silver due to the mismatch in their electrochemical potential. In addition, the oxides are non-conductive and create an insulating barrier at the adhesive metal interface. The test boards were constructed by stenciling the adhesives onto the metallised pads and across the gaps to complete the circuit (150 μm adhesive layer). The test boards were then cured to the recommended cure schedule for each adhesive.

3.2. Contact Resistance Stability Under Heat Storage And Thermoshock Testing :

A daisy chain horseshoe pattern (with 10 resistor positions) of the conductive adhesive was printed with a thickness of 150 μm on an FR4 substrate. The circuit was completed using Sn terminated null Ohm resistors (standard 0805) for bridging the gaps. The test boards were cured according to the recommended cure schedule for each adhesive.

For the new adhesives D and E, a similar test device has been used. A daisy chain pattern has been printed on ceramic instead of FR4.

4. ADHESION TESTING

Adhesion is an important property for CSMAs to insure circuit integrity during normal handling of today's electronic devices. Component shear strength testing was conducted after 85°C / 85 % RH aging, high temperature aging at 150°C and thermoshock testing from –40°C to +150°C. The test device used for this evaluation is the same device used for the contact resistance testing. Components were Sn terminated 0805 chip resistors. An average of 30 components was measured for each data point.

5. RESULTS AND DISCUSSION

The contact resistance stability and shear strength of recently developed conductive adhesives in contact with non-noble metallisations such as tin and solder has been evaluated. The contact resistance stability under 85°C and 85 % RH with Sn and SnPb will be discussed first. Secondly the performance of these materials after heat storage at 150°C and thermoshock between –40°C and 150°C is evaluated and possible failure scenarios will be discussed. Finally, data on new formulations based on patented technology giving improved mechanical performance will be presented.

5.1. Contact Resistance Stability Under 85°C / 85 % RH Testing

A first test device containing traditionial 63/37 SnPb solder surface metallisation as described above was used with 3 different conductive adhesives. The low electrochemical potential of the SnPb alloy makes it a potential problem when using CSMAs. Contact resistance data up to 1000 hours at 85°C and 85 % RH are shown in Figure 1 [5,6].

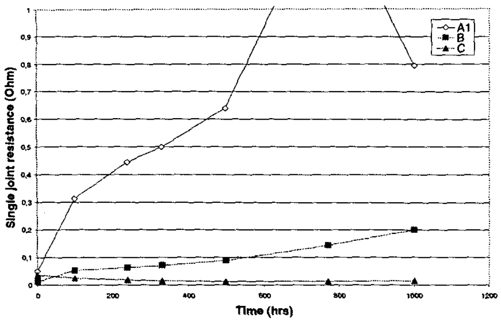

Figure 1: Contact resistance with SnPb solder as function of time under 85 °C / 85 % RH test conditions.

The control adhesive A1 shows a low initial joint resistance that is increasing rapidly under 85°C / 85 % RH. This increase can be attributed to the electrochemical corrosion process forming an insulating oxide layer at the adhesive/solder interface. The new adhesives B and C containing anti-corrosion agents display a stable contact resistance up to 500 hours aging. After 500 hours, the contact resistance of adhesive B is increasing whereas adhesive C shows outstanding performance on SnPb even after 1000 hours aging under the severe condition of 85°C and 85 % relative humidity.

A second metal surface evaluated is tin. This surface was selected for its potential to replace lead-containing terminations on electronic components. It has been well documented that high tin alloys will most certainly be used by the electronic industry in the future [7,8]. High tin alloys will pose similar corrosion issues due to its low electrochemical potential. Generally, acceptable contact resistance has been more difficult to obtain on high tin surfaces (see Figure 2).

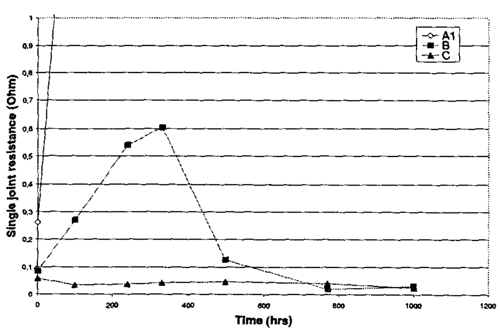

Figure 2: Contact resistance with tin as function of time under 85°C / 85 % RH test conditions.

The contact resistance of the control adhesive A1 is increasing even more rapidly when tin is used as the contact metal. The performance of adhesive B shows a peculiar behaviour as it appears to detoriate rapidly but then briefly performs acceptable for a short time. Overall the performance of adhesive B with tin metal cannot be considered as being acceptable. Although the contact resistance is higher on Sn as compared to SnPb, adhesive C shows an acceptable low initial joint resistance that maintains its low value through the aging study.

5.2. Contact Resistance Stability Under Heat Storage And Thermoshock Testing

Further work has been performed on the contact resistance stability after heat storage at 150°C and thermoshock between –40°C and 150°C. In a first series of tests an adhesive daisy chain pattern printed on FR4 was completed using Sn terminated null Ohm resistors. This also allowed to measure the component shear strength after the contact resistance was measured.

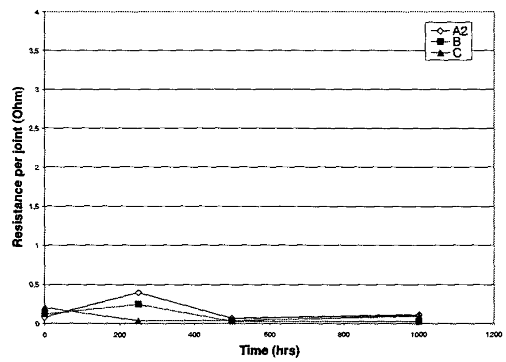

Figure 3: Resistance per joint with Sn terminated null Ohm resistors as function of time after 150°C heat storage.

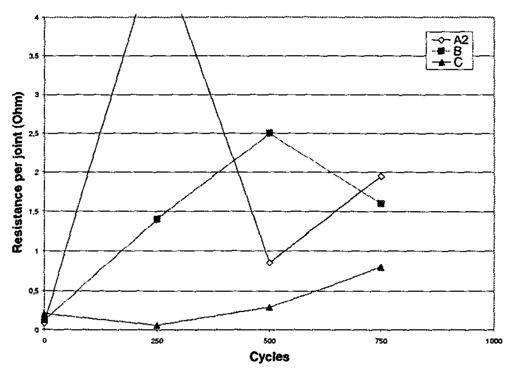

Figure 4: Resistance per joint with Sn terminated null Ohm resistors as function of number of thermoshocks.

Figures 3 and 4 show test results on resistance per joint after 1000 hours heat storage at 150°C and 750 thermoshocks between –40°C and 150°C. The resistance data are somewhat higher using this experimental set-up because besides the joint contact resistance the bulk resistance of the adhesives contributes as well to the measured data. It has been shown that the bulk resistance of all evaluated adhesives is not changing under the applied test conditions.

The contact resistance displays no pronounced increase during heat storage at 150°C for all studied materials indicating that electrochemical corrosion is not taking place. The requirement of both high temperature and high humidity was not fulfilled under these test conditions. Thermoshock testing between –40°C and 150°C results in a performance which is more or less similar to that of 85°C / 85 % RH testing. Both adhesives A2 and B perform unacceptable and only adhesive C is not increasing its contact resistance rapidly. However a slight increase of the resistance of adhesive C is seen in contrary to the 85°C / 85 % RH test condition.

The increase in contact resistance during thermoshock testing might be explained by the accumulation of humidity at the adhesive/tin interface and will be facilitated by the difference in thermal expansion between the FR4, the adhesive and the null Ohm resistor. However, as reported in the past by Jagt et al [9], the formation of microcracks at the interface can also influence the resistance measured. To achieve a better understanding, an evaluation of the shear strength of the null Ohm resistors under the various test conditions was carried out.

5.3. Component Shear Strength After 85°C / 85 % RH, Heat Storage And Thermoshock Testing

The component shear strength has been measured after 85°C / 85 % RH, 150°C heat storage and –40°C up to 150°C thermoshock testing. Test results are shown in Figure 5.

Similar results are achieved under all test conditions. The control adhesive A2 has the lowest initial adhesion and decreases only slightly after testing. Adhesive B has a slightly higher adhesion but shows a larger decrease and adhesive C has the highest adhesion but displays the largest decrease in bond strength as well. Whereas adhesive A2 and B are (slightly) flexibilised adhesives with improved thermoshock resistance, adhesive C is a non-flexibilised brittle material which is more sensitive to thermoshock testing. However adhesive C still displays the best adhesion after reliability testing. These data show that there is no direct relation between the contact resistance stability and the component shear strength. Adhesive C with excellent contact resistance stability is displaying an adhesion decrease indicating that other processes might be involved in lowering the adhesion strength.

The decrease of the adhesion of a silver epoxy conductive adhesive in contact with tin surfaces when subjected to high temperatures near 150°C or to humid atmospheres even below 100°C has been reported earlier [10 to 13]. Several hypotheses have been posted to explain the decrease in adhesion strength after high temperature annealing.

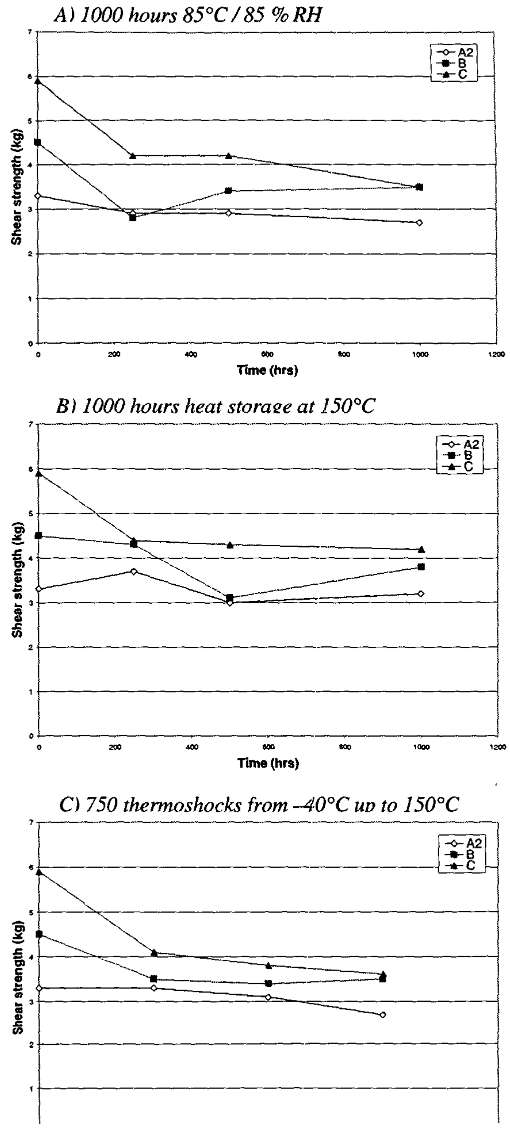

Figure 5: Component shear strength with Sn terminated null Ohm resistors under different test conditions

A) Diffusion of Sn from the Sn surface to the conductive adhesive can occur at higher temperatures resulting in the formation of Kirkendale voids at the interface. In addition the formation of brittle intermetallic Ag_3Sn can further decrease the bond strength [14,15].

B) Sn and SnPb plated components usually have a Ni plating below. Diffusion of Ni into the Sn layer can create a brittle SnNi intermetallic layer and result in a decrease of the adhesion strength [16].

The recently developed materials containing anti-corrosion agents display excellent contact resistance stability under 85°C / 85 % RH test conditions. However when thermoshock performance between –

40°C and 150°C is required, both adhesion and contact resistance can be of concern. It should be mentioned that the outcome of such an evaluation can depend strongly on the type of component that is studied. It has been observed that some components perform well whereas others perform poor after thermoshock testing using the same adhesive.

5.4. Contact Resistance Stability And Component Shear Strength After Thermoshock Testing : New Formulations

So far, adhesive C shows the best overall performance after 85°C / 85 % RH, heat storage at 150°C and thermoshock testing from –40°C up to 150°C. The performance after thermoshock testing seems to be most critical and needs further improvement.

New developed formulations have been evaluated under these test conditions. A daisy chain pattern has been printed on ceramic and Sn terminated null Ohm resistors have been placed to complete the pattern. The single joint resistance and the component shear strength have been measured after thermoshock testing from –40°C to 150°C.

The conductive adhesive C has been compared with adhesive D containing a low melting alloy. This material has been studied at two different cure temperatures ; one above and the other below the melting point of the low melting alloy. Adhesive E with an increased glass transition temperature (Tg) but not containing a low melting alloy has been evaluated as an alternative route to improve the mechanical performance. All adhesives C, D and E contain anti-corrosion agents. Results of the component shear strength are shown in Figure 6.

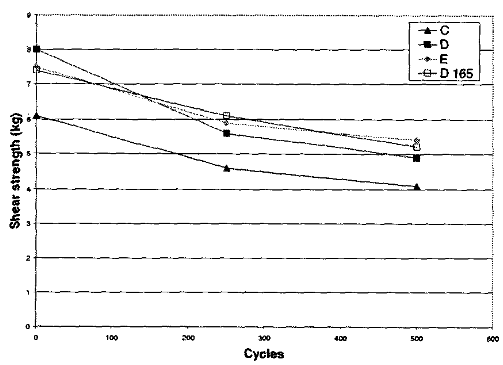

Figure 6: Component shear strength with Sn terminated null Ohm resistors after thermoshock testing.

The new formulations D and E display an increased initial bond strength as compared to adhesive C. Adhesive D cured at 150°C shows a decrease comparable to the decrease of adhesive C. However when the material is cured at 165°C which is above the melting point of the low melting alloy a different performance is observed. The initial adhesion is slightly lower but the decrease is more limited than when cured at 150°C. Adhesive E with a higher Tg also shows an improved mechanical performance similar to that of adhesive D cured at 165°C. The contact resistance stability of these materials is shown in Figure 7.

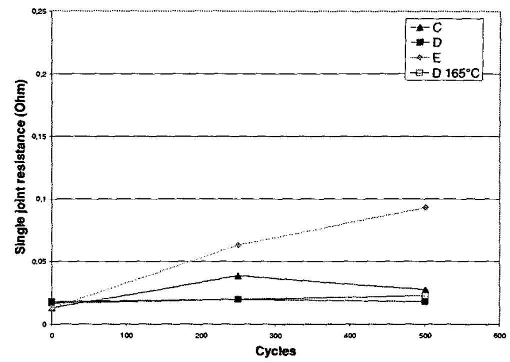

Figure 7: Contact resistance stability with Sn terminated null Ohm resistors after thermoshock testing.

Adhesive C displays a small increase in contact resistance after 250 thermoshocks but is not increasing further after 500 shocks. Adhesive D has a low and stable contact resistance for both cure temperatures. Adhesive E is showing a small increase in contact resistance.

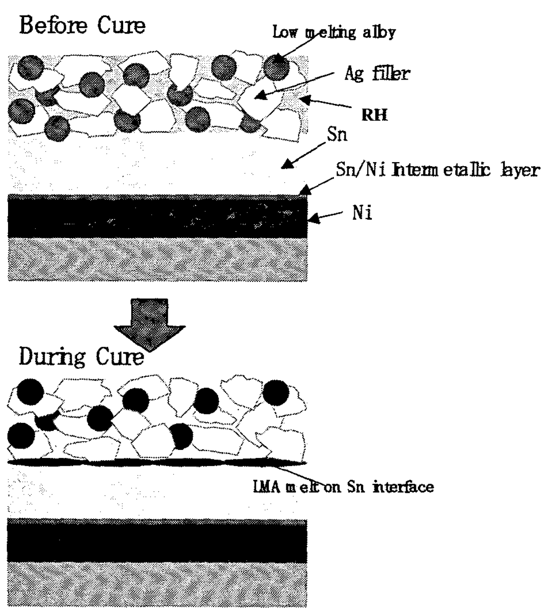

Figure 8: Formation of intermetallic layer of low melting alloy at interface between silver adhesive and Sn surface preventing Sn migration.

Adhesive D cured at 165°C, above the melting temperature of the low melting alloy shows the best overall result. The contact resistance is stable and the mechanical performance has been significantly improved. The improved performance might be explained by : a) the soft low melting alloy stops the formation of microcracks at the interface and b) the low melting alloy formation can form a metallic layer at the interface preventing diffusion of Sn into the conductive adhesive (see Figure 8).

6. CONCLUSIONS

The purpose of this study was to evaluate the performance of commercial and recently developed conductive adhesives in contact with non-noble metallisations such as Sn and SnPb solder.

It was shown that adhesive C containing anti-corrosion agents displays excellent contact resistance stability with both Sn and SnPb metallisations under 85°C and 85 % RH conditions up to 1000 hours.

When heat storage at 150°C and thermoshock aging between –40°C and 150°C are applied, a decrease of the adhesion strength is measured and some concerns about contact resistance stability under thermoshock testing have been defined. It has been mentioned that these phenomena depend on the type of components used.

Recently developed formulations are showing an improved mechanical performance. When anti-corrosion agents and low melting alloys are combined, the contact resistance is stable after thermoshock and the adhesion strength is significantly improved. The anti-corrosion agent is preventing electrochemical corrosion at the interface with the non-noble metal. The low melting alloy improves the contact resistance and the mechanical strength by the formation of a metallic layer at the interface preventing diffusion of Sn to the silver adhesive. Further work is required to define if the proposed model explaining the improved mechanical performance is valid.

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