ThreeBond
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Recent Technical Trends in Conductive Adhesives

Introduction

Three Bond has been supplying conductive adhesives for about 15 years. Most of these products take the form of paste containing silver powder. They are used for mounting quartz oscillators and semiconductors. Today, new technologies are developing very rapidly in the electric and electronic industries, creating faster and lighter products, especially in the field of information. Accordingly, electric connectivity, which is not its original purpose, is required of the adhesives.

This issue of *Recent Technical Trends in Conductive Adhesives* discusses conductive adhesives. The first half describes the relation between volume resistance and connection resistance. The second half introduces two adhesives: silicone-based conductive adhesive, which is still under development, for use in the SMD quartz oscillator, and two-part low-outgas conductive adhesive (ThreeBond is abbreviated to TB hereafter).

Contents

1. Conductivity theory

There are two theories about why a conductive adhesive is conductive. One is that conductive fillers become connected to one another as the adhesive contracts as it cures. The other is that an insulation between conductive fillers breaks down because conductive fillers are scattered in the binder and are surrounded by nonconductive organic (or inorganic) binder even after the adhesive is cured.

2. Composition of the conductive adhesives

2-1. Conductive filler and binder

A conductive filler can be composed of powder of gold, silver, copper, nickel, aluminum, plated particles, carbon, graphite, and so on. The sizes and shapes of these differ; the typical shapes are flakes, balls (granular), and arboroid. For most conductive adhesives, conductive fillers of different size and shapes are blended for dense packing. Flake fillers provide lower resistance after the adhesive is cured, because they provide facial contacts, compared with ball-shaped fillers that provide point contacts, as shown in Fig. 1. When only flake fillers are used, however, the thixotropy ratio rises, and might reduce ease of handling. To achieve an appropriate leveling, it is better to use flaked and ball-shaped fillers together.

The binder binds the conductive fillers, and it is used to connect the conductive fillers to one another within the curing adhesive, as well as to the adherend when it cures and shrinks. Thus the binder has a very important influence on conductivity.

Organic binders are the most popular binders. Epoxy resin is common, but depending on the required property or use, urethane, silicone, acrylic, or polyimide might be used, as well as other heat-curing resin or thermoplastic resin. As with inorganic materials, glass of low melting point is used as a secondary binder for a conductive adhesive that is manufactured by high-temperature baking.

2-2. Conductive filler and binder

The resistance of the cured adhesive varies according to the type of binder used (see Fig. 2). There are three factors:

(1) Each binder shrinks at a different rate while curing.
If that rate is high, conductive fillers stay closer to each other. This makes it easier to break the insulation and thus to reduce the resistance.

(2) Each binder (resin) has different wettability for the conductive fillers.
Wettability is affected by the polarity (hydrophilicity and hydrophobicity) of the surface of the conductive filler and the binder, and by the difference of activeness. If wettability is poor, the binder (resin) rejects the conductive fillers during the curing process. The conductive fillers cannot stay close to each other, and therefore the resistance of the cured adhesive increases.

(3) Each binder has different resistance.
The conductive fillers are surrounded by insulating binders. The lower the resistance of the cured binder, the more easily the insulation can break down.

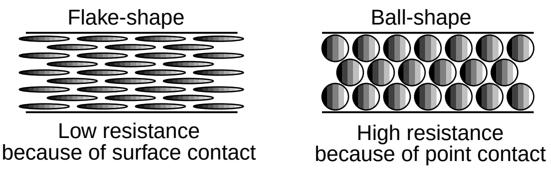

Fig. 1. Difference of conductivity caused by the difference of filler shapes

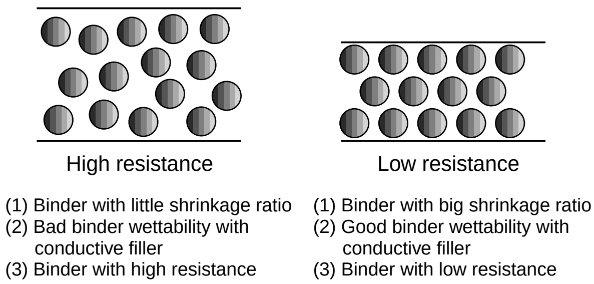

Fig. 2. Difference of conductivity caused by difference between binders

3. Conductivity

3-1. Volume resistance

The conductivity of conductive adhesive is usually described by the volume resistance, and as was explained above, the resistance of the cured adhesive varies according to the blend. Figure 3 shows the method to measure the volume resistance of a test piece. In general, such an adhesive has a volume resistance between 10^0 and 10^{-5} Ω·cm. When it is used for bonding electrodes, however, the volume is between 10^{-3} and 10^{-5} Ω·cm.

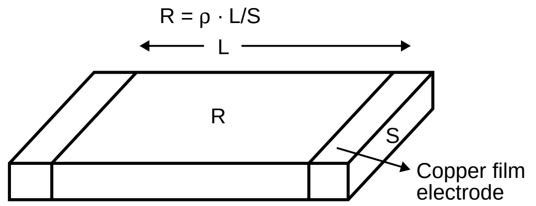

Fig. 3. Method of measuring volume resistivity

3-2. Electrode and connection resistance

When electrodes are bonded with a conductive adhesive, the resistance measured is the sum of the resistance of the conductive adhesive itself and the connection resistance (contact resistance) between the adherend (electrode) and the conductive adhesive. Therefore, not only the lower volume resistance of the conductive adhesive, but also its lower connection resistance to the adherend are important when it is used as the electrode adhesive.

Table 1 shows the volume resistance of conductive adhesives for different conductive fillers. As can be seen from Table 1, silver powder is used for the conductive adhesive because it reduces the volume resistance the most. Table 2 shows the connection resistance between various boards and adhesives with various conductive fillers. To measure the connection resistance, a test piece was prepared (Fig. 4). For these measurements, prototypes of conductive adhesive were prepared with the same epoxy-based binder, blended with the appropriate amount of powder of silver, nickel, gold plating, palladium, carbon, or other material. The results showed that the adherend and the conductive adhesives caused large differences. Clearly, then, low volume resistance does not always mean low connection resistance. For a nickel board, for example, the connection resistance with nickel paste (2.7 × 10^{-1} Ω·cm) was lower than with silver paste (1.1 × 10^{-4} Ω·cm). The reason for this is not yet known, but it suggests that one main factor is the energy activating the dispersion between metallic materials (base materials)--the combination that is easier to make an alloy--in addition to the surface conditions of metallic boards.

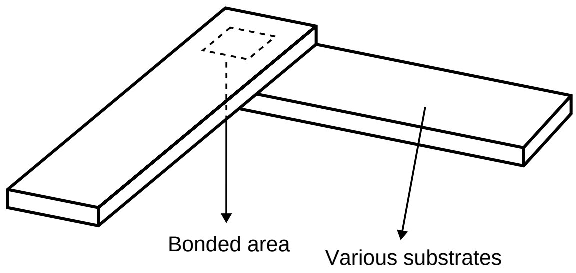

Fig. 4. Method of measuring bonding resistance

On the basis of this conductivity theory, Three Bond is developing new conductive adhesives. Two of these new adhesives are introduced here.

Table 1. Volume resistivity (ρ) of various conductive adhesives

	Silver paste	Nickel paste	Gold paste	Palladium paste	Carbon paste
Volume resistivity (Ω·cm)	1.1 × 10^{-4}	2.7 × 10^{-1}	2.1 × 10^{-2}	8.2 × 10^{-2}	1.3 × 10^{-1}

Table 2. Bonding resistance (mΩ) between various conductive adhesives and various substrates

Type of substrate	Silver paste	Nickel paste	Gold paste	Palladium paste	Carbon paste
Nickel	700	140	61	27	12000
Silver	1.0	2000	1.4	1.7	900
Gold	0.60	6.5	0.83	1.9	170
Aluminum	6000	200	1200	10000	0.80
Copper	0.33	8.3	18	34	3900
Tin	4.0	22	4900	1400	26000
Solder	34	1800	1800	4200	10000
Phosphor bronze	2.9	23	520	1700	60000

4. Conductive adhesives for quartz oscillators

4-1. Recent trends in quartz oscillators

Most Three Bond's conductive adhesives are used to assemble quartz oscillators. Figure 5 shows the typical structure of a quarts oscillator with a support. Recently, as electric units have become smaller and thinner, the production of quartz oscillators of the surface mount device (SMD) type (Fig. 6), which have no lead, has been increasing. One big reason for this increase is the rapid popularization of mobile communication equipment such as mobile phones.

4-2. Characteristics required for the adhesives

The conductive adhesives for the SMD quartz oscillator present the following problems not encountered with the one for the support type:

(1) The adhesive must not only support the quartz, but also bond it to the base, providing the electrical connection.

(2) Because the electrode is gold-plated, and gold does not adhere well, the adhesive has to provide a special kind of adhesion,

(3) The adhesive must be resistant to heat and disintegration. To be made airtight, it has to be exposed to high temperature, though only for a short time.

The adhesive, therefore, plays an important role with SMDs. Silicone-based and polyimide-based conductive adhesives are the potential candidates. Both have advantages and disadvantages. Recently, higher frequencies are required for quartz oscillators, and the drop test has become more severe. But the sealing condition has been moderated in terms of heat. For this and other reasons, it is likely that the silicone-based conductive adhesive will become the mainstream adhesive for SMDs. Three Bond has developed such an adhesive.

4-3. Silicone-based conductive adhesive under development (TB3303E)

The one-part solvent-type, silicone-based conductive adhesive that Three Bond is developing for the SMDs has the following improvements:

(i) To improve ease of handling, a solvent with low volatility is used.

Usually, the solvent used to dissolve silicone resin has low affinity and so is more volatile. If it is left too long after it is applied, its wettability deteriorates. TB3303E maintains wettability. Figure 7 shows the results of measurements of the strength of a bond between a ceramic chip and a sheet of glass. Chips were coated with the adhesive, but attached only after a period of time shown on the horizontal scale. As the chart shows, the bonding strength after a wait of up to 10 minutes between coating the chip and attaching it showed almost no change. Even after longer intervals, the bonding strength did not change substantially.

(ii) Improving adhesion to gold plating

Table 3 shows the strength of a bond between a ceramic chip and a gold-plated panel. The adhesion strength is higher than that of products of other manufacturers.

(iii) Preventing deterioration at high temperature

The effects of temperatures from 300 to 400˚C are shown in Fig. 8 for volume resistance, in Fig. 9 for bonding strength, and in Fig. 10 for outgas (weight reduction by heating). From these results, it can be assumed that the adhesive can hold for 20 minutes at 300˚C, 10 minutes at 350˚C, and 5 minutes at 400˚C.

Table 3. Strength of chip bonding to a gold-plated board obtained with the Three Bond product and with the vendor product

	Unit	On a glass board	On a gold-plated board
Developed product (TB3303E)	MPa	3.6	3.4
Other vendor product	MPa	2.0	2.0

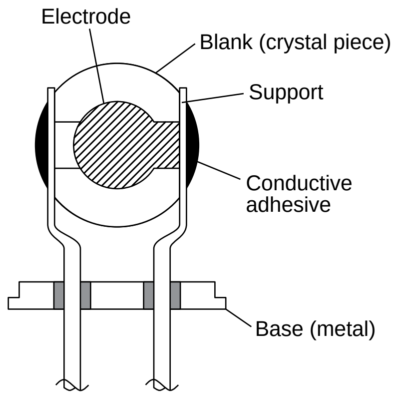

Fig. 5. Structure of crystal oscillator of support type

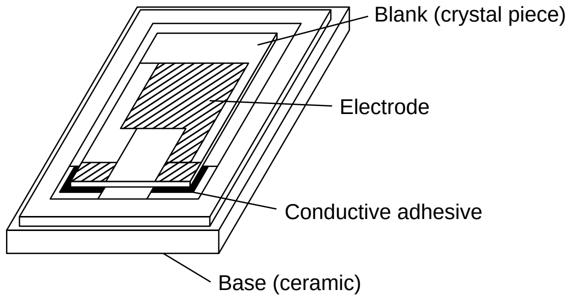

Fig. 6. Structure of crystal oscillator of SMD type

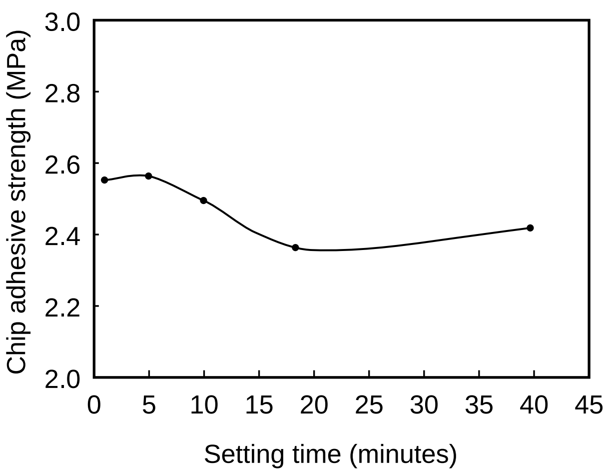

Fig. 7. Relation of chip adhesive strength to leaving time

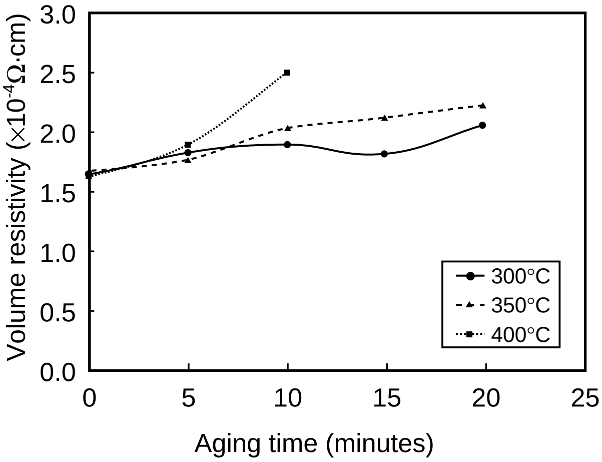

Fig. 8. Variation of volume resistivity during high-temperature aging

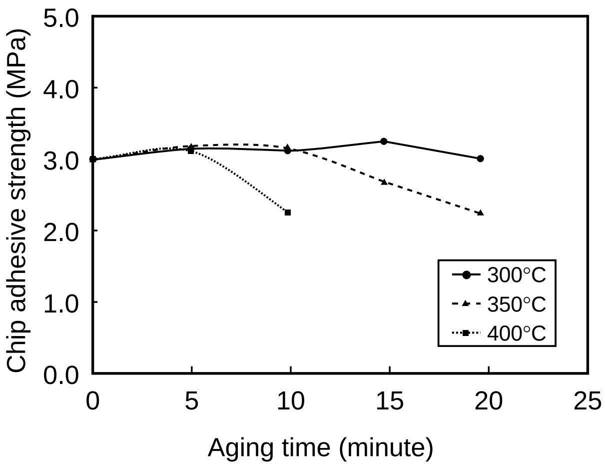

Fig. 9. Variation of chip adhesive strength during high-temperature aging

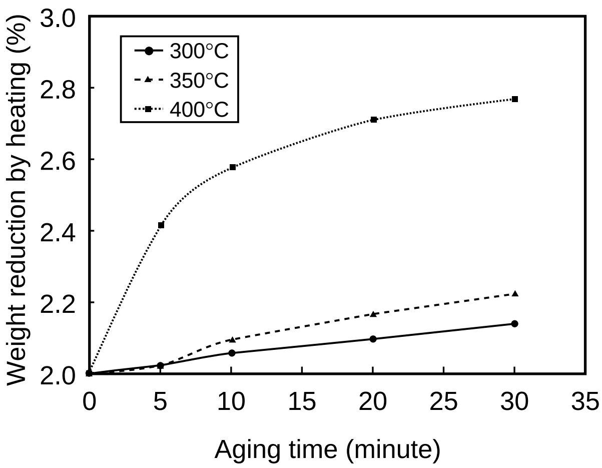

Fig. 10. Variation of weight reduction during high-temperature aging

5. Conductive adhesives for grounding

5-1. Recent trends of grounding

Electric products often need to be grounded. Grounding is especially important during the assembly of small motors, HDD magnetic heads for PCs, and VTR magnetic heads for video players. In such electric products, conductive adhesives can be used not only to make electrical connections, but also to simplify the manufacturing process. For example, an adhesive can be used for grounding as well as for sealing.

5-2. Properties required of adhesives

To counteract the effects of the heating process and the working conditions, adhesives are required to have the following properties:

(1) Improved ease of handling
(2) Low curing temperature, 60 - 80˚C
(3) Low outgas
(4) No solvent

Figure 11 shows the organization of the TB3300 series of conductive adhesives. Among these, the epoxy-based two-part conductive adhesive meets the requirements. TB3380, however, does not meet all the requirements, and so a new epoxy-based two-part conductive adhesive is under development.

5-3. Two-part conductive adhesive under development (TB3380B)

(i) Viscosity after mixing

After a two-part conductive adhesive is mixed, it continues its reaction at room temperature. With such an adhesive, therefore, workability is an important factor. Figure 12 shows how the viscosity changes after the two-fluids are mixed and left at 25˚C. As chart shows, the adhesive has low initial viscosity, and even after one hour, it has viscosity low enough to be coated with a dispenser.

(ii) Curing conditions and properties

Figure 13 shows the volume resistance for different curing conditions. Figure 14 shows the bonding strength for the chips. Table 4 shows the weight reduction after aging at 120˚C for 30 minutes, and Table 5 shows the weight reduction after aging at 120˚C for 60 minutes.

To summarize the results, the curing time must be 2 hours or more when the curing temperature is between 60 and 70˚C, or 1 hour if at 80˚C. The property seems to stabilize fastest at 80˚C.

Also, the amount of outgas tends to increase when an adhesive containing solvent is cured at low temperature. That is because solvent cannot vaporize completely when the curing temperature is not high enough, and this causes more outgassing. The two-part conductive adhesive offered by Three Bond uses no solvent, and so is suitable for curing at low temperature.

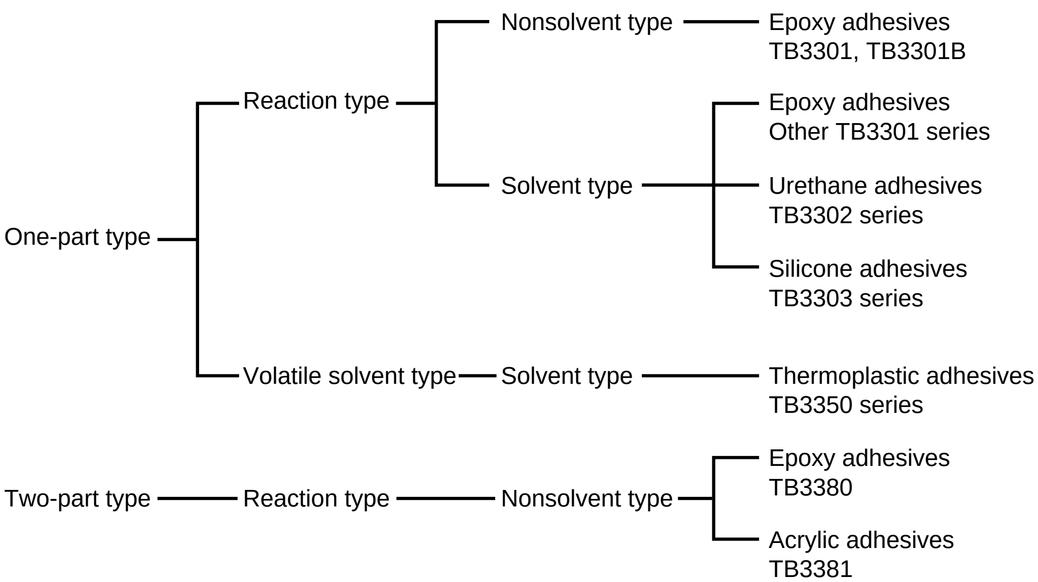

Fig. 11. Various products of silver paste

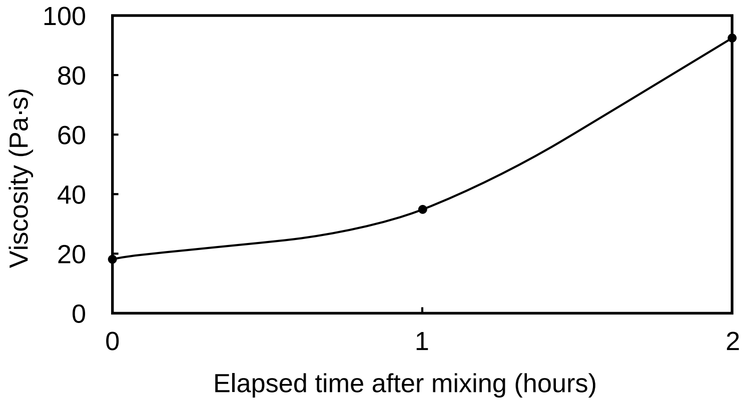

Fig. 12. Viscosity variation after mixing two fluids

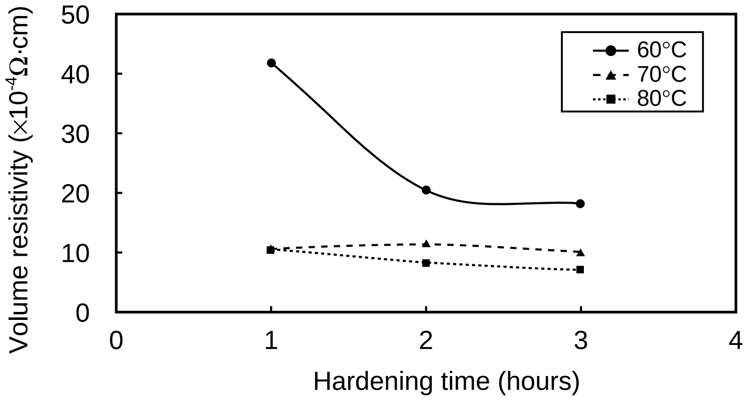

Fig. 13. Relation of volume resistivity to hardening conditions

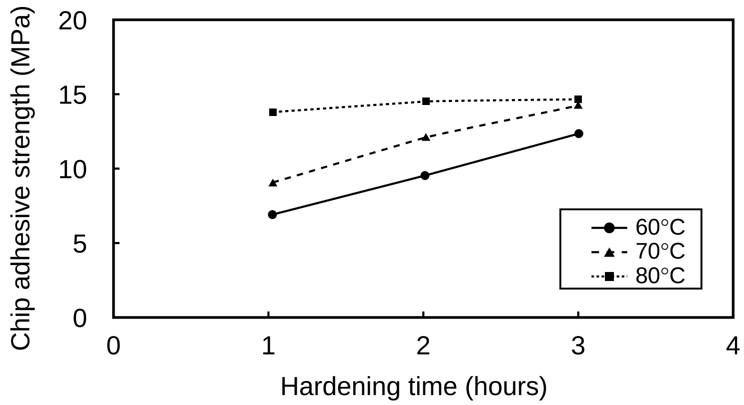

Fig. 14. Relation of chip adhesive strength to hardening conditions

Table 4. Weight reduction after aging at 120˚C for 30 minutes

	1-hour hardening	2-hour hardening
60˚C	0.41	0.25
70˚C	0.36	0.24
80˚C	0.22	0.13

Table 5. Weight reduction after aging at 120˚C for 60 minutes

	1-hour hardening	2-hour hardening
60˚C	0.53	0.34
70˚C	0.47	0.33
80˚C	0.29	0.19

6. Conclusion

The requirements for conductive adhesives are becoming more and more sophisticated nowadays, and the adhesive is becoming an integral part of the functional device. Thus, each electric or electronic part needs its own specific conductive adhesive. Future conductive adhesives need to be developed specifically for each application as well as for their conventional general properties.

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