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Electrically Conductive Adhesive Market Trends and Low Temperature Curing Electrically Conductive Adhesives ThreeBond 3331D

Introduction

Conductive adhesives both bond materials and conduct electricity, so they are utilized across a multitude of electrical and electronic applications. These adhesives generate conductivity at curing temperatures that are lower than other conductive bonding methods and materials, such as soldering or welding, and changing binder components enables them to conductively bond a variety of metals.

Furthermore, because a variety of binder components are available, conductive adhesives can be matched to ensure application and curing in any conditions for enormous workability and productivity.

In this article, we will introduce ThreeBond 3331D, a conductive adhesive with properties that make it well suited to the requirements of today's market, such as low-temperature curing, high reliability and precise applicability.

Hereafter, ThreeBond is abbreviated as TB.

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1. Conductive Adhesives that Fulfill Market Needs

Conventionally, Sn-Pb solder had been used to bond electronic components. However, the use of lead in electronics was restricted by the EU's RoHS directive in 2006, so looking at such a societal perspective and the corporate responsibility associated with it, lead-free electronics development was required. Accordingly, conductive adhesives have been gaining attention as lead-free alternative. In the electronics market of recent years, the following characteristics are required for conductive adhesives.

Required Characteristics

Beside the required lead-free materials there are four main aspects that a suitable product should feature on.

(1) Low temperature curing

In recent years, smartphones, computers and other electronic devices have become lighter and thinner and the use of resin and other non-heat-resistant materials is increasing. Therefore, in order to reduce impact on these materials, curing at low temperatures of 100°C or less is required in conductive bonding with conductive adhesives.

(2) Highly reliable

Lead-free solder is used for mounting general equipment, but Pb solder is more reliable, therefore, it is more commonly used for vehicle electrical components. Further considering the RoHS directive stance on eliminating Pb, a highly reliable conductive adhesive is needed to replace Pb solder.

(3) Precise applicability

With electronic components becoming smaller in recent years, so too has the need for thin wires and films, leading to further diversification in what is required of adhesive application. In many cases, dispensers are used to apply small quantities in small diameters, but rheological control is required to prevent the conductive filler from separation and precipitation that such applications require.

(4) Solvent free

In recent years, solvent free conductive adhesives have been in demand considering the working environment in which such adhesives are used. By the use of solvent free adhesive it possible to reduce or eliminate issues such as the formation of voids inside the cured product that occur due to solvent evaporation.

ThreeBond developed the new TB3331D to meet these and future market needs. In this article, we will discuss TB3331D, our new electrically conductive adhesive that meets modern requirments in the electronics market.

2. ThreeBond's Conductive Adhesive Lineup

ThreeBond's current lineup consists of the following conductive adhesives, which handle various applications (Fig. 1)



Fig. 1 ThreeBond's Conductive Adhesive Lineup

3. Product Comparison

We show the comparison TB3331D with other representative ThreeBond products in terms of electrically conductive adhesive characteristics needed on the market (Table 1). TB3350B, a solvent-type acrylic conductive coating, has excellent workability due to low-temperature curability and low viscosity. On the other hand epoxy resins are more reliable. TB3301W and TB3301F are both epoxy based and show very good reliability and workability. Their standard curing temperature is quite high from 120 to 150°C, so they are difficult to use with sensitive applications.

As a result, we developed TB3331D, an epoxy resin with

excellent low-temperature curability that is extremely reliable. It perfectly combines the low-temperature curability with the high reliability. So, it fulfills the demands of the modern electronics market. In addition, in order to make it easy to applying, we packaged TB3331D in a syringe.

4. TB3331D Characteristics

4-1. Properties and Characteristics

The charts below show TB3331D's properties (Table 2) and physical characteristics (Table 3).

Item	TB3331D	TB3350B	TB3301W	TB3301F
Binder resin	Ероху	Acrylic	Ероху	Ероху
(1) Low temperature curing (standard curing condition)	 (80°C×60min.)		× (120°C×60min.)	× (150°C×30min.)
(2) High reliability	O	\bigtriangleup	O	O
(3) Precision application (viscosity)	 (25Pa∙s)	© (2.5Pa∙s)	 (37Pa∙s)	(23Pa⋅s)
(4) Solventless	O	×	\bigcirc	×

Table 1. Conductive Adhesives for Electronics Market

Table 2. Properties of TB3331D

Test items	Unit	ThreeBond 3331D	Testing method	Remark(s)
Appearance	-	Silver	3TS-2100-020	-
Viscosity	Pa∙s	25	3TS-2F00-007	Shear velocity 10.0 s ⁻¹
Structural Viscosity Rate	-	4.0	3TS-2F10-007	-

Test items	Unit	ThreeBond 3331D	Testing method	Remark(s)
Chip bond strength test	MPa	15	3TS-4180-002	Ni plated board/2Φ ceramic chip
Volume Resistivity	Ω·m	0.5×10 ⁻⁵	3TS-5100-002	-
Tg	°C	90	3TS-4730-001	DMA tensile mode (tanδ peak: 1 Hz)
Standard curing conditions	-	80°C×60min.	-	Hot air oven
Recommended nozzle diameter	mm	0.29 or more (inner)	-	25G needle
Pot life	h	48	-	25°C

4-2. Low Temperature Curing

We show the volume resistivity (Fig. 2) and change in bond strength (Fig. 3) in the 80°C environment. We can see from the result, volume resistivity become stable in approximately 30 min. and bond strength become stable in approximately 60 min. Accordingly, TB3331D's standard curing condition has been set at 80° C x 60 min. to ensure stable volume resistivity and bond strength.

Low temperature curing (100°C or lower) is required in the electronics market. TB3331D designed as can be cured at 80°C, reducing risk of damage to materials that are not heat resistant, such as electronics and plastic parts.

4-3. High Reliability

4-3-1. High Heat and Humidity Testing

We show changing of volume resistivity and bond strength in 85°C, 85% RH environment (Fig. 4). In both cases, performance does not deteriorate after 1,000 hours.

4-3-2. Heat Cycle Testing

We show changing of volume resistivity and bond strength in a -40°C \Leftrightarrow 85°C heat cycle (30 min. ea.) (Fig. 5). Performance does not deteriorate after 2,000 cycles.



Fig. 2. Volume Resistivity in an 80°C Environment



Fig. 3. Chip Bond Strength in an 80°C Environment Ni plated board/2φ ceramic chip



Fig. 4. Volume Resistivity and Chip Bond Strength in an 85°C, 85% RH Environment



Fig. 5. Volume Resistivity and Chip Bond Strength in a Heat Cycle Test (-40°C 85% ⇔ 85°)

4-3-3. Heat Resistance Testing

We shows changing of volume resistivity (Fig. 6) and bond strength (Fig. 7) in 100°C, 120°C and 150°C environments. In both cases, performance does not deteriorate, and characteristics are stable.

Conductive adhesives are required a high reliability can replace lead solder. Above durability tests results show the good stability in terms of conductivity and bond strength of TB3331D under various conditions. We recommend as a good alternative of lead solder with confidence.

4-3-4. Strength of Bond to Variety of Metals

TB3331D have good bond strength to variety of metals in addition to curing at low temperature. We show changing of bond strength to a variety of metals in an 85°C, 85% RH environment (Fig. 8). For all metals, it shows stable bond strength in reliability tests.



Fig. 6. Volume Resistivity in 100°C, 120°C, 150°C Environments



Fig. 7. Chip Bond Strength in 100°C, 120°C, 150°C Environments



Fig. 8. Bond Strength to Adherends and 85°C, 85% RH Environment Test

4-3-5. Connection Resistivity

When conductive adhesive is used to connect electrodes, the resistance measured through the electrodes (Fig. 9) is a combination of two resistances:

the resistance of the conductive adhesive itself (volume resistivity) and

the resistance generated at the point of connection between the adherend (electrode) and the adhesive (connection resistivity).

In recent years, in the electronics market, with components becoming smaller and thinner, the volume of conductive adhesive applied is decreasing. This means that the influence of volume resistivity, once dominant, has decreased, while the influence of connection resistivity has increased. Accordingly, it is increasingly necessary to measure reliability, both for the volume resistivity of the resin itself as well as the connection resistivity generated at the point of connection to the adherend.

We show our measurement method of connection resistivity

Ω Volume resistivity (Rv) Electrode Conductive adhesive Connection resistivity (Rc) Connection resistivity (Rc) Rall Ω WW M ۱A.A. Ŕċ Rv

 $Rall = Rv + 2Rc \cdots (Formula 1)$

Fig. 9. Volume (Rv) and Connection Resistivity (Rc)



 $Rall = 2Rc \cdots (Formula 2)$

From formula 1, we can see that $Rv \doteq 0$ by reducing the thickness of the conductive adhesive



and our reliability data of TB3331D.

<Measurement method of connection resistivity>

test conditions: 3TS-5110-004

Masking tape with a 2mm hole is attached to a conductive adherend (metal, etc.) and a squeegee is used to uniformly apply the resin. After the conductive adhesive is apply with the squeegee, the tape is peeled off to form a thin layer of conductive adhesive with the hight of the thin film on the adherend. Next, it is cured in standard conditions. A measurement instrument is connected to the adjacent conductive adhesive to measure connection resistivity (Fig. 10). This method ensures a sufficiently thin layer of resin, ignores volume resistivity and enables a simulated evaluation of the connection resistivity.

A test piece is created in the above way and left in an 85°C, 85% RH environment, then taken out at specified intervals and measured. The results are as indicated below (Fig. 11). As it is shown the connection resistivity to the adherends is also extremely stable over time.



Fig. 11. Change in Connection Resistivity in an 85°C, 85% RH Environment

4-4. Workability

In many applications of the electronics market, dispensers are used to apply conductive adhesives in lines and dots. Many conventional conductive adhesives are housed in glass or plastic containers, so stirring and transfer to a separate container for application (such as a syringe) is required prior to use. To further improve workability TB3331D is available in syringes which greatly improve work efficiency by eliminating stirring and transfer before use.

Conductive adhesive is composed of a combination of adhesive components with low specific gravity and conductive filler with high specific gravity. In conventional conductive adhesives, it was possible for the filler to separate and settle, requiring stirring to return it to a uniform and well dispersed state before application. However, it is not possible to stir and fix separation issues due to the syringe container, so rheology control is necessary to suppress separation and settling during the shelf life of the product. We used proprietary rheology control to suppress separation and settlement in TB3331D and ensure stability within the syringe. Below we show changes in viscosity (Fig. 12) as well as changes in volume resistivity and chip bond strength (Fig. 13) after storage in a room temperature environment (25°C). When TB3331D is poured in a syringe, viscosity does not change within 48 hours at room temperature (25°C), and both volume resistivity and chip bond strength remain stable during that time. We also checked change in volume of dispensing after 48 hours at room temperature (25°C) (Fig. 14). Discharge rate did not change, and TB3331D contains no solvent by design, so there is no danger of solvent drying making the product difficult to apply when there is a break during applications, indicating stable workability when applying.



Fig. 12. Change in Viscosity at Room Temperature (25°C)



Fig. 13. Volume Resistivity and Chip Bond Strength at Room Temperature (25°C)



Fig. 14. Change in Discharge at Room Temperature (25°C)

<Test conditions> Nozzle 25G, inner diameter 0.29 mm 0.3 MPa, 5 sec. (air dispenser)

Closing

The characteristics required of conductive adhesives increase year by year with the heightened performance and complexity of electronics. To handle these changes, it is necessary to design a resin that can correspond increasingly smaller and thinner electronic components. Here, we introduced our method for measuring connection resistivity. With further performance increases in future electronic components, other measurement method may be needed to develop. We are already designing resins that match even more to the advancing in electronic components whilst optimizing test methods in order to obtain data that closer correlate to actual usage.

Moving forward, we expect use of these adhesives to expand into automobiles, so more reliable conductive adhesives will be indispensable. Furthermore, it will be necessary to address future issues by developing conductive adhesives outside those with typical characteristics that are suitable for every expanding application in this evolving range.

<References>

- 1) Nishikawa, Hiroshi. Relation Between Metal Filler and Electrical Conductivity for Electrically Conductive Adhesives, Journal of Smart Processing 139 (2012)
- 2) Kohinata, Shigeru. Fundamentals of Isotropic Conductive Adhesive Paste (Part 3), Vol. 10, No. 1, 88 (2007)
- Fuji Keizai Co., Ltd. Overview of the Special Adhesive and Sealant Market and Application Development 2014, p. 183 (2013)
- 4) Technical Information Institute Co., Ltd. Improvement of Dispersal, Evaluation and Application of Conductive Fillers and Aids, p3 (2015)
- 5) Nakaya, Manabu and Suzuki, Hironori. ThreeBond Technical News: Technological Trends in Modern Conductive Adhesives (1999)
- The Adhesion Society of Japan. Journal of The Adhesion Society of Japan: Adhesion Technology, Vol. 37, No. 2, pg. 26 (2017)

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