ThreeBond TECHNICAL NEWS

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Conductive Adhesives for Quartz Oscillators

1. Classification of Quarts Oscillators and Quartz Application Products

The products using a quartz oscillator can be roughly divided into (1) industry use, (2) consumer use, and (3) quartz application products with the classified contents listed below.

1-1. Industry Use

a. Quartz Oscillators for Industry Use

Radio communication equipment, wire communication equipment, electronic application equipment, pagers, facsimiles, measuring instruments, automobile controls, telephones, automatic vending equipment, cash registers, and computers.

1-2. Consumer Use

a. Tuning Fork Type Quartz Oscillators

Wrist watches, clocks, electronic calculators, and other products using a tuning fork type oscillator.

b. Quartz Oscillators for Clocks

For table clocks, wall clocks, travel clocks, timers, car clocks, and other clocks not using a tuning fork type quartz oscillator.

c. Quartz Oscillators for Color TVs and VTRs

Color TVs, VTRs, RF converters for VTRs.

d. Quartz Oscillators for Consumer Use

Transceivers, radio controls, amateur radios, players, radios, microphones, tape decks, home electric appliances, and microcontrollers.

e. Quartz Oscillators for Toys

Transceivers and radio controls.

Contents

1-3. Quartz Application Products

a. Oscillators

b. Filters

Crystal Oscillators and Crystal filters are classified as listed below according to the functions.

a. Crystal Oscillators

General Simple Packaged Crystal Oscillator (SPXO), Voltage Controlled Crystal Oscillator (VCXO), Temperature Compensated Crystal Oscillator (TCXO), and Oven Controlled Crystal Oscillator (OCXO).

b. Crystal Filters

General crystal filters and monolithic crystal filters (MCF).

2. Composition of Conductive Adhesives

2-1. Binders

The binder bonds the conductive filler to the adherend, and at the same time, connects the conductive filler in chains to obtain conductivity, providing physical and chemical stability to the conductive adhesives.

Resins of epoxy-based, urethane-based, and silicone-based are selected according to the structure of the supporter used for the quartz oscillator or the crystal oscillator and thickness of the quartz chunk, etc. with consideration of the hardness and the bonding strength of the cured object.

2-2. Conductive Filler

Typical examples of the conductive filler include silver, copper, carbon, and graphite, etc. Their characteristics of conductivity and bonding strength differ according to the differences of the type, the shape, and the particle size.

As conductive adhesives for quartz oscillators, silver particles are used because of the reliability and the specific volume resistance value.

2-3. Solvent and Additives

The solvent is added to improve workability. It takes the role of a kind of viscosity adjustment. When selecting the solvent, solubility to the binder is important. In case of no solubility, cohesion of resins occurs, which prevents chain connections among the conductive filler, leading to unstable conductivity and the loss of physical and chemical stability of the adhesive.

In addition, the solvent, which volatiles within the curing time at the curing temperature, should be selected. If the solvent remains in the cured object, it affects the reliability and the like.

There are many kinds of additives such as the dispersing agent, which improves the dispersibility of the conductive filler, the leveling agent, and the reinforcing agent, which improves bonding strength. These additives are added to supplement the characteristics of the binders. Therefore, only extremely small amount should be added because too much amount may affect the conductivity.

3. Conduction Mechanism

The conduction mechanism of the adhesives starts with the contact of the conductive filler. The contact of the filler is brought about by the baking of the binder. Before baking, since the conductive filler and the binder exist in the solvent independently without any contact, they are in the insulated state. After baking, due to evaporation of the solvent and the curing shrinkage of the binders, the conductive filler connects each other in chain to bring about conductivity. In this case, if the amount of the binder is too much for the conductive filler, the chain connection cannot be obtained during curing, it becomes isolated or unstable. On the contrary, if the conductive filler is too much, physical and chemical stability of the coating film is lost and it becomes brittle, at the same time, the conductivity becomes unstable because of no strong connection among the conductive filler. Therefore, the conductive filler and the binder should be mixed with the proper ratio.

The relationship between silver content and the specific volume resistance value is listed below. The silver content of 70 to 90 wt% (volume ratio of 20 to 50%) is recommended. Below 70 wt%, the resistance is high, which means unstable, and above 90 wt%, the resistance increases again.

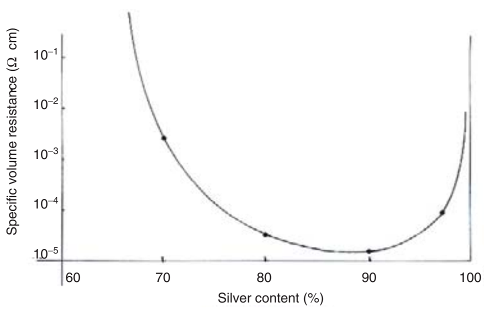


Figure 1. Relationship between silver content and specific volume resistance value

Connection state of the conductive filler depends on the shape of the filler. There are such as spherical, granular, dendritic, flaked, angular, spongy, and irregular shapes, in which the surface contact type such as the flaked shape has better conductivity compared with the point contact type such as the spherical one. Furthermore, the particle size of the conductive filler also influences the conductivity. The state of closest filling with the proper dispersion of particles less than 10μm has the highest conductivity. With the particle size of equal or less than 0.01μm, the contact resistance increases, which reduces the conductivity.

Besides the contact theory of the conductive filler, there is a theory that the electrical conductivity is brought about by thermal electron irradiation through the air or the inner space of the dielectric and the tunneling effects as well.

4. Classifying Conductive Fillers

The conductive filler is divided as listed below according to the manufacturing process and the particle shape. When using the conductive adhesives, two to three types are mixed to be used in consideration of the specific volume resistance and liquid properties.

4-1. Classification by Manufacturing Process

A. Electrolytic Process

A-1. Electrolytic Powder (Figure 2)

It is the metal powder deposited in powder by the electrolysis, and many of the particles are in the dendritic shape.

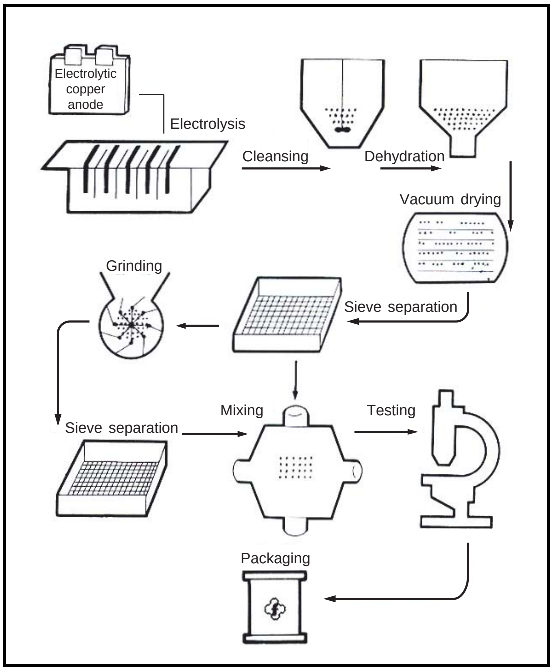


Figure 2. Electrolytic Powder

A-2. Pulverized Electrolytic Powder (Figure 3)

It is made by electrolysis as the brittle electrodeposition on the cathode. After the electrolysis, it is pulverized into angular or irregular shape.

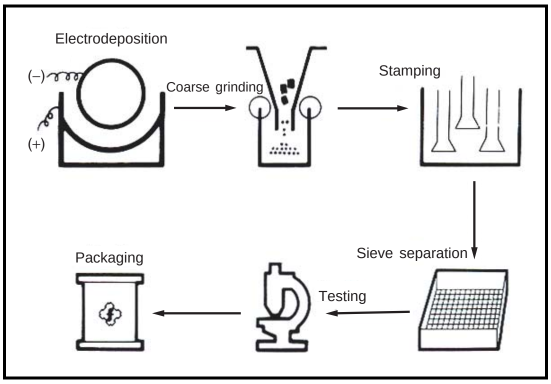


Figure 3. Pulverized Electrolytic Powder

B. Mechanical Comminution Process

B-1. Stamped Powder (Figure 4)

It is the metal powder pulverized by the impact of the falling stamper, many of which are in the flaked shape.

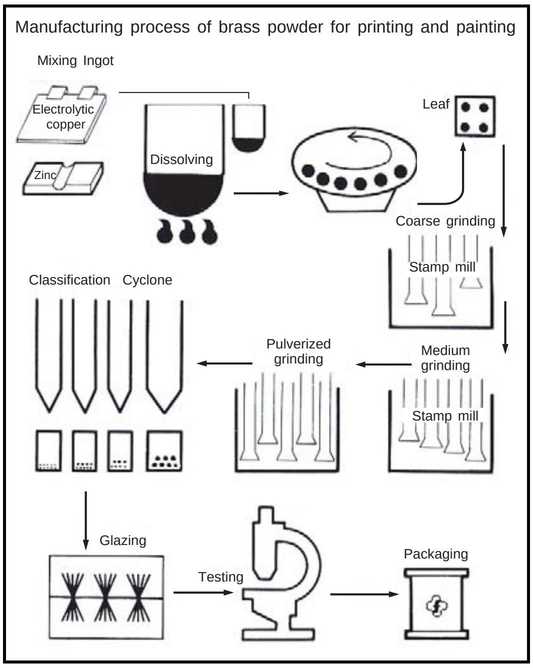


Figure 4. Stamped Powder

B-2. Comminuted Powder (Figure 5)

It is the metal powder made by pulverizing using a grinder such as a ball mill or a crusher (except a stamper).

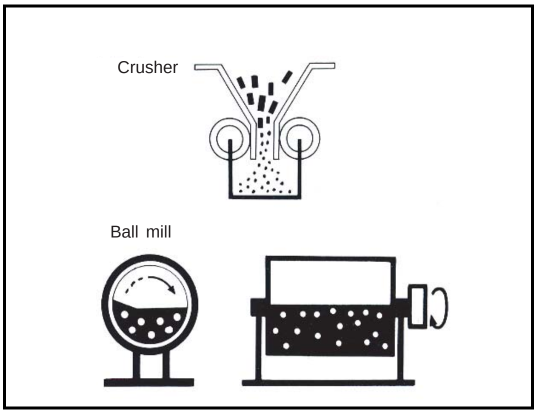


Figure 5. Pulverized Powder

C. Molten Metal Powdering Process

C-1. Atomized Powder (Figure 6)

It is a process to powder melted metal using high-speed fluid for dispersion and coagulation. The shape of the powder is spherical, granular, nodular, or irregular according to the surface tension of the atomized metal and the atomization conditions.

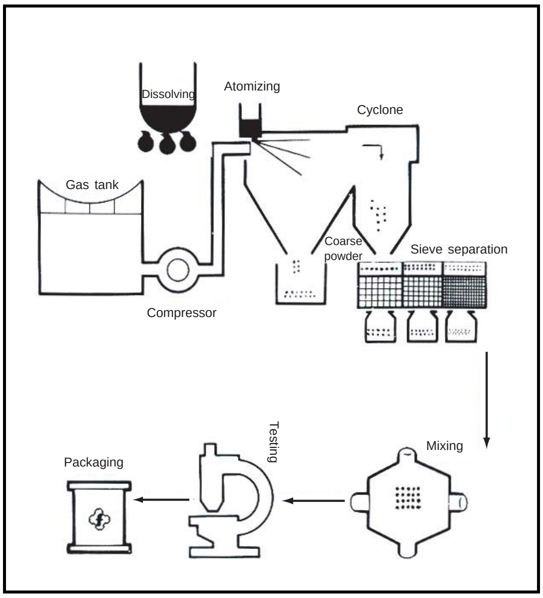


Figure 6. Atomized Powder

C-2. Granulated Powder

It is a process to make powder by dropping the molten metal into water and by stirring vigorously during coagulation.

D. Chemical Manufacturing Process

D-1. Reduced Powder (Figure 7)

It is a powder made by the dry method, in which metal compound (normally oxide) is reduced by reducing gas at high temperature. The shape is normally spongy (porous).

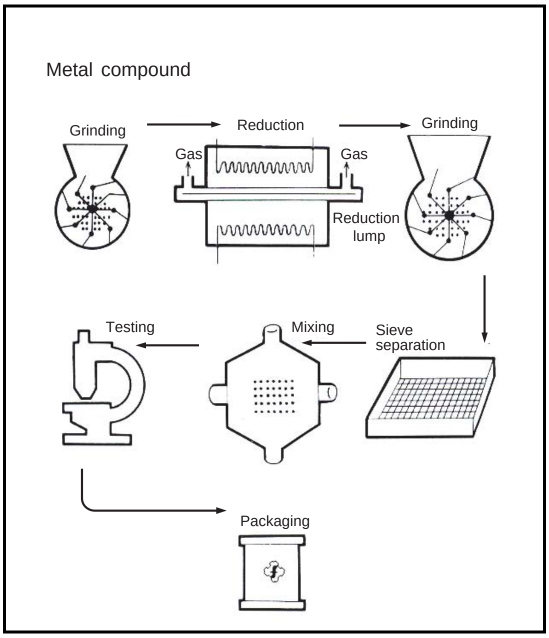


Figure 7. Reduced powder

D-2. Electrolytically Replaced Powder

It is a metal powder made by electrolytical replacement, where the other metal is added to the metal saline solution for deposition using the difference of ionization tendency of these metals.

4-2, Classification by the Particle Shape

A-1. Spherical Powder (Photo 1)

Powders of spherical particles, made by atomization process of such as copper or bronze.

A-2. Granular Powder (Photo 2)

Such as tin and lead powder made by atomization process has this near-spherical or nodular shape.

A-3. Dendritic Powder (Photo 3)

The typical example is the electrolytic copper powder obtained in powder as the deposition directly to the cathode by electrolytic process.

A-4. Flaked Powder (Photo 4)

It is a powder extended to very thin thickness made by mechanical comminution process from brass, aluminum, zinc, and nickel, etc.

A-5. Angular Powder (Photo 5)

It is a powder of angular particles. Typical examples are mechanically comminuted iron, silicon, chromium and the like.

A-6. Spongy Powder (Photo 6)

It is a powder of porous particles. Iron, nickel and the like made by reduction process have this shape.

A-7. Irregular Powder (Photo 7)

It is a powder composed of the particles without symmetry. The typical examples are copper alloy powder, stainless powder and the like by atomization process.

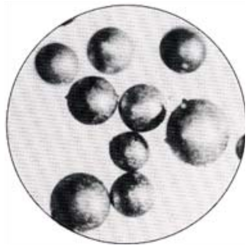


Photo 1
Spherical powder

Photo 2
Granular powder

Photo 3
Dendritic powder

Photo 4
Flaked powder

Photo 5
Angular powder

Photo 6
Spongy powder

Photo 7
Irregular powder

5. The Structure and the0 Name of Each Part of Quartz Oscillators

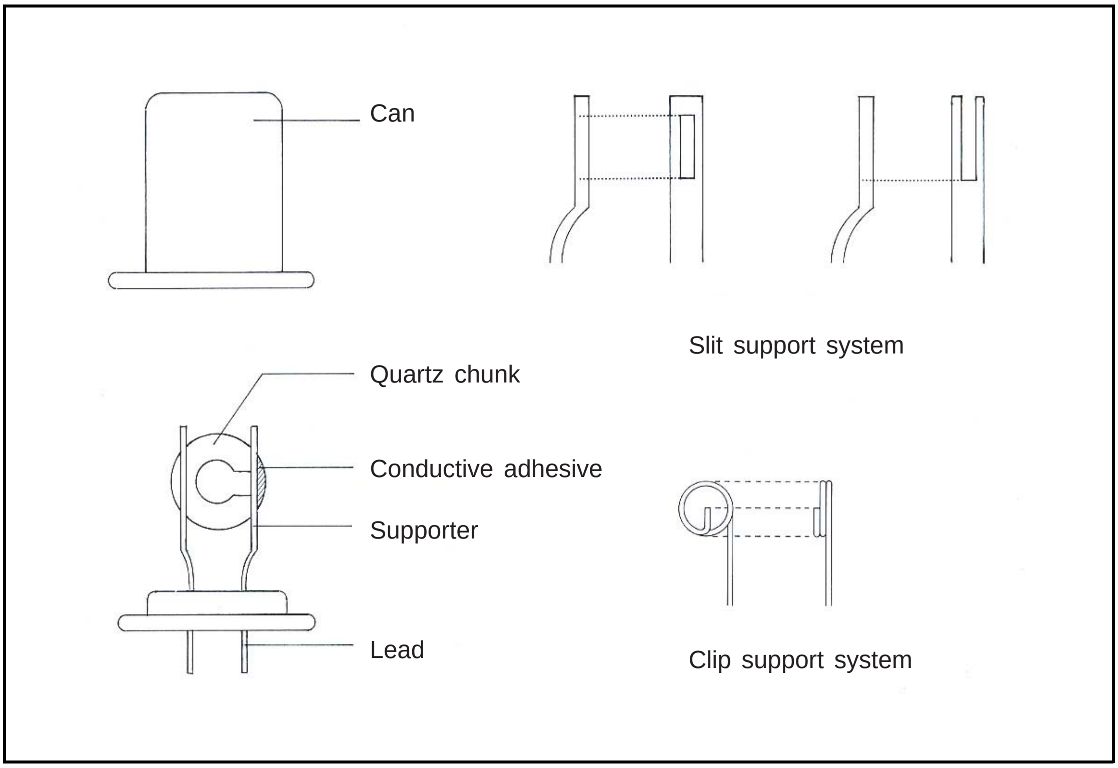


Figure 8. Vertical quartz oscillator

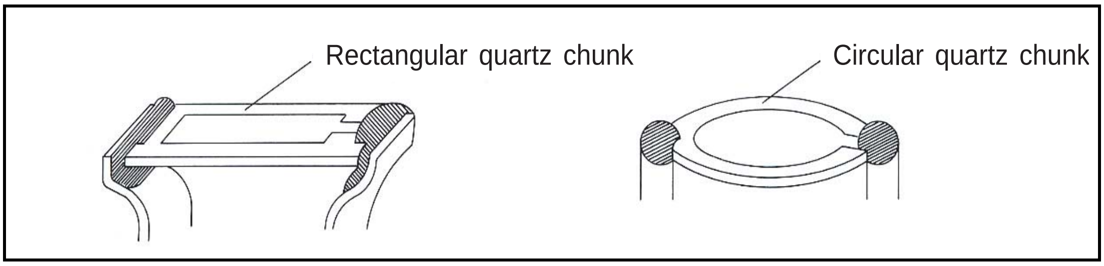


Figure 9. Horizontal quartz oscillator

It is roughly classified into the vertical type and the horizontal type as mentioned above. The clip support system is replaced by the slit support system because of the miniaturization and the thinning of the quartz chunk and the convenience of the mass production. With the slit support system, because of the shape of the supporter with poor shock absorption and poor curing shrinkage, the conductive adhesive needs to take that role.

6. The Characteristics Required for Conductive Adhesives for Quartz Oscillators

The characteristics required for the conductive adhesives (for quartz oscillators) are divided into the characteristics as liquid and the characteristics of the cured objects.

6-1. Liquid Characteristics

A) Workability

It should be considered that the conductive adhesive has no cobwebbing because they are coated by a dispenser. The degree of the leveling due to thixotropy also should be considered. However, the proper viscosity differs depending on the diameter of the needle used and the coating process.

B) CI Characteristics

If bleeding or sagging occurs during coating, during exposure time before curing, and during curing, CI (Crystal Impedance) value deteriorates. Therefore, the liquid characteristics without bleeding and sagging are needed. Since the viscosity is related with bleeding and sagging, workability also should be considered.

6-2. Characteristics for Cured Objects

A) Shock Resistance

If hardness of the cured object is high, the stress during curing tends to become large, which leads to the destruction of a quartz chunk or the smash of a quartz chunk at the impact test. However, if the soft conductive adhesive is used to relieve stress, the quartz chunk may be dropped from the supporter because the adhesive may not stand the drop impact of the quartz chunk.

B) Aging Characteristics

If aging variation of the conductive adhesive is large, the frequency characteristics and the CI value varies. Lack of heat resistance especially causes generation of decomposition gas or weak bonding strength.

In addition, in case where evaporation of the solvent is not conducted sufficiently during curing or the uncured object remains, the can may be filled with the solvent during thermal aging and the uncured component may evaporate, which deteriorate aging characteristics.

C) Temperature Characteristics

Characteristics of the cured object, which does not affect temperature characteristics (differs depending on the cutting method or the shape) of the quartz chunk, are needed. It means that the temperature dependence of the cured object should be low. It is because if it becomes hard due to the low temperature, free vibration of the quartz chunk may be affected.

In consideration of the above-mentioned characteristics of the cured object, the hard type or the soft type should be selectively used according to the thickness of the quartz chunk or the support system.

7. Advantages of One-part Conductive Adhesives

One-part conductive adhesives have the following advantages compared with the two-part conductive adhesives.

1) Although the two-part type requires extra work of mixing because the main agent and the curing agent are mixed to be used, which may cause the mistake of the mixing ratio, etc., the one-part type requires no mix work. However, dispersion of the filler is required.

2) Since the two-part type has concern of the pot stability, the mixed adhesives should be used within the pot life. Furthermore, since the reaction proceeds even at room temperature, the workability deteriorates due to viscosity increase. Since with the one-part type, the reaction does not proceeds until the designated temperature, the workability is not affected by the viscosity increase at room temperature. However, in case where the solvent that evaporates at room temperature is used, the thickening due to the evaporation of the solvent occurs.

3) With the two-part type, the quality of the cured object may tend to vary if the mixing was not sufficient. In addition, it is much affected by the ambient temperature and the curing time. Since the one-part type uses heat-cure reaction, quality of the cured object does not vary much.

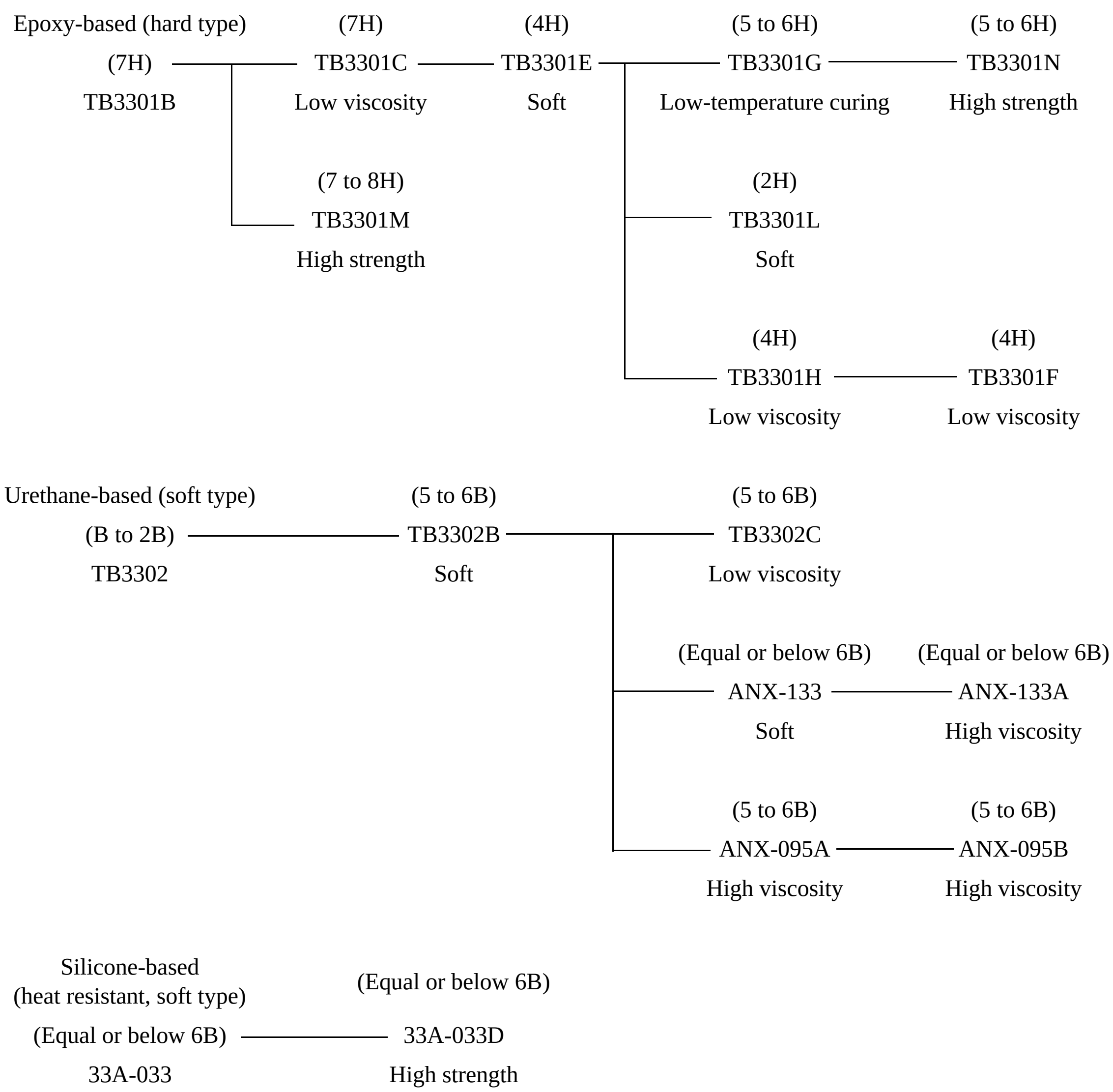
8. Selection and Product Lineup of Conductive Adhesives for Quartz Oscillators

To select conductive adhesives for quartz oscillators, the size and the thickness of the quartz chunk, the shape of the supporter, and the aging temperature, etc. should be considered.

In general, in case of the large and thick quartz chunk, the hard epoxy-based type is eligible, due to irrespective of the results of the impact test. In case of the small and thin quartz chunk, urethane-based or silicon-based is eligible because stress due to curing shrinkage and the temperature dependence of adhesives are important.

In case where stress and the impact to the quartz chunk can be absorbed because the supporter has enough length, the epoxy-based is eligible. In case of the supporter with short length or the supporter using the pole (horizontal type), the urethane-based or the silicon-based is eligible because the conductive adhesives have to absorb stress and the impact.

Three Bond's products are classified by binder shown below.



Note: Inside the ( ) shows the pencil hardness

9. Development Trend of Conductive Adhesives for Quartz Oscillators

Following the miniaturization of quartz oscillators, the shape and the support system of the quartz chunk is changing. The miniaturization of the package has been realized by changing the shape of the quartz chunk from round to rectangular. Regarding the slit support system and the clip support system, the horizontal type has become mainstream and the supporter itself may extinguish in future. In addition, because the aging temperature is becoming higher, the soft conductive adhesives with excellent heat resistance are needed.

We expect that a low-melting glass sealing method should be used as a sealing method in order to obtain high precision and high reliability, and surface mounting will be performed by reflow soldering in order to improve mass productivity. It means that higher heat resistance than the current heat resistance level would be required.

≪ References ≫

(1) Kazuta Hanabusa, “New Technology to Provide Conductivity to Polymers”

(2) FUKUDA METAL FOIL POWDER Co., Ltd., “METAL POWDER HAND BOOK”

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