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# Technical Trends in Silicone-Based Conductive Adhesives for Crystal Devices and ThreeBond 3304J, a Conductive Adhesive Suitable for Minute-Amount Application

## Introduction

ThreeBond develops and sells conductive adhesives that have been widely adopted for a range of market applications. They are often used for crystal devices, particularly crystal oscillators.

The electrical and electronics market is currently seeing remarkable technical innovations, and use of mobile devices such as smartphones, tablets and smartwatches is spreading rapidly. As mobile devices become smaller and capable of increased performance, the size and thickness of the crystal devices must also reduce. Today's devices are between half and a third the size of those from ten years ago. As of March, 2020 the smallest crystal oscillator in the world is 1.0 mm × 0.8 mm and further miniaturization is expected in future (according to ThreeBond's research).

This article introduces ThreeBond 3304J, which is suitable for use with the world's smallest crystal oscillators and compares it to examples of previous products released by ThreeBond for use with crystal oscillators.

Hereafter, ThreeBond is abbreviated as TB.

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## 1. Market Trends and Required Characteristics

The field of crystal devices is undergoing a significant shift towards smaller and thinner devices. Surface mounted device (hereafter referred to as “SMD”) crystal oscillators for mobile devices can be taken as an example. In 2010, the smallest sizes were 2.5 mm × 2.0 mm or 2.0 mm × 1.6 mm. Over the following ten years, the smallest size decreased to 1.0 mm × 0.8 mm, less than half the size. Development work is also being carried on reducing sizes to 0.8 mm × 0.6 mm Although crystal devices are becoming smaller and thinner, their functionality has been maintained and performance is improving.

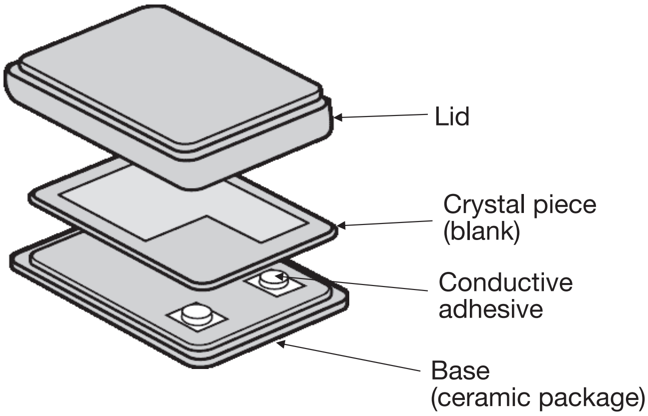



**Fig. 1 SMD Crystal Oscillator Structure**

As crystal devices become smaller, the size (application diameter) of conductive adhesives will also inevitably be reduced. In the case of 2.5 mm × 2.0 mm or 2.0 mm × 1.6 mm SMD crystal oscillators, the application diameter of the conductive adhesive is about Ø200 to 250 µm. If the size is reduced to 1.0 mm × 0.8 mm, the application diameter is about Ø100 to 150 µm (Table 1). Conductive adhesives used in such fields require various characteristics. Some examples of required characteristics are shown in Table 2.

## 2. Conductive Adhesive Lineup

Examples of previously-released products for SMD crystal devices are listed in Table 3. Because many SMDs only hold the crystal piece on one side, silicone resin with excellent stress relaxation is used as a binder. Another reason for using silicone resin is that there is little change in its characteristics even at the high temperatures (265°C or higher) produced during reflow soldering. The example products have been broadly classified into generations based on their proportion and process design. This classification equates to the size of supported SMD crystal device and is carried out independently by ThreeBond.

The binder design is the element that underwent the largest improvement between the first and second generations. By limiting the size of the components contained in the binder that provide adhesion, the size of supported SMD crystal devices was reduced. The biggest improvement from the second to the third generation is the filler design. Limiting the size of the filler (particularly coarse powder), allows

**Table 1 SMD Crystal Oscillator Size and Conductive Adhesive Application Diameter**

| Crystal oscillator size | mm | 2.5 × 2.0 | 2.0 × 1.6 | 1.0 × 0.8 |
|---|---|---|---|---|
| Conductive adhesive application diameter | µm | Ø200 to 250 | | Ø100 to 150 |

**Table 2 Required Characteristics for Conductive Adhesives for SMD Crystal Oscillators**

| Classification | Item | Required characteristic |
|---|---|---|
| Workability | (1) Discharge performance | The nozzle does not clog during use |
| | (2) Application performance | Optimum application diameter |
| | (3) Shape retention | Shape is maintained after application |
| Characteristic | (4) Adhesion | Does not peel off due to impact when dropped |
| | (5) Conductivity | Low CI (crystal impedance) value is maintained |
| | (6) Heat resistance | Little change in characteristics during reflow soldering |
| | (7) Low outgassing | Low levels of outgassing from cured materials |

application with nozzles with smaller inner diameters than before, enabling support for the miniaturization of SMD crystal devices. In this case, filler is a general term for conductive fillers and other functional fillers.

## 3. Product Characteristic Comparison

A list of characteristic values of example products from each generation is shown in Table 4. In order to respond to the miniaturization of SMD crystal devices, the particle diameter of the components that make up the conductive adhesive is also getting smaller. As a result, the chip bond strength (bond strength) tends to decrease up to the third generation.

In general, when comparing adhesives containing large filler particles and small filler particles, the bond strength tends to decrease as the filler particle size decreases. This is because the ratio of the binder component at the adhesive interface with the adherend is higher when the filler contains particles with a large diameter.

Figure 2 shows a model of a spherical filler. Focusing on the binder component at the adhesive interface, comparing the diameter of the filler particles shows that the ratio of the binder component at the adhesive interface with the adherend is higher when the filler contains particles with a large diameter, resulting in greater bond strength. On the other hand, fillers containing particles with smaller diameters have less of the binding component at the adhesion interface. This reduces contact between the binder and the adhered, thereby reducing the bond strength.

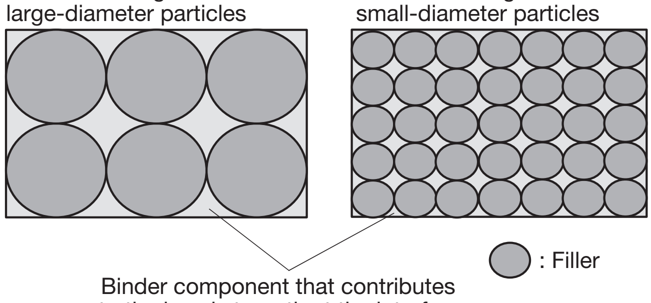



**Fig. 2 Effect of Filler Size on Bond Strength**

**Table 3 Examples from Product Lineup**

| Classification | First generation | Second generation | Third generation |
|---|---|---|---|
| Product | TB3303M<br>TB3303N<br>TB3303R | TB3303G (NEO)<br>TB3303Y<br>TB3304 | TB3303Z<br>TB3304C<br>TB3304D |
| Binder resin | Silicone-based | Silicone-based | Silicone-based |
| Minimum supported crystal oscillator size | 5.0mm × 3.2mm, 3.2mm × 2.5mm | 3.2mm × 2.5mm, 2.5mm × 2.0mm | 2.5mm × 2.0mm, 2.0mm × 1.6mm |
| Features/improvements from previous generation | Good adhesion to gold-plated electrodes | Reduced size of adhesion-imparting component in binder | Reduced filler size (coarse powder) |

**Table 4 List of Characteristic Values of Example Products**

| Test item | Unit | TB3303M | TB3303G (NEO) | TB3304D | TB3303Z | Testing method | Remark(s) |
|---|---|---|---|---|---|---|---|
| Viscosity | Pa•s | 40 | 40 | 50 | 70 | 3TS-2F00-007 | Shear velocity: $1.92\ s^{-1}$ |
| Structural viscosity ratio | — | 2.8 | 2.8 | 3.2 | 3.1 | 3TS-2F10-004 | |
| Volume resistivity | $10^{-6}\Omega$•m | 1.9 | 2.5 | 1.3 | 0.6 | 3TS-5100-002 | |
| Chip bond strength | MPa | 3.2 | 3.0 | 2.4 | 1.4 | 3TS-4180-002 | 2Ø gold-plated chip/ gold-plated plate |
| Standard curing conditions | — | 180°C × 60min | 180°C × 60min | 180°C × 60min | 210°C × 60min | — | |
| Recommended nozzle inner diameter | μm | 210 | 210 | 140 | 130 | — | |

■ Curing conditions
Curing equipment: Hot air drying oven
Curing atmosphere: Air

*Physical properties listed above are representative values.

## 4. TB3304J

### 4-1. Features

TB3304J was released in February 2020. It is a silicone-based conductive adhesive with the following features.

(1) High precision minute-amount application

(2) High structural viscosity ratio

(3) High bond strength

(4) High heat resistance

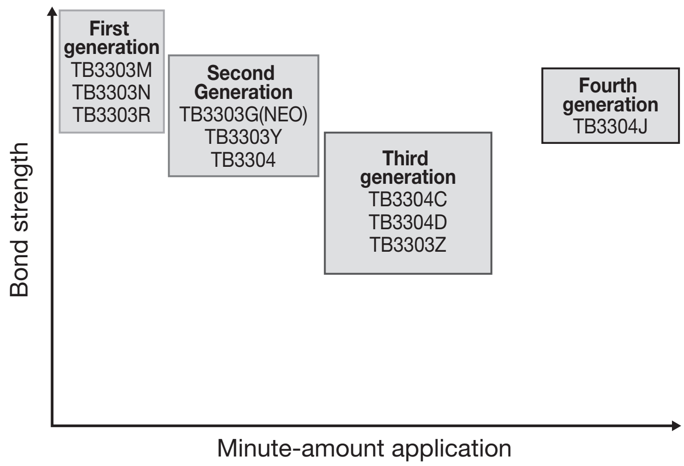
In order to respond to increased miniaturization of SMD crystal oscillators, improvements to various physical properties such as bond strength are necessary in addition to allowing minute-amount application. For this reason, many elements of the binder and filler design have been improved during the development of TB3304J. In the product lineup, it is classified as part of the new fourth generation.

### 4-2. Characteristics

The characteristic values of TB3304J are shown in Table 5. A nitrogen atmosphere was used for measurement to match the curing environment when used with crystal oscillators. In TB3304J, the design of the filler has been greatly improved in order to allow for high precision minute-amount application. As a result, bond strength, which previously had to be reduced as a trade-off for achieving minute-amount application, has been successfully maintained while limiting the maximum particle size of the filler to 10 µm or less. In addition, because it is necessary to hold the crystal piece firmly even when minute amounts are applied, it was designed to have a high structural viscosity ratio in order to improve shape retention after application.

The bond strength and minute-amount application of the example products mentioned above and TB3304J are mapped in Figure 3.

As shown in Table 2, low outgassing from cured products is required in the crystal device field. One characteristic of crystals is that they have a fundamental frequency that depends on mass. The sensitivity is extremely high, and the frequency fluctuates even with nanogram-order changes in mass. Because the crystal device has a closed structure, if outgas generated from the material cured with adhesive after assembly adheres to the crystal piece, the frequency will deviate from the design value. The mass of the attached substance and the change in frequency can be calculated using the Sauerbrey equation shown in Figure 4. With a 50 MHz crystal oscillator, this corresponds to a change of about 1 Hz per 1/100 nanogram.




* Bond strength: Measured with 2Ø gold-plated chip/gold-plated plate

**Fig. 3 Relationship between bond Strength and Minute-Amount Application for Each Product**

**Table 5 TB3304J Characteristic Values**

| Test item | Unit | TB3304J | TB3303G (NEO) | Testing method | Remark(s) |
|---|---|---|---|---|---|
| Maximum filler particle diameter | µm | ~10 | ~50 | — | D100 value of laser diffraction |
| Viscosity | Pa•s | 80 | 40 | 3TS-2F00-007 | Shear velocity: 2.0 $s^{-1}$ |
| Structural viscosity ratio | — | 5.2 | 2.6 | 3TS-2F10-004 | Shear rate ratio: 2.0/20 $s^{-1}$ |
| Volume resistivity | $\times 10^{-6}\Omega$•m | 4.5 | 2.3 | 3TS-5100-002 | |
| Chip bond strength | MPa | 2.2 | 2.4 | 3TS-4180-002 | 2Ø gold-plated chip/gold-plated plate |
| Dynamic mechanical analysis (DMA) measurement | GPa | 0.3 | 0.3 | 3TS-4730-001 | DMA method E' at 25°C |
| Recommended nozzle inner diameter | µm | 50 | 210 | — | |

■ Curing conditions

*Physical properties listed above are representative values.

Curing equipment: Hot air drying oven

Curing atmosphere: Nitrogen

Curing temperature: TB3304J: 60 min at 210°C and 30 min at 300°C

TB3303G (NEO): 60 min at 180°C and 30 min at 300°C

$$\Delta F = \frac{2 \times F_0^{\,2}}{A\sqrt{\mu \times \rho}} \times \Delta m$$

ΔF: Oscillation frequency change
$F_0$: Crystal oscillator frequency
A: Electrode area
μ: Shear stress of crystal ($2.947 \times 10^{10}$ kg•ms)
ρ: Crystal density (2,648 kg/$m^3$)
Δm: Mass change

**Fig. 4 Sauerbrey Equation**

Annealing treatment is generally performed in order to reduce outgas from the cured material as much as possible. The annealing temperature varies between crystal device manufacturers, but is higher than that for reflow soldering. For this reason, annealing treatment was performed for 30 minutes at 300°C after curing under standard curing conditions and the characteristic values were checked for any changes in order to ensure that TB3304J was able to withstand annealing treatment (Table 6). It was confirmed that the characteristic values do not change due to the annealing treatment. The amount of outgas from the cured product with and without annealing treatment was also measured. Equipment capable of simultaneous thermogravimetric and differential thermal analysis (TG-DTA) was used for measurement. The results of the TG-DTA measurements are shown in Figure 5. They show that annealing treatment reduces the amount of outgas from the cured material.

## 4-3. Application Performance

The following three elements can be considered as necessary for high precision minute-amount application.

(1) Adhesive application performance
(2) Applicator performance (condition setting)
(3) Nozzle accuracy

High precision minute-amount application cannot be achieved if one of these elements is missing, and all must meet or exceed a certain standard. A further problem is when good results are not obtained when evaluating application performance. For example, when the nozzle clogs, it is necessary to determine whether this clogging is due to particles contained in the adhesive or due to surface roughness inside the needle of the nozzle. The same applies when the application accuracy is inconsistent. It is necessary to determine whether the problem is caused by the properties of the adhesive or the accuracy and setting of the applicator.

The following were used for the three elements when evaluating the application performance of TB3304J on this occasion.

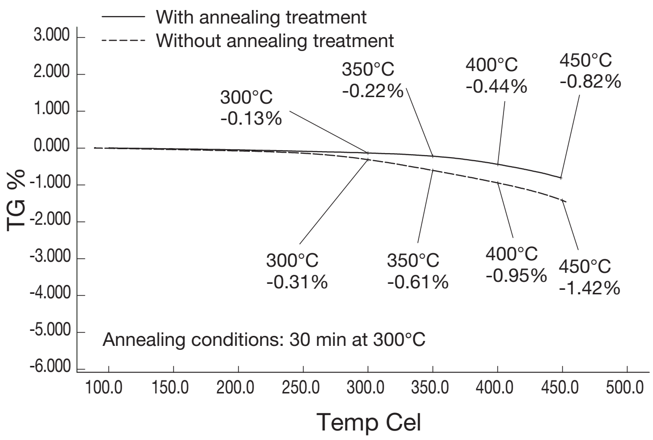



**Fig. 5 Outgassing Volume following Annealing Treatment**

**Table 6 Change in Characteristic Values of TB3304J following Annealing Treatment**

| Test item | Unit | Without annealing treatment | With annealing treatment | Testing method | Remark(s) |
|---|---|---|---|---|---|
| Volume resistivity | $\times 10^{-6}\Omega$•m | 4.5 | 4.5 | 3TS-5100-002 | |
| Chip bond strength | MPa | 2.3 | 2.2 | 3TS-4180-002 | 2Ø gold-plated chip/gold-plated plate |
| Dynamic mechanical analysis (DMA) measurement | GPa | 0.3 | 0.3 | 3TS-4730-001 | DMA method E' at 25°C |

■ Curing conditions
Curing equipment: Hot air drying oven
Curing atmosphere: Nitrogen
Curing temperature: Without annealing treatment: 60 min at 210°C
With annealing treatment: 60 min at 210°C and 30 min at 300°C

*Physical properties listed above are representative values.

■ Application test conditions - three elements

Adhesive: TB3304J

Applicator: Air-type dispenser, manufactured by PFA Corporation (hereafter referred to as “PFA”)

Nozzle: Manufactured by Tecdia Co.,Ltd. (hereafter referred to as “Tecdia”)

Applicator selection, setting of conditions, and application tests were conducted with the cooperation of PFA. PFA applicators have a long track record in the crystal device market. Likewise, Tecdia nozzles have a proven track record in the market and the company provides nozzles designed for use with crystal devices. These test conditions were determined to be appropriate to accurately determine the application performance of TB3304J. The objectives set in this application test are shown below.

Application diameter: Ø100 µm, Ø80 µm

Number of applications: 2,000 shots

Application target: 1210PKG, manufactured by KYOCERA Corporation

Application precision: 3σ = 20 µm or less

The application test was performed by changing the nozzle type according to the target application diameter. Table 7 shows the test conditions covered in this article, and Tables 8-1 to 8-3 show the test results. Application was performed on two 1210PKG gold-plated electrodes and Point 1 and Point 2 were measured.

The test with a target application diameter of Ø100 µm using a nozzle with an outer diameter of Ø100 µm achieved good results, with accuracy of 3σ = approximately 13 µm compared to a target accuracy of 3σ = 20 µm or less (Table 8-1). Similarly, Table 8-2 shows the results of the test using a nozzle with a smaller outer diameter of Ø80 µm with a target application diameter of Ø100 µm. Application was even more accurate, with an accuracy of 3σ = approximately 11 µm. In the final test, the target application diameter was Ø80 µm. This test assumes that the SMD crystal oscillator has a size of 0.8 mm × 0.6 mm. In this test, a nozzle with an outer diameter of Ø80 µm was used, and a highly accurate result of 3σ = approximately 11 µm was obtained (Table 8-3).

In this application test, the adhesive shape (appearance) at the time of application is also confirmed along with the application diameter. Application in a perfect circle is desirable, however, distortion will occur if the properties of the adhesive do not match the adhesive conditions. The appearance confirmation results for TB3304J are shown in Fig. 6.

**Table 8-1 Application Test Results (Test 1)**

| Application diameter | Point 1 | Point 2 |
|---|---|---|
| Average (µm) | 101.57 | 105.79 |
| Minimum (µm) | 89.65 | 94.00 |
| Maximum (µm) | 115.43 | 123.96 |
| 3σ (µm) | 13.18 | 13.29 |

**Table 8-2 Application Test Results (Test 2)**

| Application diameter | Point 1 | Point 2 |
|---|---|---|
| Average (µm) | 108.26 | 106.02 |
| Minimum (µm) | 96.22 | 96.77 |
| Maximum (µm) | 117.89 | 113.95 |
| 3σ (µm) | 11.24 | 8.74 |

**Table 8-3 Application Test Results (Test 3)**

| Application diameter | Point 1 | Point 2 |
|---|---|---|
| Average (µm) | 83.70 | 81.19 |
| Minimum (µm) | 68.63 | 70.28 |
| Maximum (µm) | 95.50 | 91.64 |
| 3σ (µm) | 11.51 | 9.52 |

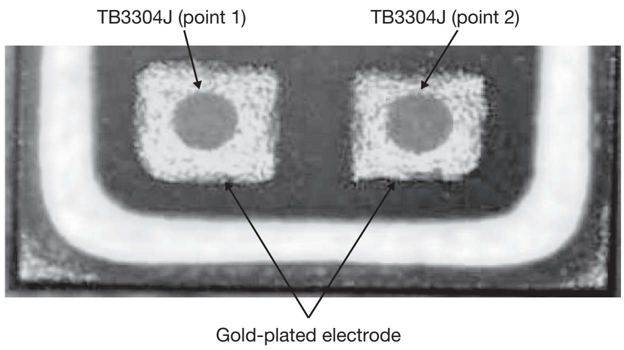



**Fig. 6 Appearance of TB3304J during Application**

**Table 7 Application Test Conditions and Nozzles Used**

| Application test number | Target application diameter (µm) | Nozzle used | Nozzle inner diameter (µm) | Nozzle outer diameter (µm) |
|---|---|---|---|---|
| 1 | ϕ100 | ARQ-S-0510-S | ϕ50 | ϕ100 |
| 2 | ϕ100 | Customize Nozzle | ϕ50 | ϕ80 |
| 3 | ϕ80 | Customize Nozzle | ϕ50 | ϕ80 |

Confirmation of the appearance of the adhesive with a digital microscope after application showed that the circle was extremely well-formed, a result that confirms the previously-established accuracy of application.

Table 9 and Figures 7-1 and 2 show the results of comparative evaluation of TB3304J, TB3303Z, and TB3304D under the conditions of Test 1, with a target application diameter of Ø100 µm. Although TB3303Z, which has the best minute-amount application among the 3rd generation, was not able to meet the target, TB3304J demonstrated extremely high precision application.

The Tecdia nozzles used in this application test are shown in Table 10. None of these products are custom made and all can be obtained for general use.

## 5. Future Development Trends

As stated above, TB3304J was been designed specifically for application precision. From 2020 onward, the spread of 5G communication networks will diversify the type of terminals connected to networks, and it is expected that greater reliability will be required in the crystal device market. In order to meet these needs, we will continue to place emphasis on high reliability as we focus on the development of products with low levels of outgassing and improved stress relaxation (reduced elastic modulus).

**Table 9 Application Test Results for Each Adhesive**

| Application diameter | TB3304J | | TB3303Z | | TB3304D | |
|---|---|---|---|---|---|---|
| | Point 1 | Point 2 | Point 1 | Point 2 | Point 1 | Point 2 |
| Average (µm) | 101.57 | 105.79 | 98.65 | 100.38 | 93.67 | 97.65 |
| Minimum (µm) | 89.65 | 94.00 | 82.40 | 82.26 | 62.90 | 67.81 |
| Maximum (µm) | 115.43 | 123.96 | 120.04 | 119.78 | 118.53 | 118.45 |
| 3σ (µm) | 13.18 | 13.29 | 20.42 | 19.03 | 25.39 | 22.06 |

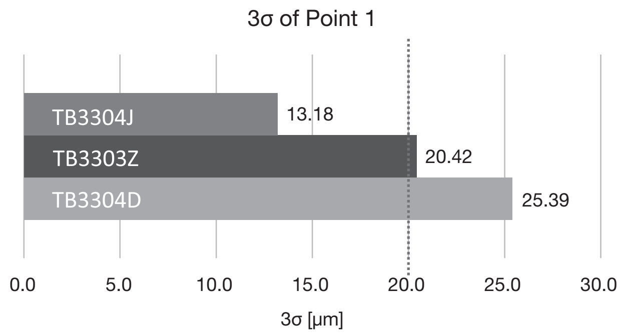



**Fig. 7-1 Application test results**

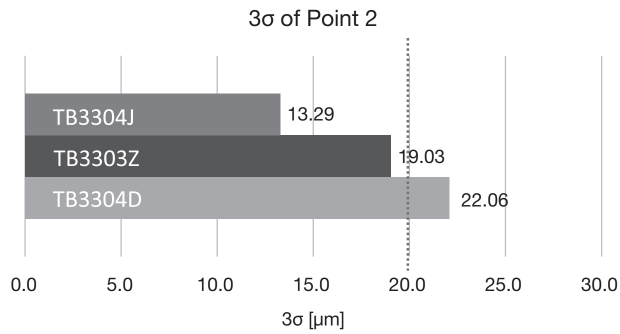



**Fig. 7-2 Application test results**

**Table 10 Information on Nozzles Used**

| Model | Diagram number | Inner diameter (µm) | Outer diameter (µm) |
|---|---|---|---|
| Customize Nozzle | TEC-4301054 #1 | 50 | 80 |
| ARQ-S-0510-S | TEC-4300872 #2 | 50 | 100 |

## Closing

This article describes a product that is suitable for use in the crystal device field, where products have undergone remarkable reductions in size and thickness. By adjusting the applicator conditions and nozzle used, high-precision application of TB3304J is possible at any diameter down to the minimum diameter of Ø80 μm. This opens up the possibility of a wide range of future applications in crystal devices.

We at ThreeBond will continue to focus our efforts on product and technology development in line with market trends in order to ensure the contribution our products make to the industry.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