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Effects of Corrosive Gases on Corrosion & Adhesion Properties of Conductive Pastes

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Abstract

We have investigated the effects of corrosive gases on corrosion and adhesion properties of the conductive pastes used for electronic device interconnection wires and electrodes. We examined three different polymer-type conductive pastes. All three pastes contain silver particles as their conductive filler. In one of the pastes, polyester is used as the binder; in another, silicone; and in the third, epoxy resin. We applied each conductive paste to a flexible bilayer polyimide printed-circuit board and then let them cured. We then subjected the cured conductive pastes to an acceleration test, placing the board in a tank filled with a mixture of corrosive gases. The test conditions we set up were equivalent to exposing a sample of silver to a typical Southeast Asian environment for five years, as follows: 2 ppm hydrogen sulfide gas, 4 ppm nitrogen dioxide gas, a temperature of 30°C, a relative humidity of 70%, and testing duration of 77.3 hours. To analyze the resulting corrosion, we cut samples, using the SAICAS slant-cut method, and checked the sulfur component in the cut section of each sample by using both the scanning electron microscope and the EDX component analysis method. We found that, for each of the pastes, the corrosion reached a depth of about 2 μ m, as expected. We also measured the adhesion properties of each conductive paste, using the SAICAS method. As a result, we have confirmed that the conductive paste which contains epoxy resin as its binder has a higher adhesion with respect to horizontal peeling than the other types, and that its adhesion does not deteriorate, even after the corrosion test.

1. Introduction

Currently popular products incorporating electronic devices, as typified by mobile phones and computers, are used in diverse environments throughout the world. In Southeast Asia, it is characterized by a high surrounding concentration of corrosive gases, such as sulfur dioxide and nitrogen dioxide, as well as a high-temperature and high-humidity climate. We have been concerned about the corrosion of conductive materials used there in electronic devices. Conductive paste is used as a conductive material in a wide variety of products, such as electronic parts and sets. Before being ap-

plied, the conductive paste is liquid. After being applied, it is dried and cured, and then it becomes conductive. These conductive pastes are either high-temperature acclimated types that contain an inorganic binder, or polymer types that contain an organic binder. Both types achieve their conductivity by firmly fixing a conductive particle, such as silver, gold, or copper, with the smallest amount of binder possible. The conductive particle as typified by silver particles easily corrodes under the influence of surrounding corrosive gases. There are many types of surrounding corrosive gas test. The test used for this study was an acceleration test in which samples were placed in a gas mixture for 77.3 hours, that is, the test equivalent to five years of exposure to an average Southeast Asian environment. In this study, after the completion of the test, the detailed changes in the adhesion properties of the polymer-type conductive paste relative to the

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polyimide board and observations of how deeply the conductive paste had been corroded, were evaluated by using a scanning electron microscope (SEM) and the SAICAS (Surface And Interfacial Cutting Analysis System) method¹⁾.

2. Experiment

2.1 Preparation of test pieces

The flexible printed-circuit (FPC) board used in our tests was a bilayer board made of SC1850 (Sony Chemicals Corporation). Its polyimide layer is $15\ \mu\text{m}$ thick and the copper foil on the board is $18\ \mu\text{m}$ thick. The board has no bonding layer. We degreased the surface of the polyimide layer by washing it with acetone. We applied a string of each of the conductive pastes listed in Table 1, about 1 mm wide and about 0.1 mm thick to the polyimide surface of the FPC board. We then placed the FPC board in a hot air circulating oven at 150°C for 30 minutes to drive off the solvent from the conductive paste strings and form cross-links between the binder together, thereby causing the conductive pastes to stick to the FPC board and form our test pieces. As non volatiles of each paste differ from each paste as shown in Table 1, the string thickness measured closely after dried differed from 40 to $110\ \mu\text{m}$.

Table 1 Characteristics of conductive paste

Type	Conductive particle	Particle size (μm)	Polymer type of binder	Curing temp. & time	Non volatile ratio (wt-%)
Paste A	Silver	Mixed about 0.3 & 4	Polyester	150°C 30min.	50
Paste B	Silver	Mixed about 0.3 & 4	Silicone	150°C 30min.	50
Paste C	Silver	about 4	Epoxy *1	150°C 30min.	95

Epoxy*1: liquid resin of cresol novolac type

2.2 Corrosion test method

As shown by measured data in Fig. 1²⁾, samples of silver were exposed to an natural Southeast Asia and Japan/Europe/USA each environment for one year. The each samples averaged $0.42\ \mu\text{m}$ and $0.12\ \mu\text{m}$ of corrosion thickness. In this study, we selected $0.42\ \mu\text{m}$ in Southeast Asia where corrosive environment is severer for standardized corrosion thickness. As the corrosion of the silver progresses linearly over time, it would be about $2.1\ \mu\text{m}$ deep after five years of exposure to the environment. Through the experiment, we determined the accelerated mixed gas corrosion test conditions that cause the corrosion to grow to about $2.1\ \mu\text{m}$, according to the mixed gas condition-to-corrosion

Fig. 1 Ag-corrosion in Southeast Asia and in Japan/Europe/USA (1 year)

Fig. 2 Accelerative corrosion test at 96 hours

thickness relationship shown in Fig. 2³⁾. Specifically, we subjected the test pieces to a 77.3 hour acceleration test under a mixed gas condition (30°C and 70%RH) with 2 ppm of hydrogen sulfide gas and 4 ppm of nitrogen dioxide gas. We observed the surface of the conductive paste on each test piece, using a SEM (Quanta 200FEG manufactured by FEI Company), both before and after the test. We also performed a component analysis on the test pieces, using an energy dispersive X-ray microanalysis (EDX, Genesis4000 manufactured by AMETEK, Inc.). Furthermore, we performed an EDX component analysis on the test pieces that had been subjected to the corrosion test at a range of depths, measured in micron units, to find out how

deep the corrosion progressed, by cutting each test piece with diamond-blade (1 mm wide) of a SAICAS (DN-20 manufactured by Daipia Wintes Co., Ltd.) at a vertical speed 1/100 as high as $3\mu\text{m}/\text{sec}$ of the horizontal speed. Then, we performed sulfur mapping and obtained the component-area ratio for the sulfur at each depth, measured in micron units, using image analysis software manufactured by Keyence Corporation.

2.3 Adhesion test method

To obtain the adhesion property between the conductive paste and the polyimide, we performed measurements on the test pieces both before and after the corrosion test. To measure the adhesion, we performed a peeling test, using the SAICAS method, with a diamond-blade of 1 mm wide and at a horizontal speed of $5\mu\text{m}/$

sec with initial vertical speed of $0.5\mu\text{m}/\text{s}$, and the blade only moving horizontally for peeling.

3. Results and discussion

3.1 Corrosion test results

Fig. 3 shows the SEM photographs⁴⁾ and Fig. 4 shows the EDX spectra of conductive pastes A, B, and C, obtained before and after the corrosion test. We could observe the mixed silver particle as shown in Fig. 3a and 3b. And Fig. 3c shows about $4\mu\text{m}$ flake of silver particle of paste C. After the corrosion test, the surfaces were roughened than before the test, which made focusing more difficult. We believe that this is because the silver particles increased in volume and its surface became rough through being converted to silver sulfide during the corrosion test. The result of com-

Fig. 3 SEM Photographs before and after corrosion test (3a, 3b & 3c : before corrosion test; 3d, 3e & 3f : after corrosion test)

Fig. 4 EDX spectra before and after corrosion test (4a, 4b & 4c : before corrosion test, 4d, 4e & 4f : after corrosion test)

Fig. 5 Measuring position ①, ②, ③, ④ of depth profile analysis by EDX spectra after cutting by SAICAS
5a: Paste A, 5b: Paste B, 5c: Paste C

Fig. 6 EDX spectra of mark position
① Surface and ② 1~2 μm depth

ponent analysis using an EDX confirmed this speculation, because the sulfur-component spectrum was high for all the pastes as shown in Fig. 4. Fig. 5 shows the measuring position (①, ②, ③, ④) of EDX mapping of the sulfur components at each depth profile, as measured from the surface. Fig. 6 shows EDX spectra of mark position ① and ② at each pastes. Table 2 shows the component-area ratio (%) for the sulfur at each depth about each pastes after corrosion test. For all the pastes, the sulfur component spectrum was observed at a depth of 1 to 2 μm . The spectrum for paste

Table 2 Component-area ratio (%) for the sulfur of depth profile analysis about each pastes after corrosion test.

Depth Profile	Paste A	Paste B	Paste C
① Surface of Paste	7.11	7.47	5.32
② 1~2 μm Depth	3.55	4.48	2.11
③ 3~5 μm Depth	1.17	1.21	1.11
④ 10~20 μm Depth	0.94	0.78	1.07

B was the highest; followed by paste A, and then paste C, the latter using the epoxy binder. At a depth of 3 μm or more, the spectrum of all the pastes was about 1%, which was within the measurement error range. The sulfur component depth profile analysis, performed after the corrosion test, also showed that paste C has a lower sulfur component than the other paste types at a depth of 1 to 2 μm . This could be because the cohesion and adhesion properties of paste C were high when it was cut diagonally, as shown in Fig. 7c and Fig. 8c.

3.2 Adhesion test results

Table 3, Fig. 7 and Fig. 8 show the results of the peeling adhesion test which we did using the SAICAS method. Peel force of paste B, with the silicone binder, was the lowest and the failure was adhesive failure⁵⁾. Paste B peeled off from the FPC board in condition that diamond-blade does not reach the FPC board. Fig. 7b and Fig. 8b show them. The information of depth showed in Fig. 8b was about 20 μm lower than true depth upon closer study. Peel force of paste C, with the epoxy binder, was highest. We believe that this is because polyimide of the FPC board and epoxy binder of the conductive paste are both high-polarity polymers. After corrosion test, peel force of paste A and C were lower a little than before test. We believe that this is because the polyimide film absorbed humidity during the corrosion test. Because the water absorption measured by JIS C 6481 of SC1850 used in this study was about 1.5 wt-%. In Fig. 8; only 8c, vertical force at 80 to 160 sec showed high. This is because paste C with epoxy binder was its high agglutinability when it was cut diagonally. And also, we did not observe an alien substance upon closer study. Corrosion and adhesion test results showed that adhesion property by SAICAS method of each paste was in proportion to corrosion resistance.

Fig. 7 Peel force by SAICAS method before corrosion test (Peel condition ; Horizontal speed : $5\mu\text{m/sec}$, Vertical speed: $0.5\mu\text{m/sec}$)
Horizontal force : ———
Vertical force : - - - - -
Depth : ······

Fig. 8 Peel force by SAICAS method after corrosion test (Peel condition ; Horizontal speed : $5\mu\text{m/sec}$, Vertical speed: $0.5\mu\text{m/sec}$)
Horizontal force : ———
Vertical force : - - - - -
Depth : ······

Table 3 Peel force (kN/m) by SAICAS method

Type	before corrosion test	after corrosion test
Paste A	1.7 Cf*2	1.6 Cf
Paste B	0.16 Af*1	0.21 Af
Paste C	8.5 Cf	7.4 Af

Af*1 : Adhesive failure , Cf*2 : Cohesive failure⁵⁾

4. Conclusions

- We have succeeded in ion mapping in the depth direction according to the results of component analysis by means of the SAICAS slant-cut method, to determine the progress of corrosion.
- We have found out by SAICAS method that adhesion of each paste was in proportion to corrosion resistance.
- We have found out that a 77.3 hour acceleration test using a mixture gas consisting of 2 ppm H_2S gas and 4 ppm NO_2 gas caused the conductive paste corrosion to reach a depth of about $2\mu\text{m}$.
- We have found that the adhesion property of the conductive paste with an epoxy binder was degraded less as a result of the corrosion test than the other types of conductive paste.
- SEM observations of the test pieces subjected to the corrosion test showed that the gas test changed the volume of the silver particles partly and made its surface roughen.

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Additional remark

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<論文>

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導電ペーストのコロージョンおよび接着特性に
及ぼす腐食性ガスの影響

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要 旨

電子デバイスの配線や電極などに使用されている、導電ペーストの腐食性ガスによるコロージョン試験と接着性について研究した。導電ペーストとしては、導電フィラーとして銀が使用され、バインダーとしてポリエステル、シリコンならびにエポキシ樹脂が使用されているポリマータイプの3品種を使用した。2層ポリイミドフレキシブルプリント配線板上に塗布、硬化した導電ペーストを、腐食性混合ガスを用いた槽内加速試験で腐食させた。この時、腐食性混合ガス試験は、東南アジアにおける一般環境5年暴露に相当の、硫化水素ガス 2ppm、二酸化窒素ガス 4ppm、試験温湿度 30℃、70%RH の条件で、77.3 時間行なった。腐食度合いの分析は、サイカス斜め切削法により深さ方向に対して、電子顕微鏡の EDX 成分分析で硫黄成分の分析を行なった。その結果、いずれの導電ペーストも、想定した深さ約 2 μ m まで腐食が進んでいることが明らかになった。接着性についても、サイカス法により測定した。水平剥離強さは、エポキシ樹脂をバインダーに使用した導電ペーストの接着が、最も強固で、コロージョン試験後においても、大幅な強度低下は見られないことが確認できた。

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