New Technology Introduction

● Effect of the ion exchanger "IXE®", "IXEPLAS®" for the reliability of the copper wiring package

Yasuharu Oono

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1. Introduction

Toagosei's IXE® and IXEPLAS® ion exchangers have excellent heat resistance and ion selectivity, and are used to improve the reliability of electronic materials, such as semiconductor package encapsulants[1].

In recent years, the switch from gold to copper wire for semiconductor package wiring has accelerated. Copper wire has many advantages over gold wire, including lower cost, higher electrical conductivity, and superior thermal conductivity. On the other hand, copper wire is known to be more susceptible to oxidation than gold wire, resulting in inferior package reliability. Recently, research has been conducted on the reliability degradation mechanism of copper wire packages and countermeasures against such degradation. Some reports suggest that free Cl^- ions and the pH level in the encapsulation resin are contributing factors[2, 3].

We therefore verified the impact of Cl^- ions and pH on reliability using copper wiring test pieces instead of copper wire, and assessed the effect of IXE and fine-particle IXEPLAS.

To examine differences in scavenging performance based on particle size, migration tests were also conducted by adding IXE and IXEPLAS to the adhesive layer of a flexible printed circuit (FPC) containing copper wiring.

2. Experiments

2.1 Ion exchangers used in the experiment

Table 1 shows the ion exchangers used in the experiment. IXE and IXEPLAS are additives that scavenge trace amounts of impurity ions in electronic materials and are composed of specific inorganic ion exchangers.

In general, inorganic ion exchangers reversibly exchange ions in their surrounding environment with the ions they contain. IXE and IXEPLAS have the following characteristics, and were used in the experiments on this basis.

Ⅰ. Low impurity content and free of RoHS restricted substances

Ⅱ. Once ions are captured, they are difficult to release

Ⅲ. Selectively scavenges impurity ions such as Cl^- and Na^+ that cause defects in electronic materials, releasing in exchange either harmless ions or none at all

IXE and IXEPLAS can enhance the reliability of various encapsulants by combining these necessary characteristics.

Table 1: Ion exchangers used

	Ion exchanger	Component	Average particle diameter
A	IXEPLAS-A1	Zirconium/magnesium-based	0.5 μm
B	IXEPLAS-A2	Zirconium/magnesium-based	0.2 μm
C	IXEPLAS-B1	Zirconium-bismuth-based	0.4 μm
D	IXE-600	Antimony-bismuth-based	1.0 μm
E	IXE-100	Zirconium-based	1.0 μm
F	IXE-100F (developed product)	Zirconium-based	0.2 μm
G	Competitor ion exchanger	Magnesium-based	0.5 μm

2.2 Sample preparation for evaluation

2.2.1 Preparation of test pieces and cured materials

To observe the impact of the Cl^- ion concentration and the pH level, the bisphenol A liquid epoxy resin (72 parts) shown in **Table 2** was used. In addition, amine curing agent (28 parts), fused silica (100 parts), epoxy coupling agent (1 part), and ion exchanger (0.5 parts) from **Table 1** were blended, which were mixed in three rolls (**Table 3**).

Table 2: Epoxy resins used in reliability evaluation tests

	Hydrolyzable chloride	pH of the extract	Notes
(1)	500 ppm	4.7	Bisphenol A
(2)	300 ppm	4.7	↑
(3)	50 ppm	4.8	↑
(4)	300 ppm	5.9	↑
(5)	300 ppm	6.9	↑

New Products Research Laboratory, General Center of R&D, Toagosei Co., Ltd.

The mixed resin was applied in a 1 mm thick layer onto 2 copper wires (line width: 20 µm, film thickness: 0.15 µm, length: 1000 mm, line spacing: 20 µm, resistance ≈7 kΩ) printed on a glass plate and cured at 130°C (hereinafter referred to as "test piece"). Additionally, the mixed resin was cured to a size of 1 cm (length) x 33 cm (width) × 1 mm (thickness) and used for the extraction test (hereinafter referred to as "cured material").

Table 3: Compositions of resin formulations for test pieces and cured materials

Epoxy resin	Curing agent	Fused silica	Coupling agent	Ion exchanger
(1) / 72 parts	28 parts	100 parts	1 part	None
(2) / 72 parts	↑	↑	↑	None
(3) / 72 parts	↑	↑	↑	None
(4) / 72 parts	28 parts	100 parts	1 part	None
(5) / 72 parts	↑	↑	↑	None
(1) / 72 parts	28 parts	100 parts	1 part	A/0.5 parts
↑	↑	↑	↑	A/1.0 part
↑	↑	↑	↑	B/0.5 parts
↑	↑	↑	↑	B/1.0 part
↑	↑	↑	↑	C/0.5 parts
↑	↑	↑	↑	C/1.0 part
↑	↑	↑	↑	D/0.5 parts
↑	↑	↑	↑	D/1.0 part
↑	↑	↑	↑	G/0.5 parts
↑	↑	↑	↑	G/1.0 part

2.2.2 Preparation of electrochemical migration evaluation samples

Epoxy acrylate and urethane acrylate resin compositions and ion exchangers were blended according to **Table 4** and coated onto interdigitated copper electrodes (spacing between electrodes = 50 µm/50 µm) at 35 µm film thickness. Then, the samples underwent UV curing at 2,000 mJ and thermal curing at 160°C for one hour to produce mock film substrates for evaluation.

Table 4: Types of ion exchangers used in the tests and amounts added

Ion exchanger	Average particle diameter	Additive amount
None	-	-
A (IXEPLAS-A1)	0.5 µm	0.5 parts
B (IXEPLAS-A2)	0.2 µm	0.5 parts
E (IXE-100)	1.0 µm	0.7 parts
F (IXE-100F)	0.2 µm	0.7 parts
G (competitor ion exchanger)	0.5 µm	0.7 parts

2.3 Evaluation method for test pieces and cured materials

2.3.1 Extraction test (evaluation of Cl^- concentration and pH)

Ten pieces of cured material were placed in a Teflon container and five times their weight of pure water was added. Then, they were tightly sealed at 130°C for 100 hours and underwent an extraction treatment.

The concentration of Cl^- ions in the extract was measured using ion chromatography. The pH was also measured.

2.3.2 Reliability (defect rate) evaluation

The test pieces underwent HAST testing at 130°C, 85% RH, with an applied voltage of 40 V for 100 hours. Test pieces that experienced open or short-circuits were considered defective, and the defect rate was calculated for ten samples.

2.3.3 Electrochemical migration evaluation

Migration tests were conducted on mock film substrates at 85°C, 85% RH, with an applied voltage of 50 V for 500 hours.

Migration is a phenomenon in which an electric field or mechanical stress repeatedly causes the dissolution and precipitation of metal, eventually leading to a short circuit[4]. Since copper deposits appear between the electrodes when migration occurs, the electrodes were evaluated by observing them under a microscope after the test.

3. Results and discussion

3.1 Impact on reliability

3.1.1 Impact of free Cl^- ions

Table 5 shows the hydrolyzable chloride content of the epoxy resin, the extraction test results, and the reliability (defect rate) evaluation results. For epoxy resins with similar extract pH, the higher the hydrolyzable chloride content, the higher the Cl^- ion concentration.

Table 5: Extraction and reliability test results

Epoxy resin No./ Hydrolyzable chloride	Extracted Cl^- ion concentration (ppm)		Defect rate (%)
	Measured value	Average	
(1) 500 ppm	5.1	5.2	100
	5.3		
(2) 300 ppm	2.9	3	80
	3		
(3) 50 ppm	0.9	1	30
	1.1		

Figure 1 shows the relationship between the concentration of Cl^- ions of the epoxy resin extract and the defect rate. The higher the concentration of Cl^- ions in the extract, the higher the defect rate. We believe that Cl^- ions cause copper wiring to dissolve, contributing to the corrosion and migration phenomena expressed by the following formulas[4, 5].

- **Anode:** $Cu \rightarrow Cu^{2+} + 2e^-$ (Cu elution)
- **Cathode:** $Cu^{2+} + 2e^- \rightarrow Cu$ (Cu deposition)

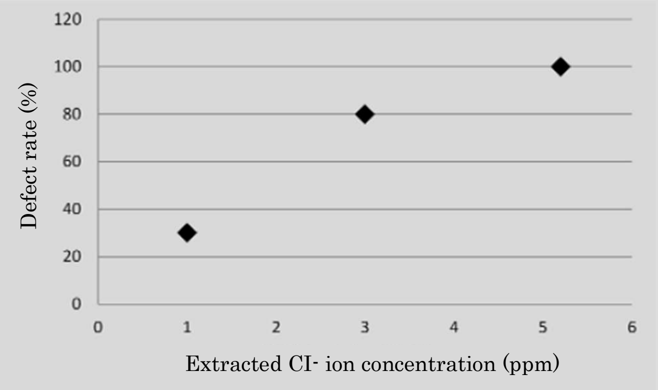

Figure 1. Relationship between the Cl- ion concentration in the extract and the defect rate

3.1.2 Impact of the pH level of the encapsulation resin

Table 6 shows the results of the extraction test and reliability (defect rate) evaluation for epoxy resin compositions with similar hydrolyzable chloride content but different pH levels.

Table 6: Extraction and reliability test results

Epoxy resin No./ Hydrolyzable chloride	Extraction test results		Defect rate (%)
	Cl^- concentration	pH	
(2) /300 ppm	3	4.7	80
(4) /300 ppm	3.1	5.9	70
(5) /300 ppm	3.2	6.9	50

The concentration of Cl^- ions was almost the same across resins with different pH values of the extract. **Figure 2** shows the relationship between the pH of the extract and the defect rate. The defect rate tended to be higher at lower pH levels.

Since copper is more soluble at lower pH levels, corrosion and migration are considered to be more likely to progress.

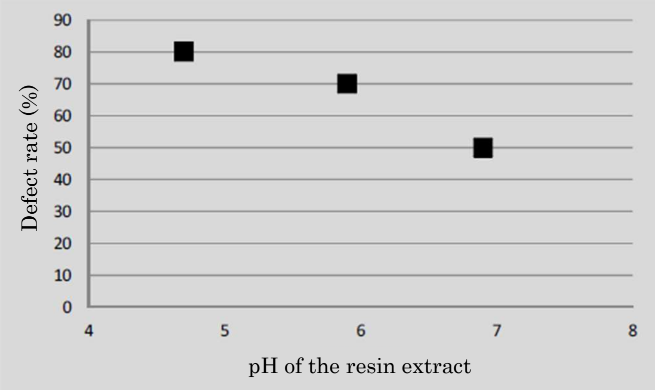

Figure 2: Relationship between the pH of the resin extract and the defect rate

3.2 Verification of the effect of adding ion exchangers

Table 7 shows the Cl^- ion concentration, pH, electrical conductivity (EC), and reliability test results of the epoxy resin extract when the ion exchangers are added. The base epoxy resin used was (1) hydrolyzable chloride at 500 ppm as listed in **Table 2**, and the ion exchangers used were A through D and G (competitor product).

Table 7: Extraction and reliability test results

Ion exchanger /additive amount	pH of the extract	Cl^- concentration in the extract (ppm)	EC of the extract (μS/cm)	Defect rate (%)
None	4.7	5.2	30	100
A/0.5 parts	5.5	5.1	26	50
A/1.0 part	6.1	4.5	20	30
B/0.5 parts	5.4	4.5	25	20
B/1.0 part	6.1	3.7	19	0
C/0.5 parts	4.8	3.2	22	20
C/1.0 part	5	2.6	15	10
D/0.5 parts	4.5	2.6	30	40
D/1.0 part	4.1	1.9	31	30
G/0.5 parts	5.8	5.2	29	70
G/1.0 part	6.7	5	29	50

Figure 3 shows the relationship between the concentration of Cl^- ions in the resin extract and the defect rate. Adding the ion exchanger lowered the concentration of Cl^- ions in the extract, and the defect rate generally decreased accordingly. Among them, ion exchanger B was the most effective. Ion exchangers A and B have the same composition. However, their particle sizes differ, with B being smaller. We believe that the smaller particle size increases the specific surface area, thereby improving the ability to scavenge Cl- ions.

On the other hand, the test piece containing competitor ion exchanger G showed almost no reduction in Cl^- ion concentration, and its defect rate was high.

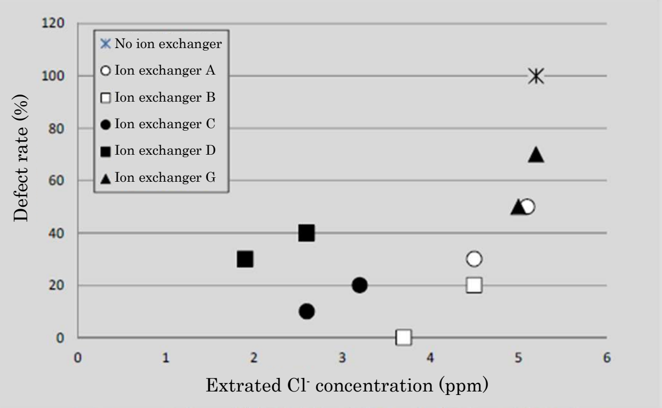

Figure 3: Relationship between the Cl^- ion concentration in the resin extract and the defect rate with the ion exchangers added

Figure 4 shows the relationship between the pH of the resin extract and the defect rate. For all test pieces except for ion exchanger D, the defect rate tended to decrease with increasing pH.

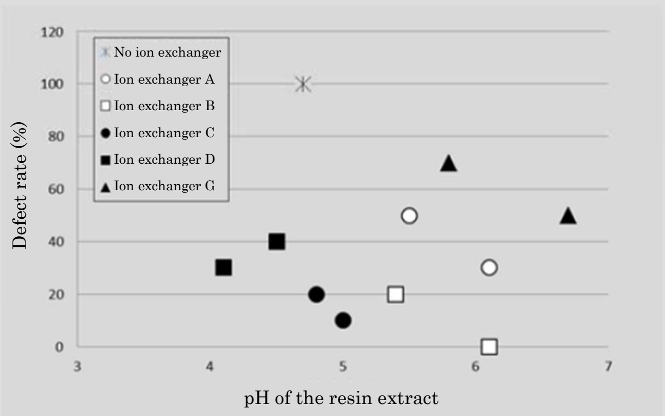

Figure 4: Relationship between the pH and the defect rate with the ion exchangers added

Figure 5 shows the relationship between the electric conductivity (EC) of the extract and the defect rate. For all test pieces except for ion exchanger D, the defect rate tended to decrease with lower EC. We assume that the ion exchangers scavenge Cl$^-$ ions in the resin, resulting in decreased EC. With ion exchanger D, Cl$^-$ ions are exchanged for ions that do not affect corrosion rather than being scavenged, and we have confirmed that the EC and pH do not decrease.

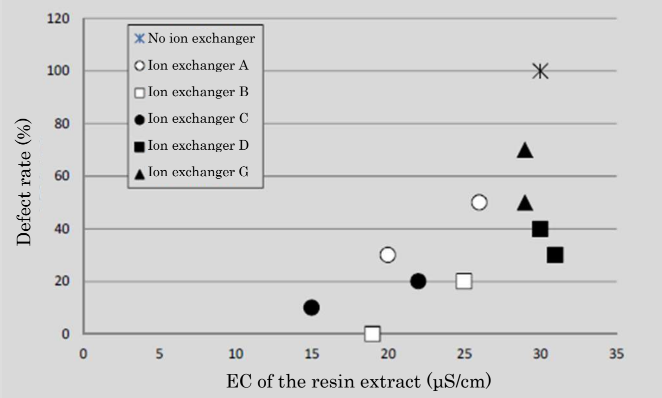

Figure 5: Relationship between the electrical conductivity (EC) of the resin extract and the defect rate

3.3 Electrochemical migration evaluation results

Figure 6 shows the migration test results. In all cases, the addition of ion exchangers suppressed migration.

Ion exchangers A and B have the same composition, but B has a smaller particle size. In other words, fine particles are more effective at suppressing migration. As with the results of the test pieces, we believe that this occurs because fine particles have a larger specific surface area and provide more opportunities for contact with impurity ions, such as Cl$^-$ ions, even with the same amount of additive, making them easier to scavenge.

Similarly, the zirconium-based ion exchangers E and F were also highly effective in inhibiting the migration of fine particles. E and F are cation exchangers, and we believe that they exhibit migration prevention effects by scavenging eluted Cu.

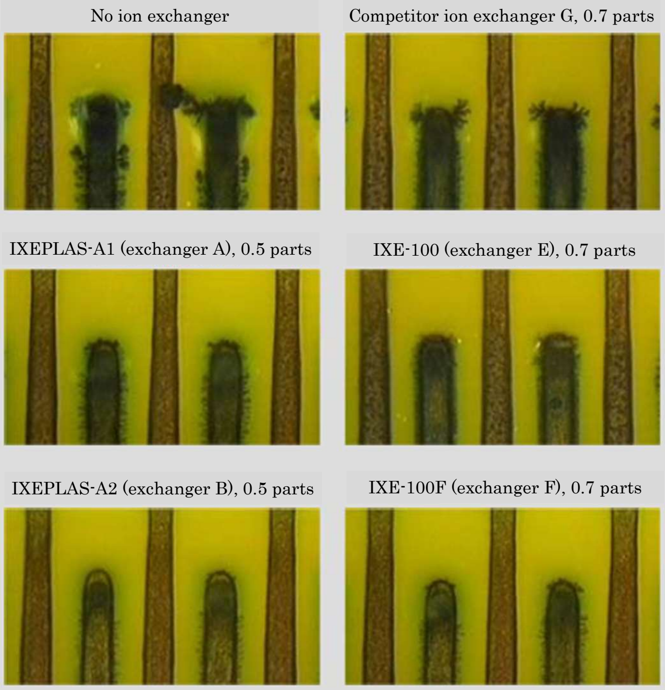
No ion exchanger
Competitor ion exchanger G, 0.7 parts
IXEPLAS-A1 (exchanger A), 0.5 parts
IXE-100 (exchanger E), 0.7 parts
IXEPLAS-A2 (exchanger B), 0.5 parts
IXE-100F (exchanger F), 0.7 parts

Figure 6: Migration test results

4. Summary

To verify the factors contributing to the reliability degradation of copper wire packages, we prepared encapsulant test pieces, and conducted extraction tests and reliability evaluations. We also verified the effect of adding ion exchangers on improving reliability. Furthermore, we verified the effect of ion exchangers in preventing copper wiring migration in FPCs. We then obtained the following results.

- We found that a lower concentration of Cl$^-$ ions in the extract and a higher pH resulted in a lower defect rate and higher reliability. Additionally, the lower the hydrolyzable chloride content of the epoxy resin, the lower the defect rate and the higher the reliability. Based on these findings, we presume that the hydrolyzable chloride had ionized and corroded the copper wiring.
- Adding IXE and IXEPLAS suppressed the concentration of Cl$^-$ ions in the resin extract, reducing the defect rate and improving reliability. We assume that this occurs because IXE and IXEPLAS scavenge Cl$^-$ ions, thereby decreasing their concentration in the encapsulant.
- We confirmed that adding IXE and IXEPLAS inhibited migration of copper wiring. We also found that for the same composition, the smaller the particle size, the greater the suppression effect. We presume this is because the effective specific surface area increases with finer particles.

Based on the above, we recommend the ion exchanger IXEPLAS-A2 for copper wire packages due to its high Cl^- ion scavenging capability, effect of increasing pH levels, and fine particle form.

We will continue developing ion exchangers with even higher performance to help improve the reliability of electronic materials.

Reference

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