

## How impurities affect ionic migration, and how to counter their impact

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*The author has studied how impurities adhering to PCBs affect ionic migration, and presents in this report a summary of the results of his investigation.*

### 1. Introduction

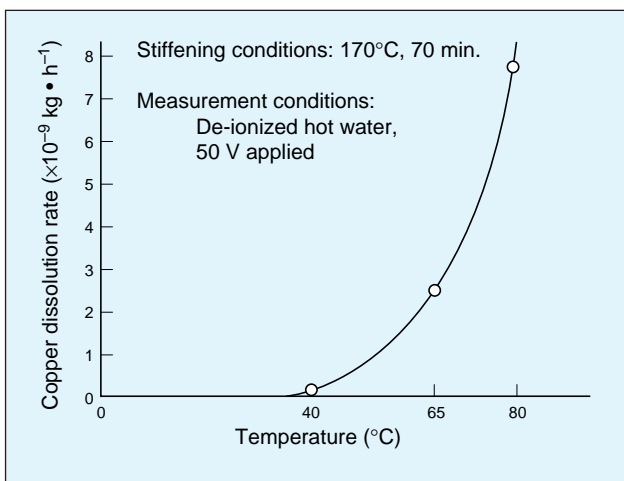
The halt in the manufacture of specific CFCs (chlorofluorocarbons) has forced electronics manufacturers to turn to alternate CFCs or water to wash electronic parts and equipment, or even not to wash at all. The Insulation technology investigation committee (chaired by Professor Tsukui of Tokai University) of the Institute of Electrical Engineers of Japan inaugurated an investigation of this situation, and from April 1993 through March 1996 carried out a thorough study of the literature on washing and soldering methods for PCBs (printed circuit boards) related to the effects of ionic migration. This report presents the results of that study.

### 2. Mechanisms generating ionic migration, and factors influencing those mechanisms

#### 2-1 Mechanisms generating ionic migration

High temperature and high humidity test conditions are generally employed in accelerated testing for ionic migration.

Fig. 1 shows the temperature dependence of the dissolution rate of copper in PCBs when voltage is applied.



**Fig. 1** Temperature dependence of copper dissolution rate

In this case, ionic migration is caused by an electrochemical reaction. Using electrolytes to apply direct current voltage across electrode intervals causes the dissolution of the electrode metals in the high region of standard potential (as seen in the list of standard potentials in Table 1).<sup>1)</sup>

( $E_0^0$  represents the equilibrium electrode potential of metals with standardized hydrogen electrodes in normal conditions. The ranking of  $E_0^0$  constitutes standard potentials, and forms the basis for the degree of the tendency to ionize.<sup>2)</sup>)

The degree of the tendency for ionic migration is known to differ according to the type of electrode metal, and normally can be ordered as  $\text{Ag} > \text{Pb} > \text{Cu} > \text{Sn}$ , which differs from the order of the standard potentials listed in Table 1. Metals such as Fe, Pd, and Pt are classified as having a weak tendency for ionic migration.

The following three items are thought to have a causal connection to determining the order of the tendency to form the above-mentioned ionic migration.<sup>1)</sup>

- (a) Standard potential, along with the electrode reactions in Table 1
- (b) The effect of pH on electrode reactions
- (c) The speed of electrode reactions

Based on the material presented above, the following items are thought to be related to the causes of the occurrence and growth of ionic migration.

- (a) The application of direct current voltage
- (b) The type of conductive metal
- (c) Insulation layer: differences in materials, composition, and manufacture
- (d) Processes: E.g., contamination by foreign particles, ionic residue, the occurrence of cracking, and the degree of washing
- (e) Environment: temperature, humidity, and ionic components (particles in the atmosphere such as SO<sub>x</sub> and NO<sub>x</sub> that dissolve and form ionic components). In other words, matter that is supposed to form the primary insulation layer is believed to yield ionic components from the items listed in (c) through (e), and the formation of electrolytes is thought to generate ionic migration and spur its growth.

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**Table 1 Standard electrode potential (25°C, 0.1 MPa, V vs. SHE)**

Electrode reaction	E°	Electrode reaction	E°
Li = Li <sup>+</sup> + e <sup>-</sup>	-3.05	Fe = Fe <sup>2+</sup> + 2e <sup>-</sup>	-0.440
K = K <sup>+</sup> + e <sup>-</sup>	-2.92	Cd = Cd <sup>2+</sup> + 2e <sup>-</sup>	-0.403
Ca = Ca <sup>2+</sup> + 2e <sup>-</sup>	-2.87	In = In <sup>3+</sup> + 3e <sup>-</sup>	-0.342
Na = Na <sup>+</sup> + e <sup>-</sup>	-2.71	Co = Co <sup>2+</sup> + 2e <sup>-</sup>	-0.277
Mg = Mg <sup>2+</sup> + 2e <sup>-</sup>	-2.36	Ni = Ni <sup>2+</sup> + 2e <sup>-</sup>	-0.250
Be = Be <sup>2+</sup> + 2e <sup>-</sup>	-1.85	Mo = Mo <sup>3+</sup> + 3e <sup>-</sup>	-0.200
Hf = Hf <sup>4+</sup> + 4e <sup>-</sup>	-1.70	Sn = Sn <sup>2+</sup> + 2e <sup>-</sup>	-0.136
Al = Al <sup>3+</sup> + 3e <sup>-</sup>	-1.66	Pb = Pb <sup>2+</sup> + 2e <sup>-</sup>	-0.126
Ti = Ti <sup>2+</sup> + 2e <sup>-</sup>	-1.63	H <sub>2</sub> = 2H <sup>+</sup> + 2e <sup>-</sup>	±0.000
Zr = Zr <sup>4+</sup> + 4e <sup>-</sup>	-1.54	Cu = Cu <sup>2+</sup> + 2e <sup>-</sup>	0.337
Mn = Mn <sup>2+</sup> + 2e <sup>-</sup>	-1.18	2Hg = Hg <sub>2</sub> <sup>2+</sup> + 2e <sup>-</sup>	0.778
V = V <sup>2+</sup> + 2e <sup>-</sup>	-1.175	Ag = Ag <sup>+</sup> + e <sup>-</sup>	0.798
Nb = Nb <sup>3+</sup> + 3e <sup>-</sup>	-1.1	Pd = Pd <sup>2+</sup> + 2e <sup>-</sup>	0.987
Zn = Zn <sup>2+</sup> + 2e <sup>-</sup>	-0.763	Pt = Pt <sup>2+</sup> + 2e <sup>-</sup>	1.188
Cr = Cr <sup>3+</sup> + 3e <sup>-</sup>	-0.744	Au = Au <sup>3+</sup> + 3e <sup>-</sup>	1.498

**2-2 Tendency to form ionic migration**

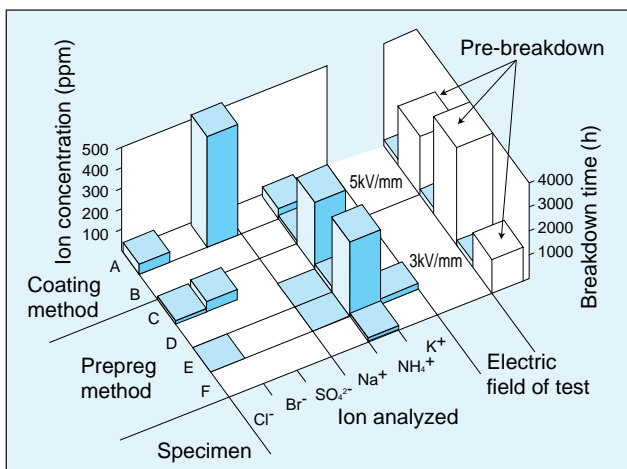
The effect of pH on electrode reactions is one factor that determines ranking in the tendency to form ionic migration.

Many impurities and ionic components are encountered in PCB materials and in processing.

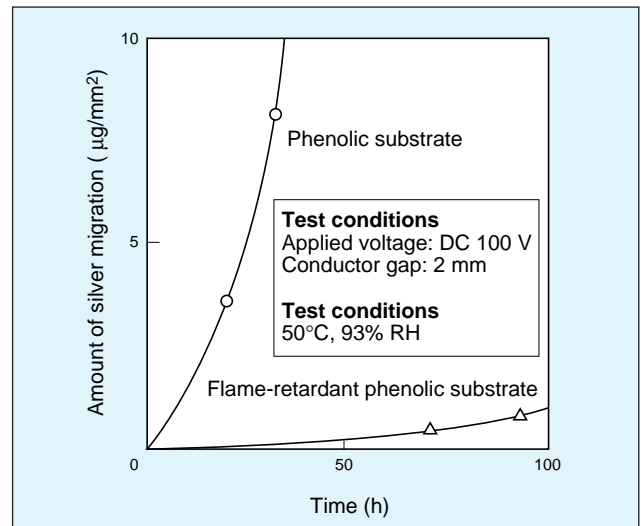
Fig. 2 shows examples taken from studies of the effects of all types of ions on copper migration. These examples demonstrate the relationship between ion residue in the insulation adhesion layer of metal-based PCBs and the time leading to insulation breakdown.

Systems with a high concentration of Cl<sup>-</sup>, Br<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and NH<sub>4</sub><sup>+</sup> have a short insulation breakdown period, suggesting a correlation with copper migration.<sup>2)</sup>

Fig. 3 shows the effects of PCB type on ionic migration. Flame-retardant phenolic substrate exhibits far less tendency to form ionic migration than non-flame-retardant substrate.



**Fig. 2 Ionic components and insulation life of insulation materials**

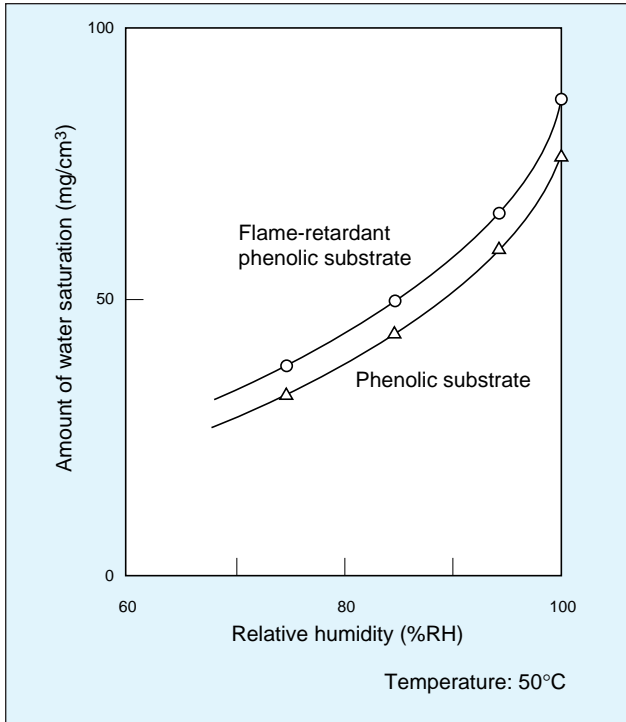


**Fig. 3 Time-based characteristics of silver migration quantities**

Based on studies to determine the reasons underlying this phenomenon, Fig. 4 shows measurements of substrate saturation moisture absorption, and Table 2 presents an analysis of leached water from PCB phenolic layers.<sup>3)</sup>

Even if the water adhering to the surface of the substrate is pure, substances leaching from the substrate, as well as gases from the ambient atmosphere, will dissolve into the water.

The pH of the water will vary markedly depending on the type and the amount of ambient gas.



**Fig. 4** Measurements of substrate saturation moisture absorption

**Table 2** Analysis of leached water from the PCB phenolic layers

	Conductance (μS)	pH	Detected anions
Phenolic substrate	32.9	6.56	Cl <sup>-</sup> 2.5ppm SO <sub>4</sub> <sup>2-</sup> 0.8ppm
Flame-retardant phenolic substrate	47.3	5.13	Cl <sup>-</sup> 3.6ppm Br <sup>-</sup> 12.5ppm

Leach conditions: 1 g PCB/100 mL purified water, 50°C, 100 h

### 2-3 Coverlay bond copper migration

The coverlay bond has an extremely large impact on copper migration, and with epoxy/nitrile adhesives, scrupulous attention must be given to the amount of nitrile rubber and the ionic impurities it contains. Nitrile rubber contains such ionic impurities as Cl, S, Ca, and Na, and these impurities accelerate copper migration.

## 3. Effects of ionic impurities

### 3-1 An investigation of copper eluting quantities

The quantity of copper ions in solution and the quantity of copper in insoluble matter vary greatly depending on the type of activator. The greater the quantity of copper ions in aqueous solution, the greater the tendency for ionic migration to occur.

Table 3 presents some examples of copper eluting quantities.<sup>4)</sup>

The moisture absorption characteristics of the resin strongly affect moisture penetration into the electrode gaps. The ionic substances are the components that cause metal elution characteristics to vary, and the activators

**Table 3** Copper eluting quantities in aqueous solution

Units: mg

Specimen solution No.	Quantity of copper ions in solution (A)	Quantity of copper ions in insoluble matter (B)	Total quantity (A + B) of copper eluted from copper plate
1	2.0	15.0	17.0
2	48.0	7.3	55.3
3	12.0	0.0	12.0
4	3.1	14.0	17.1

creating a tendency toward ionization in the presence of moisture are proportionate to these components. The factors determining the mobility of the ions in the metal ion migration process are thought to include both resin absorption characteristics and ion acquisition capacity. Activators, supplementary components, and the resin all affect these characteristics. We must also pay attention to the quantity of copper ions existing as ions in solution. By evaluating the quantity of copper ions in the aqueous solution with dissolved activators from the flux, we can reliably determine flux migration. To sum this up:

- The greater the dissolved quantity of activator copper ions in the flux, the shorter the life of the insulation.
- The higher the concentration of activator halogen, the shorter the life of the insulation, and
- With flux employing organic acid in the activator, the life of the insulation will vary depending on the type of activator.<sup>4)</sup>

### 3-2 The effect of flux on insulation characteristics

- Ionic migration occurs after moisture penetrates the surface electrode gap and is followed by metal elution. Then, metal ions and metallic chemical compounds go through a process of migrating across the gap between electrodes. Therefore, if the flux used can suppress moisture penetration, metal elution, and metal ion migration, it can suppress the occurrence of ionic migration.

If we can find the elution characteristics of copper in response to the activators in the flux, we can make a rough estimate of the insulation life.

- Evaluating unwashed flux

The activators in flux used for soldering employs halide salts of amines and anilines or carboxylic acid, and so if the substrate is not washed, these substances remain on the substrate over a long period of the product's useful life.

Since activators ionize on contact with moisture, the moisture causes a loss of insulation in the gaps between the wiring on the substrate. Moisture may also cause ionic migration or corrode the wiring pattern and produce open circuits. These problems have necessitated the use of flux employing weak activators when using unwashed substrates, and reliability evaluations are required for humid environments. Table 4 shows these evaluation test methods.<sup>5)</sup>

**Table 4 Examples of test conditions submitted for environmental tests**

	Material	Test	Environment conditions	Potential
(1)	Glass epoxy substrate	Comb-pattern electrodes	60°C, 95% RH	DC 15 V
(2)	Glass epoxy substrate	Comb-pattern electrodes Through holes Opposing electrodes	85°C, 85% RH	DC 50 V
(3)	NBR/epoxy adhesive	Comb-pattern electrodes	85°C, 85% RH	DC 50 V
(4)	Paper phenolic substrate	Comb-pattern electrodes	40°C, 90% RH	DC 50 V
(5)	Glass epoxy substrate	Through holes Opposing electrodes	85°C, 90% RH	DC 100 V
(6)	Glass epoxy substrate	Through holes Opposing electrodes	122°C, 90% RH	DC 35 V
(7)	Glass epoxy substrate	Comb-pattern electrodes Through holes Opposing electrodes Through holes—line gaps Layer-layer gaps	85°C, 85% RH	DC 100 V

(3) Effectiveness of flux washing

Various methods are used for washing, including water and water type, standard aqueous rinse water type (rinsing with water after washing in a solvent), and solvents. Table 5 shows evaluations of some washing methods examined using various water types and standard aqueous rinses.<sup>6)</sup>

Using organic acid in the activators has made it possible to suppress the occurrence of ionic migration. This ability to suppress ionic migration has resulted in a brisk movement toward the use of unwashed parts.

**Table 5 Evaluation of water-based and standard aqueous rinses (typical examples)**

	Detergents	Wash quality			Insulation resistance degradation Ionic migration	Parts & materials damage	Dangerous substances (Explosion-proof)	Environment (odor)	Drainage control	
		Rosin flux	Rosin paste	Ion residue					Separation	Biodegradability
Water-based detergents	Water/surfactants	○	○	○	○	○	○	○	○	△→○
	Water/chelating agents Alcohol Surfactants	○	×	△	○	△	○	○	×	×
	Water/glycol High-quality alcohol Surfactants	○	○	○	○	×	○	△	×	×
	Water/alkaline detergents Surfactants	○	×-△	△	○	△	○	○	×	△
	Water/neutral detergents	△	×	×	△	○	○	○	×	○
Standard aqueous rinses	d-limonene (terpene)/ surfactants	○	○	○	○	△	×	△	○	○
	Aliphatic petroleum hydrocarbon/surfactants	○	○	○	○	△	×	△	○	○
	High-grade alcohol/ surfactants	○	○	○	○	△	×	×	△	△
	Acetophenone/surfactants	○	○	○	○	△	×	×	×	×

○: Good, △: Fair, ×: Poor

### 3-3 Ionic components

#### (1) Methods of detecting the quantity of ionic residue, and its impact

The detergent can be judged by the dielectric dissipation factor ( $\tan \delta$ ) of its low-frequency range. When the wash is insufficient, moisture absorption can be seen, and the  $\tan \delta$  of the low-frequency range is large.<sup>6)</sup>

When there is a large quantity of ionic components in the insulation material, regardless of whether they are cations or anions, there is a tendency for ionic migration to occur, and the insulation life is greatly reduced.

For ion types, the effects of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  as well as  $\text{NH}_4^+$  are clearly evident.

By measuring the  $\tan \delta$  and volume resistivity ( $\rho$ ) of the specimen in conditions of high heat and high humidity, we can predict the quantity of ionic components in the insulation layer and we can also easily determine the occurrence of ionic migration.

The measurement of  $\tan \delta$  is made at the low-frequency wavelength of 50 Hz, and in the low-frequency region a conduction current is induced that serves as a carrier for ions in the insulation material. The resultant temperature rise causes an increase in  $\tan \delta$ , and when there is a large quantity of ionic components in the insulation layer of the substrate, ionic migration occurs in the insulation layer.

#### (2) The relationship between ion concentration and $\tan \delta$ of humidity

Table 6 presents some examples of leached ion concentration in 1 g of resin.<sup>7)</sup>

Fig. 5 shows the relationship between  $\tan \delta$  and ion concentration for clearly detected  $\text{NH}_4^+$  ions.

An increase in the ion concentration in the resin produces an increase in  $\tan \delta$ , and that tendency is conspicuous under conditions of high humidity.

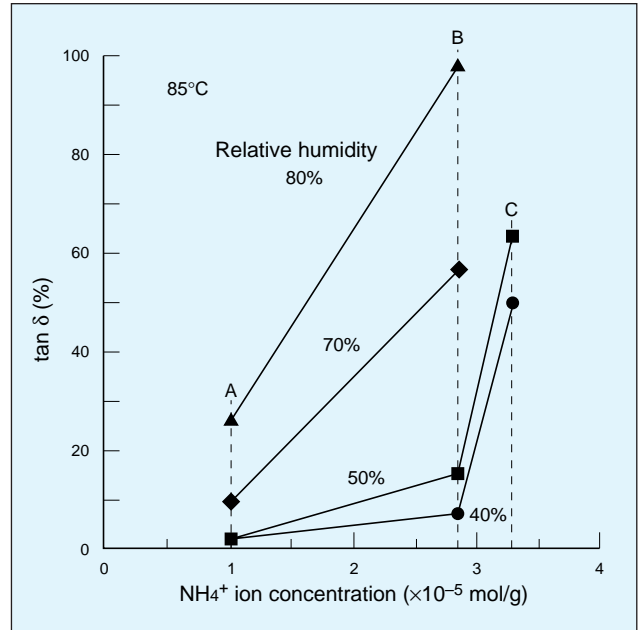
**Table 6 Concentration of leached ions in resin**

Units: ppm

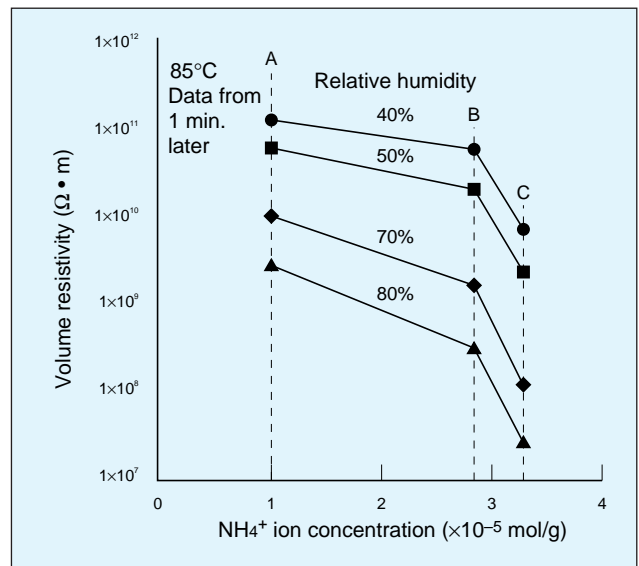
Leached ions Specimen type	$\text{Cl}^-$	$\text{NH}_4^+$	$\text{K}^+$
A	11	184	—
B	15	517	1
C	26	596	3

Fig. 6 shows the relationship between volume resistivity and the  $\text{NH}_4^+$  ion concentration.<sup>2)</sup> An increase in the ion concentration in the resin is known to produce a drop in the volume resistivity.<sup>7)</sup> Moisture from humidity absorption is also a major factor in the occurrence of ionic migration.

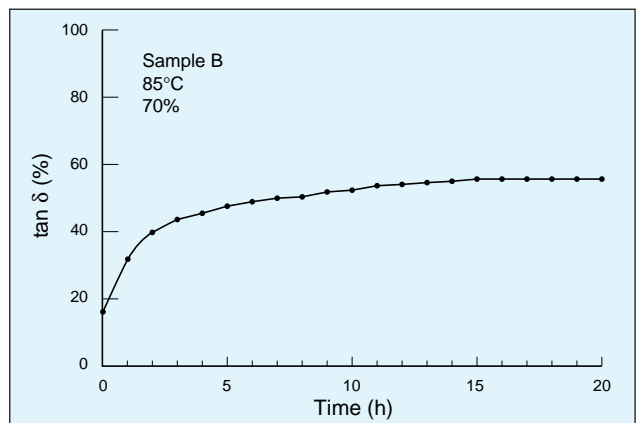
As shown in Fig. 7, by measuring the variation over time in  $\tan \delta$ , we can easily find the moisture absorption rate and the absolute moisture level. Therefore, by measuring  $\tan \delta$  and volume resistivity, we can estimate moisture absorption, and as previously noted, we can easily determine the tendency for ionic migration to occur in the insulation layer.



**Fig. 5 The relationship between dielectric dissipation factor ( $\tan \delta$ ) and ion concentration**



**Fig. 6 The relationship between volume resistivity and ion concentration**



**Fig. 7 Variation in  $\tan \delta$  over time**

## 4. Suppression methods and their effectiveness

Methods of suppressing ionic migration include means of suppressing the occurrence and growth of ionic migration, as well as extrinsic means of suppressing growth. Suppressing the occurrence and growth of ionic migration per se is achieved by introducing such steps as removing ionic impurities, adding ionic complements, and coating with migration-resistant materials. A comparison of the effectiveness of specific suppression measures is shown below.

### 4-1 Removing ionic impurities

The impact of ionic impurities on ionic migration is well known, and these ionic impurities are contained in flux, resin, and adhesives. Fig. 8 presents examples of removing ionic impurities such as Cl and Br contained in flux activators.<sup>8)</sup>

Solvents alone do not constitute sufficient washing, but the use of deionized water can suppress ionic migration. This effectiveness can be further improved by washing at higher temperatures.

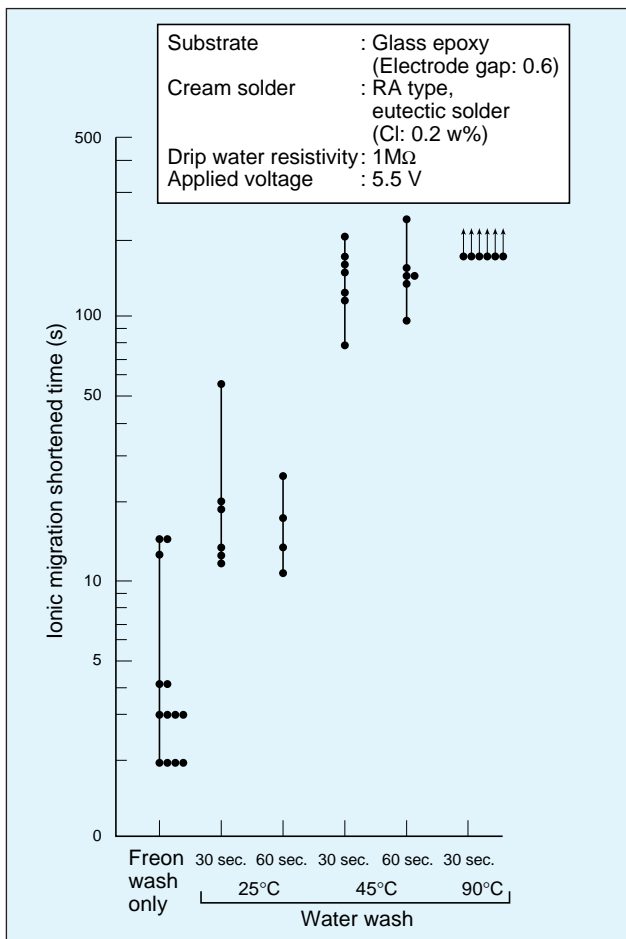


Fig. 8 Effectiveness of water wash on ionic migration

Fig. 9 shows the relationship between leaching time and detection intensity for Cl and Br ions leaching from epoxy resin, using the temperature of purified water as a parameter.

Just as in the previous examples given, these results indicate that ionic migration can be suppressed by using hot water to leach out ionic impurities from the resin.

Ionic migration occurs even in conditions of vacuum with no moisture such as found in outer space, and this leads to the conclusion that the causative agents are the non-hardened portions of the adhesives and coating materials.<sup>10)</sup>

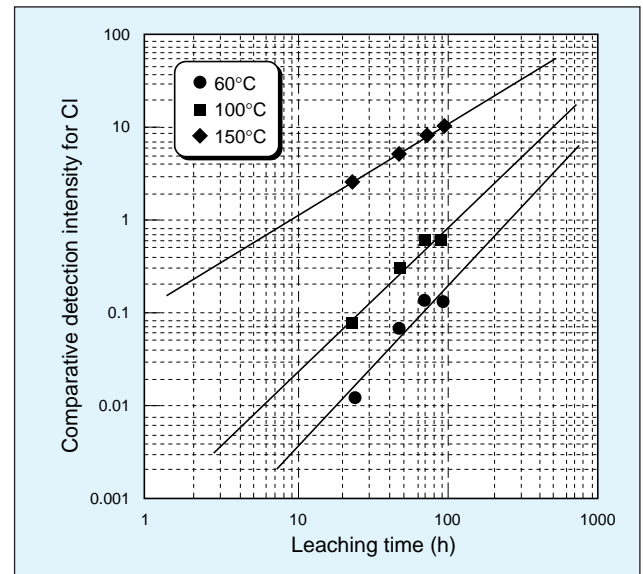


Fig. 9 Characteristics of Cl in resin leaching into purified water

### 4-2 Adding ionic complements

The sole effective method of ionic complements consists of adding ion-adsorbing inorganic substances to the resin, with the aim of reducing ionic impurities in the resin layer, suppressing ionic migration from copper wiring, and increasing insulation reliability.

Fig. 4 shows the effects of ionic migration when using silver electrodes with flame-retardant phenolic substrate and non-flame-retardant phenolic substrate.

The results indicate that flame-retardant substrate suppresses ionic migration. This effect is attributed to the Ag ion being complemented by the Br ion used in the flame-retardant additive and forming insoluble AgBr.<sup>6)</sup>

### 4-3 Other methods

Various methods of suppressing ionic migration exist, including construction material combinations, wiring metal alloys, wiring metal mixtures, solder-resistant types, and overglazing.

A comparison of three combinations of substrate construction materials, paper phenolic substrate (FN), paper epoxy substrate (PE), and glass epoxy substrate (GE) yields the ionic migration suppression order of GE > PE > FN.<sup>11)</sup>

A comparison of the wiring metal alloys Ag-Pd and Ag-Au-Pd showed the ternary alloy to be superior at suppressing ionic migration.<sup>12)</sup>

Other methods of suppressing the growth of ionic migration include the use of a variety of coating materials to prevent contamination and moisture absorption. Resin coatings are also used to prevent moisture absorption.

Coatings containing esterified epoxy with melamine resin are employed for general use.

Fig. 10 shows ionic migration results for coating thickness using silver electrodes and epoxy resin coating on phenolic (FN), epoxy (GE), and aluminum (AL) substrates under conditions of 70°C, 89% RH, and 200 V/mm, for the time (life) required for insulation resistance to drop below 100 MΩ.

The thicker the epoxy resin, the longer the insulation life, indicating that thickness is effective in suppressing ionic migration. Acrylic resin was also shown to be effective at suppressing ionic migration, but polyimide resin was reported to be almost completely ineffective.<sup>13)</sup>

The moisture resistance of epoxy resin coatings on phenolic substrate with copper electrodes has also been demonstrated.

## 5. Acknowledgement

This investigative report was produced as a cooperative effort by the members listed below, and was written up by the author and presented at the Institute of Electrical Engineers of Japan on September 11, 1996. Members cooperating in the investigation include Mr. Shinichi Kiyota (Fujikura Corporation), Mr. Suguru Hanamori (Yamanashi Avionics Co., Ltd.) Mr. Motoo Yamaguchi (Hitachi, Ltd.), and Mr. Takeshi Yanagisawa (Electron Devices Division of the Electrotechnical Laboratory Agency of Industrial Science and Technology).

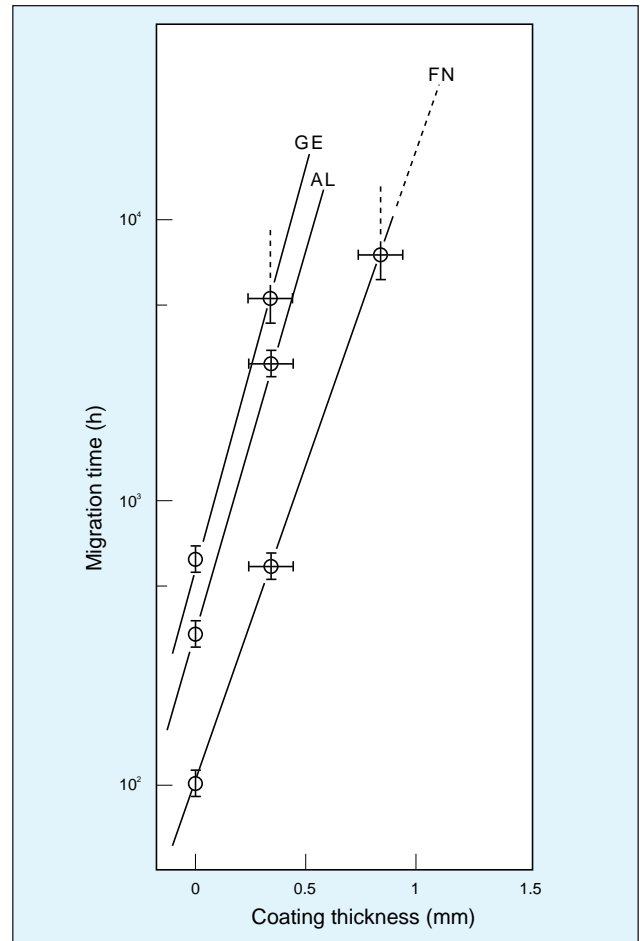


Fig. 10 Relationship between coating thickness and ionic migration time

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