Report 1

The affects of adsorbed water on printed circuit boards, and the process of ionic migration

Hiroko Katayanagi* Hirokazu Tanaka* Yuichi Aoki* Shigeharu Yamamoto*

*This report considers the insulation resistance characteristics of printed circuit boards (PCBs) and the effects of ionic migration in environmental testing. By measuring insulation resistance in a variety of environmental test conditions, the authors have determined that the initial changes in insulation resistance values is caused by water adsorption*1 and electrolysis. While investigating the occurrence of ionic migration, the authors were able to confirm that metal ions eluted in response to changes in the pH near the electrodes. These changes in pH were determined to have been caused by the electrolysis of water, which affected both pH and applied voltage.*

1. Introduction

In recent years, the trend toward compact and lightweight electronic devices has been accompanied by crucial problems in insulation reliability. Such reliability problems have been particularly noticeable with ionic migration (IM).

To properly evaluate the insulation reliability of PCBs during environmental testing, standards have been set for insulation resistance measurement in high-temperature, high-humidity tests. (Table 1)[1] These standards consist of applying flux and solder paste on prescribed electrodes and evaluating (1) the diffusion of water absorption in the flux and the resin base material, and (2) the time elapsing in the progress of the insulation deterioration due to the reduction effect of metal ion elution caused by the electric field coming from the applied voltage.

The insulation resistance values seen in environmental tests appear as a result of IM caused by (1) electrolysis due to moisture adhering to the surface of the PCB and its adsorption, and (2) by the elution and diffusion of metal ions, and their subsequent reduction. (Photos 1 and 2)

This report points out the correlation between IM and the changes in insulation resistance due to the adsorption of water. By running actual environmental tests and analyzing the IM mechanism, the authors noticed the following relationships between IM and insulation resistance values:

(1) Insulation resistance characteristics and the adsorption of water during environmental tests,
(2) Characteristics of changes in current due to the electrolysis of water,
(3) Changes in pH in the vicinity of electrodes and the elution of metal ions, and
(4) The affects of pH on the occurrence of IM.

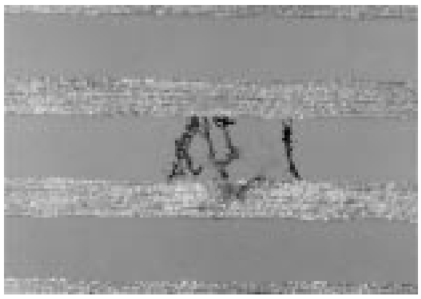


Photo 1 Dendrites occurring on a glass epoxy PCB (60×)

Table 1 Main standards for evaluating insulation resistance

Standard	Test name	Test conditions	Applied voltage	Measurement voltage
1. ANSI-J-STD-004	Requirements for Soldering Fluxes	85°C, 85% RH, 168 h	50 V DC	100 V DC
2. JIS-Z-3284 Appendix 14	Solder paste	40°C, 90 to 95% RH, 1,000 h	45 to 50 V DC	100 V DC
		85°C, 85 to 90% RH, 1,000 h		
3. IPC*-TM-650-2.6.3	Moisture and Insulation Resistance, Printed Boards	35°C, 85 to 93% RH, 4 days (class 1)	100 V DC	Decided in consultation with purchaser.
		50°C, 85 to 93% RH, 7 days (class 2)		

*IPC=The Institute for Interconnecting and Packaging Electronic Circuits

*Environmental Test Technology Center

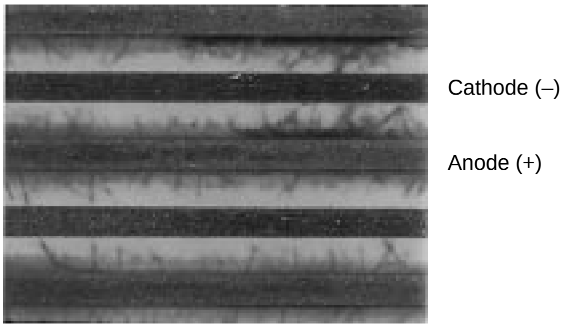


Photo 2 Example of paper phenolic board and CAF* throughout substrate material

* CAF = Conductive Anodic Filaments

2. Water adsorption and insulation resistance characteristics during environmental tests

Changes in PCB insulation resistance values during environmental tests is intimately related to the amount of water adsorption. These experiments measured both PCB resistance values and changes in the amounts of moisture absorbed under high-temperature, high-humidity test conditions. Table 2 shows the test conditions.

Table 2 Insulation resistance test conditions

Item	Details
Test conditions	3 sets of conditions: 40°C, 87% RH; 60°C, 87% RH; 85°C, 85% RH
Applied voltage	50 V DC
Measurement intervals	Every hour (measurement voltage = 50 V DC)
Specimen	Copper-clad glass epoxy (FR-4) Conductor intervals: 0.318 mm (JIS type 2)

Fig. 1 shows the insulation resistance characteristics during high-temperature, high-humidity tests. The specimens are glass epoxy PCBs with JIS type 2 copper electrodes. Measurements consisted of applying 50 V DC after the temperature and humidity had stabilized for 24 hours, and measurements were recorded hourly using an insulation resistance continuity tester. (Photo 3 shows an ionic migration evaluation system.) Fig. 1 shows a sharp rise in insulation resistance values in the initial stage of the tests, changing to a roughly stable condition after the passage of a specific amount of time. During the stable period, the insulation resistance values showed a tendency to become increasing lower in response to more severe temperature and humidity conditions.

Fig. 2 shows humidity absorption characteristics. Humidity absorption was measured by exposing the specimens to 100°C for 24 hours, then taking the initial value of the absolutely dry weight, and then measuring the weight every hour and finding the change according to the following formula, which compares the absorption weight of the PCB with its initial weight.

Change (%) in humidity absorption weight

$$= \frac{\left(\begin{array}{l}\text{weight after}\\ \text{humidity absorption}\end{array}\right) - (\text{initial weight})}{(\text{initial weight})} \times 100$$

The humidity absorption of the PCB shows a sharp increase in the initial period, followed by a gradual increase. The results also confirmed that the humidity absorption of the PCB during the environmental tests corresponded to temperature and humidity conditions.

The adsorbed water is dispersed within a solid object due to the water molecules being dispersed in the intermolecular intervals of the solid.[2)] Therefore, changes in the humidity absorption rate can be hypothesized as due to such factors as the amount of water adsorbed into the interior of the solid, the diffusion weight, and the diffusion time, and can be conjectured to be determined by the PCB materials and environmental conditions.

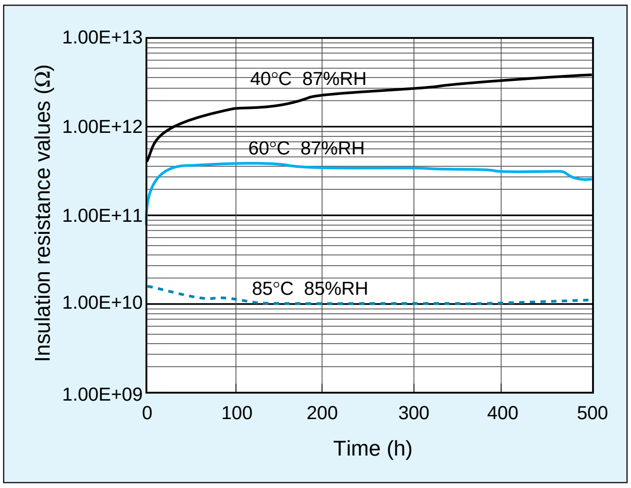


Fig. 1 Insulation resistance characteristics during environmental tests

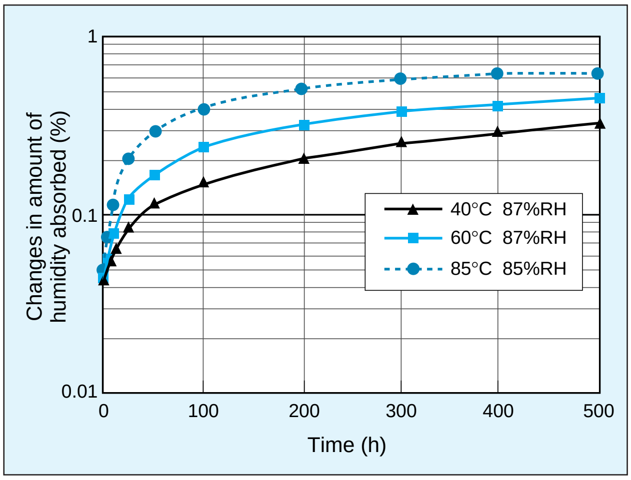


Fig. 2 Humidity absorption characteristics during environmental tests

Photo 3 Ionic migration evaluation system

3. *Verification experiments*

3-1 Electrical current characteristics resulting from the electrolysis of water

To find the characteristics of electrical current resulting from the electrolysis of water, the following type of verification experiments were carried out at room temperature. In these experiments, teflon PCBs (0.318 mm conductor intervals) with metal-plated electrodes were used to prevent water being absorbed by the PCB*2, and to prevent corrosion of the electrodes. One μL of ion-exchange water (conductivity = 2.5 μS/cm, measured pH = 6.6) was dripped between the electrodes (Fig. 3), and the elapsed time changes in electrical current were measured. Fig. 4 shows the changes in electrical current characteristics caused by the electrolysis of water when water is adsorbed on the surface of the electrodes.

The electrical current cannot be measured with a maximum applied voltage of 1 V DC, presumably because electrolysis did not occur, since the theoretical decomposition voltage of water is 1.23 V.[3)]

The trends exhibited by the electrical current characteristics included (1) rising within a few seconds, and then (2) gradually dropping, and finally (3) stabilizing.

During the initial period of voltage application, the following events occur. (1) H+ and OH- ions from water ionization quickly collect around the electric double layer*3 on the surface of the electrodes, and so the current flows rapidly. (2) Next, due to the electrolysis of water, metal ions gradually elute in the vicinity of the electrodes, and an increase in ion concentration around the electrons causes a drop in metal ion exchange and in levels of electric current around the electrodes. (3) Then, when the concentration of these ions surpasses that of metal ions, the elution and reduction of the metal ions attains equilibrium, and so the electrical current stabilizes.[4)] When stabilized, water exhibits electrical resistance, and so electrical current can be presumed to depend on applied voltage.

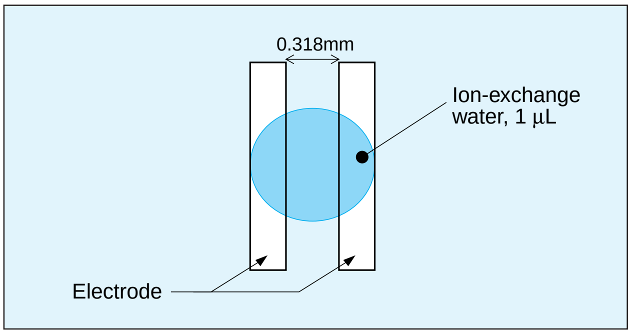


Fig. 3 Experiment conditions

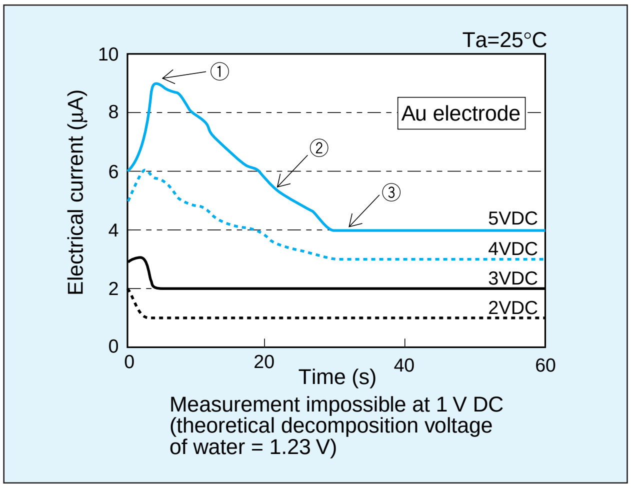


Fig. 4 Electrical current characteristics resulting from the electrical decomposition of water

These experiments concern short-period water adsorption and electrolysis, but the results of the experiments shown in Fig. 1 and 2 indicate that even during environmental testing, electrolysis of the absorbed water occurs gradually during the initial period. We can hypothesize the following process. As the elution of the metal ions begins, insulation resistance values change from low resistance to high resistance. Before long, when water adsorption becomes saturated, the elution and reduction of the metal ions reaches equilibrium, and so exhibit stabilized resistance values.

3-2 Changes in pH near the electrodes, and elution of metal ions

Based on the assumption that the electrical current characteristics are related to the elution of metal ions, these experiments regarding metal ion elution were repeated at room temperature.

Fig. 5 shows the relationship between applied voltage and the amount of metal ion elution. One μL of ion-exchange water was dripped between the electrodes of a copper-clad glass epoxy PCB (conductor intervals, 0.318 mm) and the amount of copper ion elution was measured using test sticks for the semiquantitative determination of copper. The results indicated that the amount of copper ion elution corresponded to the applied voltage.

Changes in the pH near electrodes caused by the above-noted test method were also measured using pH test paper. The pH in the vicinity of the electrodes when the applied voltage was a minimum of 2 V DC were: at the anode, acidity with a maximum of pH = 3; at the cathode, alkalinity with a minimum of pH = 10. (Fig. 6) The following reaction formula[4)] can be hypothesized.

Cathode: $4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$ (alkaline)

Anode: $2H_2O \rightarrow 4H^+ + O_2 + 4e^-$ (acid)

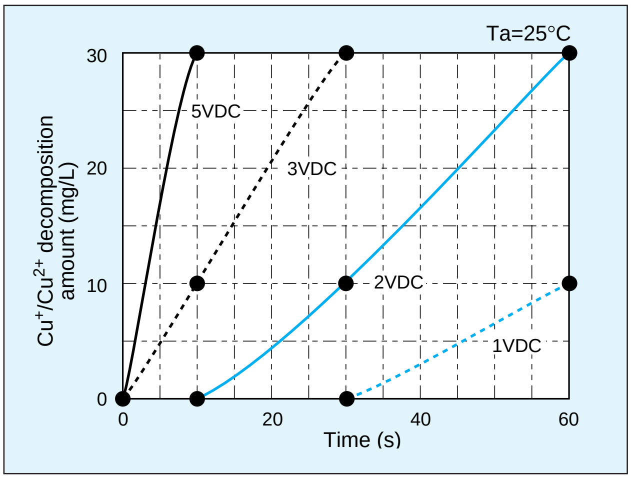


Fig. 5 Quantitative characteristics of elution: voltage and copper ions

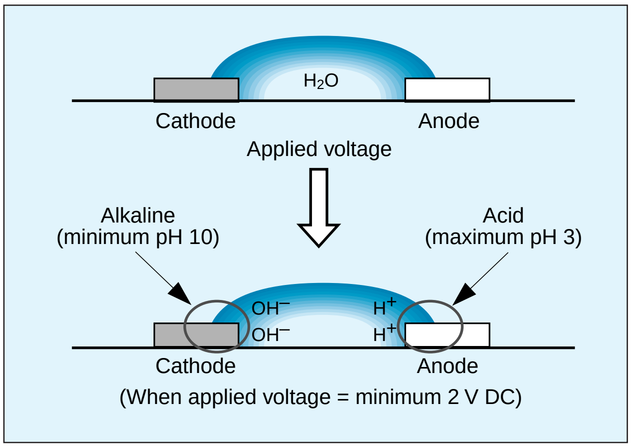


Fig. 6 Changes in pH in the vicinity of the electrodes

The surface of the copper is covered with a film of matter oxidized in the air (a compound of Cu_2O and CuO), and resists corrosion.[5)] However, this substance exhibits copper ion elution in acid and alkaline solutions. Fig. 7 shows electric potential vs. pH using an equilibrium diagram according to Pourbaix.[6)] From this graph, we can see that pH changes with the application of voltage result in the elution of Cu^{2+} on the acid side and CuO_2^{2-} on the alkaline side. Therefore, we can postulate that the electrolysis of water causes hydrogen ions form on the anode and hydroxyl ions to form on the cathode[7)], and that the film of oxidized matter on the surface of the copper is dissolved due to changes in pH in the vicinity of the electrodes, and copper ion elution is accelerated.[5)]

The standard electrode electrical potential of the metal copper dissolves in solution, Cu^{2+} at + 0.337 V (Vs.SHE[*5]), and Cu^+ at 0.520 V (vs.SHE). As a result, copper ion elution occurs even at around the minimum

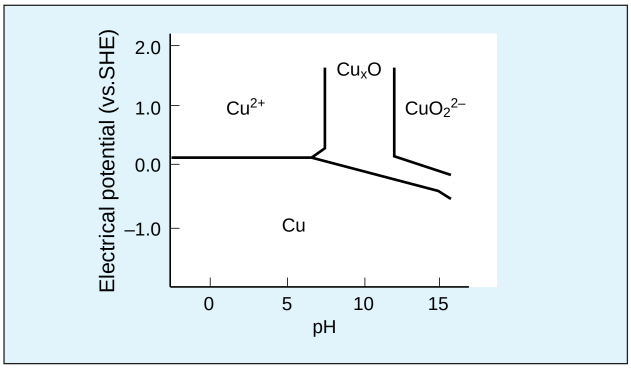


Fig. 7 Potential-pH equilibrium diagram for the system copper [6)]

theoretical voltage for the electrolysis of water, but the higher the voltage, the greater the amount of copper ion elution.

From the above considerations, we can assume that applied voltage and water adsorption are accelerating factors for the elution of metal ions from PCBs during environmental tests.

3-3 Diffusion and reduction of eluted metal ions

The diffusion and reduction of the eluted metal ions causes IM (ionic migration) to occur. Because of this, we were able to examine the process of diffusion and reduction of metal ions by causing changes in applied voltage and pH.

Fig. 8 shows the relationship between applied voltage and the occurrence of IM. One µL of ion-exchange water was dripped between the electrodes of a copper-clad glass epoxy PCB (conductor intervals, 0.318 mm) and the IM occurrence time was measured at each applied voltage level. The occurrence time was considered to be the time taken measuring from the application of voltage until IM reached the opposite electrode and short circuited.

This experiment confirmed that IM occurred at a minimum of 2 V DC, and occurrence was also reported at lower voltage.

Fig. 9 shows the relationship between pH and IM occurrence. One µL of pH 4 solution (phthalate solution), and pH 9.22 solution (borate solution), and ion-exchange water (measured pH = 6.6) was dripped

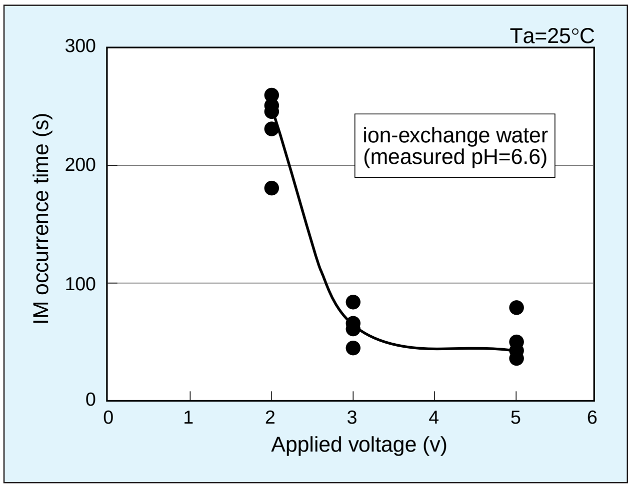


Fig. 8 The relationship between applied voltage and IM occurrence

onto the electrodes of copper-clad glass cloth epoxy PCBs (conductor intervals, 0.318 mm), and the IM occurrence time was measured at each applied voltage level.

The IM occurrence time was shorter for the pH 4 solution than for the ion-exchange water. However, IM occurred at 2 V DC in the ion-exchange water (Fig. 9), while IM did not occur in the pH 4 solution at that applied voltage. Since IM occurred in the ion-exchange water, we hypothesized that the phthalates in the pH 4 solution prevented the diffusion of the copper ions.

Bluish-white matter was observed to form on the anodes in the pH 9.22 solution. This result was considered to have been caused by copper hydroxide reduction forming on the anodes due to the diffusion time required, as copper ion elution accelerated slowly in the alkaline solution.[8)]

Applied voltage and pH are thought to greatly influence the occurrence of IM on PCBs during environmental tests.

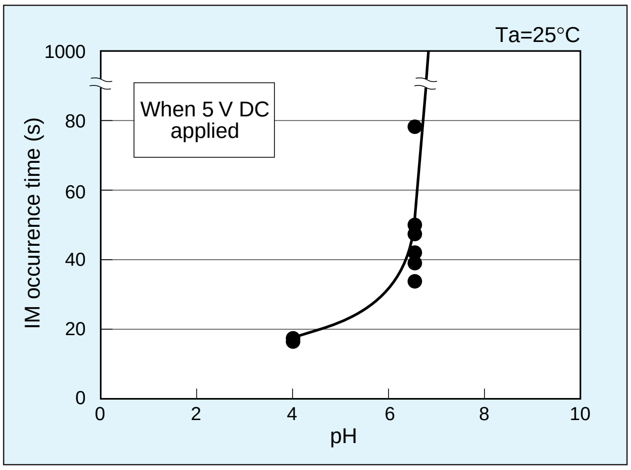


Fig. 9 The relationship between pH and IM occurrence

4. Conclusion

The insulation resistance characteristics seen during environmental testing are related to the absorption characteristics of the board and the electrical current characteristics. The absorption characteristics are determined by the PCB materials and environmental conditions, and the electrical current characteristics are affected by the elution of metal ions due to the electrolysis of water.

On the other hand, IM occurrence is caused by the process involving metal ion elution, diffusion, and reduction, which is affected by such factors as pH and applied voltage. Fig. 10 shows the mechanism of copper ionic migration.

Fig. 11 shows the relationship between the occurrence of IM and changes in insulation resistance during environmental testing. Changes in the insulation resistance values is considered to stem from the following three processes: ① The process of rising resistance values (Fig. 10, reactions 1 and 2, the elution of metal ions due to the adsorption and electrolysis of water); ② the process of stabilizing resistance values (Fig. 10, reaction 3, the elution and diffusion of metal ions): and, ③ the process of dropping resistance values and short circuiting (Fig. 10, reaction 4, metal ion reduction).

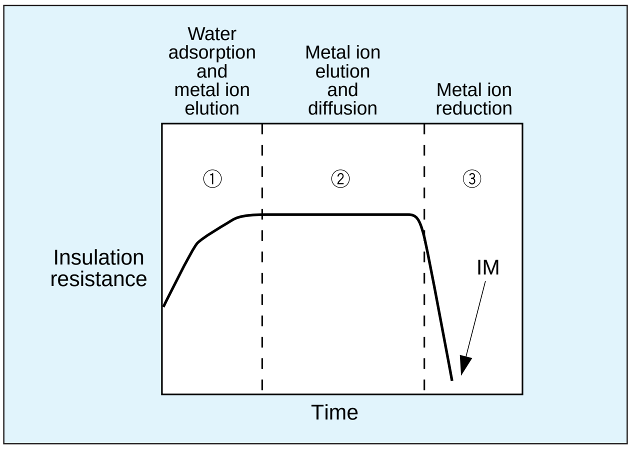


Fig. 11 The relationship between IM and insulation resistance characteristics (type diagram)

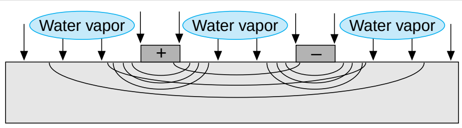
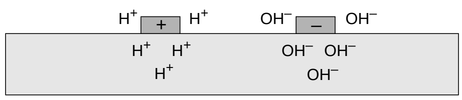
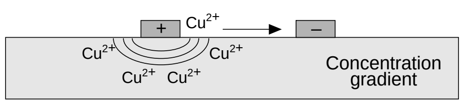
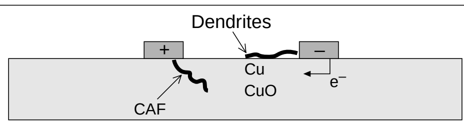
Reaction	Mechanism diagram	Acceleration factors
1. Water adsorption and diffusion		• Amount of water vapor (water amount) • Temperature • Material quality
2. Changes in pH due to the electrolysis of water (acidization)		• Voltage • Amount of water vapor (water amount) • Temperature
3. Copper elution and copper ion diffusion (diffusion)		• Voltage • Amount of water vapor (water amount) • Material quality • pH, impurity ions • Amount of dissolved oxygen
4. Electron transfer and IM occurrence (reduction)		• Voltage • Material quality • pH, impurity ions

Fig. 10 Occurrence mechanism for copper ionic migration

5. *Future themes*

During actual environmental testing, a variety of accelerating factors occur, such as adsorbed water, impurities on the board, adherence of substances and particles from inside the specimens, and the formation of dew during testing. Because of this, these factors must be considered and countermeasures must be studied when evaluating PCB insulation reliability.

Next time we would like to continue investigating IM occurrence mechanisms, and we also intend to consider some countermeasure methods.

Terms

*** 1 Adsorption**
Molecules of a gas or steam remaining on the surface of a solid or a liquid.

*** 2 Absorption**
Molecules of a gas or steam being taken inside a solid or a liquid.

*** 3 Electric double layer**
A very large electric potential gradient exists in the area extremely close to the surface of an electrode, and this is known to increase the likelihood of an electron transfer reaction. This area is called the electric double layer, and is several angstroms thick.

*** 4 Test stick for semiquantitative determination of copper**
Test paper used for qualitative analysis with a certain level of quantitative analysis added. The paper uses a color scale for comparing the changes in the color of the paper to indicate ion concentration.

*** 5 vs.SHE**
This is a method of showing the electrical potential gap by comparison to the potential of the Standard Hydrogen Electrode (SHE).

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