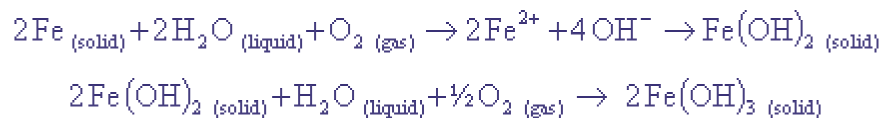
Failure Due to Humidity

Corrosion

From general experience of life, we probably have some idea about what corrosion is and have experienced the higher levels of corrosion that occur in the presence of moisture and the hostile gas species, such as chlorine, ammonia, sulphur dioxide, hydrogen sulphide and oxides of nitrogen, that are often present in the atmosphere. Whether our experience is of tarnished silver cutlery or rotting exhaust boxes, what we have seen is corrosion, defined as 'the destructive attack of a metal caused by either a chemical or an electrochemical reaction with the various elements in the environment'.

The phenomenon of corrosion involves reactions which lead to the creation of ionic species, by either loss or gain of electrons. Take the case of the rusting of iron, where metallic iron is converted into various oxides or hydroxides when exposed to moist air. The equations for this reaction are:



$$2Fe_{(solid)} + 2H_2O_{(liquid)} + O_{2\,(gas)} \rightarrow 2Fe^{2+} + 4OH^- \rightarrow Fe(OH)_{2\,(solid)}$$

$$2Fe(OH)_{2\,(solid)} + H_2O_{(liquid)} + ½O_{2\,(gas)} \rightarrow 2Fe(OH)_{3\,(solid)}$$

Because the iron loses electrons, chemists refer to this as an oxidation process. In this case, the resulting product is a mix of hydroxides; where copper reacts with acid residues creating chlorides and sulphides, this would equally (and somewhat confusingly) also be referred to as an oxidation process.

Factors affecting corrosion

Corrosion of bare conductors will happen at a rate that varies substantially, depending on the conditions. Table 1 indicates some of the factors that affect such corrosion. Note that we are considering unprotected materials, and that the addition of an effective surface coating can substantially affect the outcome for the better.

Table 1: Factors that affect corrosion

after Viswanadham, 1998

	Factor
Conductors	Nature of the material or alloy Surface condition/roughness Conductor configuration Conductor-conductor spacing
Substrate	Composition Moisture absorptivity Structure Nature of any reinforcement
Environment	Temperature Humidity Corrosive elements (type; concentration)

Another factor that affects the rate of progress of corrosion is the nature of the 'corrosion product'. If the material produced by corrosion is insoluble and forms an

impervious and tenacious layer, the corrosion reactions becomes self-limiting, as the corrosive medium can no longer diffuse through the corrosion product. A useful example of this is the oxidation of aluminium, which forms a thin protective layer of aluminium oxide; as 'anodised' aluminium, this is a good example of self-passivation.

If, on the other hand, the corrosion product is soluble or porous, corrosion will continue until the material is depleted, and no further reaction can occur. This is seen with the rusting of iron, where the oxide/hydroxide 'rust' has a different crystal structure from the iron, and creates only a porous, poorly adherent layer which does not protect against continued attack.

Galvanic corrosion

The corrosion situation is more complex if more than one metal is present within the system. Which metal will undergo oxidation is determined by the 'standard electrode potential', which is measured against an arbitrary zero created by a 'standard hydrogen electrode'. Table 2 gives standard electrode potentials for many of the metals used in electronic packaging – the more positive the electrode potential, the more 'noble' the metal is, and hence the less prone to oxidise and hence corrode.

When dissimilar materials are connected together, the less noble metal will corrode relative to the more noble one. Thus, given a corrosive environment, one would expect the tin-lead of the joints to be corroded before the copper of the tracks, and this is indeed usually the case.

Table 2: Standard oxidation electrode potentials for common metals used in electronic packaging after Viswanadham, 1998

Metal	Metal ion in equilibrium	Electrode potential at 25°C (V)
Gold	Au^{3+}	1.498
Palladium	Pd^{2+}	0.987
Silver	Ag^{+}	0.799
Copper	Cu^{2+}	0.337
	Cu^{+}	0.521
Lead	Pb^{2+}	–0.126
Tin	Sn^{2+}	–0.136
Nickel	Ni^{2+}	–0.250
Iron	Fe^{2+}	–0.440
	Fe^{3+}	0.331
Chromium,	Cr^{3+}	–0.744
Aluminium	Al^{3+}	–1.662

Conditions for corrosion

Corrosion can occur with no external applied potential, and is merely dependent on the thermodynamic free energy of the reaction – if that free energy is negative (that is, heat is given out) then the reaction will take place spontaneously.

The rate of reaction is governed by a complex set of factors, but will always increase with temperature and depend on the concentration of the reacting species. For most metals of interest in packaging, corrosion rates below 30% relative humidity are too slow to be significant.

Corrosion and semiconductors

More than just moisture is needed for corrosion to take place in a semiconductor package. Moisture needs to be *combined* with ionic contamination. The problem of corrosion in an integrated circuit can thus be split into two parts:

- The physical process of moisture penetration, which depends on the package assembly and wafer processes
- The formation of a corrosive solution and subsequent chemical reaction between this solution and the metallisation.

External sources of ionic contamination can be the result of soldering, cleaning or contact with human skin. Within the integrated circuit, contamination can potentially come from both the die and the moulding. However, in modern plastics the ionic content is very low, so corrosion is mainly the result of reactions between moisture and:

- Phosphorus in the glass of the passivation layers, which will gradually form phosphoric acid when brought in contact with moisture. [The reaction of phosphoric acid with aluminium is well known in the semiconductor industry, since it is the standard process for the wet etching of aluminium in older integrated circuit fabrication technologies]
- Residues left in the top layers during wafer fabrication. For example, chlorine ions resulting from plasma etching process of the metal can dissolve to form hydrochloric acid.

The integrity of the die passivation is a major factor in building in resistance to corrosion, and experience with plastic packages has shown a relationship between the presence of cracks in these layers, and resulting corrosion. These micro-cracks may be caused by improper handling before moulding, or be present initially. Sources of micro-cracking during wafer fab include brittleness caused by incorrect deposition conditions and topographic reasons, such as poor step coverage.

Key requirements for reliability are therefore:

- Reducing phosphorus levels in passivation
- Using nitride passivation, or dual layer passivation in critical cases
- Controlling ionic contamination in final wafer processing
- Minimising the presence of cracks by adopting a suitable wafer top layer process
- Ensuring the correct thickness and geometry of the passivation layers in relation to the metal thickness.

Electromigration

Electromigration is an electrochemical process where metal on an insulating material, in a humid environment and under an applied electric field, leaves its initial location in ionic form and redeposits somewhere else. Such migration may reduce isolation gaps and ultimately lead to an electrical short circuit.

The process begins when a thin continuous film of water has been formed and a potential is applied between oppositely charged electrodes.

Positive metal ions are formed at the positively biased electrode[1] (the anode), and migrate toward the negatively charged cathode. Over time, these ions accumulate as metallic dendrites, reducing the spacing between the electrodes, and eventually creating a metal bridge.

[1] *Electromigration is closely related to corrosion, with the anode being attacked, but which circuit element is the anode is determined by the applied field rather than the oxidation potential of the metal used.*

Whilst most often seen as a surface effect, vertical migration can also occur when moisture has penetrated into the bulk of a porous material.

Dendritic growth across tracks on a PCB

Dendrite growth across resist

The rate of electromigration increases with temperature and has four prerequisites – a mobile metal; a voltage gradient; a continuous film of moisture; soluble ions:

- Silver is the metal most susceptible to migration, since it is anodically very soluble and requires a low activation energy to initiate the migration process. Copper, zinc, and lead will also migrate, although only under much more severe conditions. Most other common electronic materials are not susceptible to migration: iron, nickel, and tin because of their low solubility in water; gold, platinum, and palladium because they are anodically stable.

- The severity of electromigration increases with applied potential gradient, the time to grow dendrites decreasing both with reducing electrode spacing and increasing voltage. The time to failure is a log-linear function of voltage at low voltages, but reaches a minimum as the effect becomes transport limited by the number of ions available.

- How much moisture is needed has been hotly debated. Whether the moisture needed represents just few monolayers, or several hundred monolayers, depends on the nature, structure, and porosity of the surface, and on its affinity for water. For example, phenolic resin laminates are more hygroscopic than ceramic substrates and are thus more susceptible to migration.

- The type of surface has another effect on electromigration, because nucleation sites are required for dendrites to initiate and grow, and these are provided by the surface roughness of the substrate and the presence of sharp corners and kinks.

- The rate of electromigration increases with relative humidity, but will become significantly worse if changing conditions encourage the formation of water droplets. This has been reported as a main factor in MLC failure due to tin and silver migration.

- A soluble ionic species is essential to provide the conductive medium for the migration to occur, and the nature of the ionic contaminants has a major impact on performance. The severity of electromigration depends on the particular ionic species involved, and factors such as its mobility, ionic radius, electronegativity, electron affinity, and charge to size. Ionic contaminants come from a wide range of sources such as activators in the flux, reaction products of the soldering process, the breakdown of cleaning solvents, and fingerprints.

The move to finer pitch components, and consequently reduced spacings, makes electromigration more likely, because the voltage gradients between conductors increase and it becomes more difficult to eliminate the minute amounts of ionic contaminants which are sufficient to cause problems.

Three main methods have been used to reduce the electromigration problem:

- Alloying any silver with an anodically stable metal such as palladium or platinum. This is one reason (as well as the improvement in solderability) why palladium-containing silver alloys are preferred to pure silver for MLC terminations

- Using a coating of solder resist to shield the PCB surface from humidity and ionic contaminants. Exposed epoxy glass is much more hydrophilic than most solder mask materials, and the improvement in Surface Insulation Resistance is typically several orders of magnitude

- Plating any silver with metals such as tin, nickel, or gold. In MLCs, the nickel barrier coating improves resistance to electromigration as well as enhancing performance on exposure to molten solder.

Moisture absorption

All polymeric materials are permeable to moisture to a lesser or greater extent, and will absorb moisture when installed in a humid environment. Moisture absorption will thus have an effect on both packages and on boards – in fact any polymeric material used in assembly.

The amount of water absorbed, and the rate at which equilibrium is reached will depend on the type of package, the material, and the conditions under which the part is stored. The normal method of evaluating moisture take-up is by measuring the percentage weight gain. For example, for a PBGA exposed at 85°C/85%RH, equilibrium at about 0.5% weight gain occurs after 1 week (168 hours), but 70% of that absorption takes place in the first day.

The ‘popcorn effect’

If plastic packaged parts have been manufactured or stored under humid conditions, they can develop cracks on soldering, by whatever method this is carried out. Absorbed moisture turns to steam when heat is applied, building up a pressure of several atmospheres in the interior of the component, which causes the housing to ‘balloon’ and crack. The stages of this so-called ‘popcorn effect’ are shown in Figure 1. Ultrasonic microscope photographs confirm that delamination has occurred, providing an easy path to the chip and bond pads both for moisture and external sources of ionic contamination.

C-scan image of PLCC, showing extensive internal delamination due to popcorning

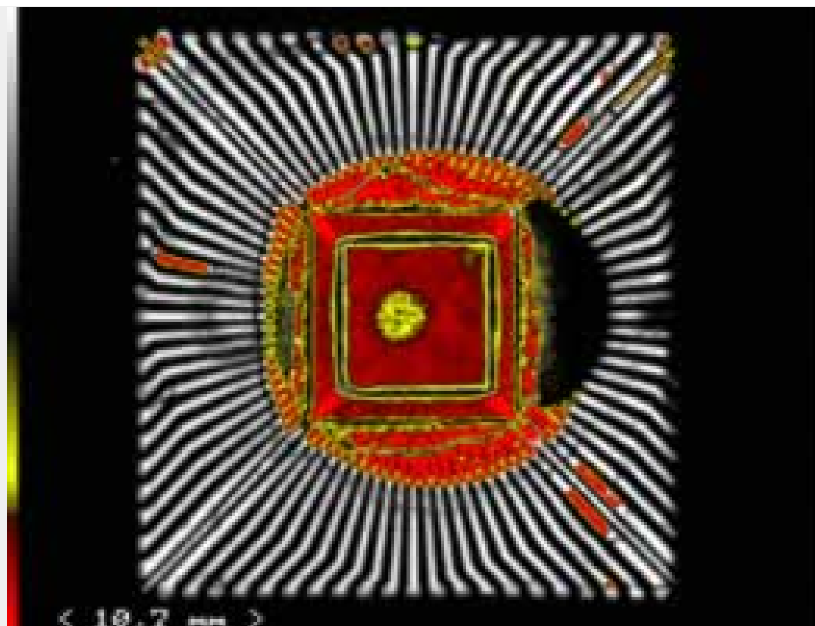
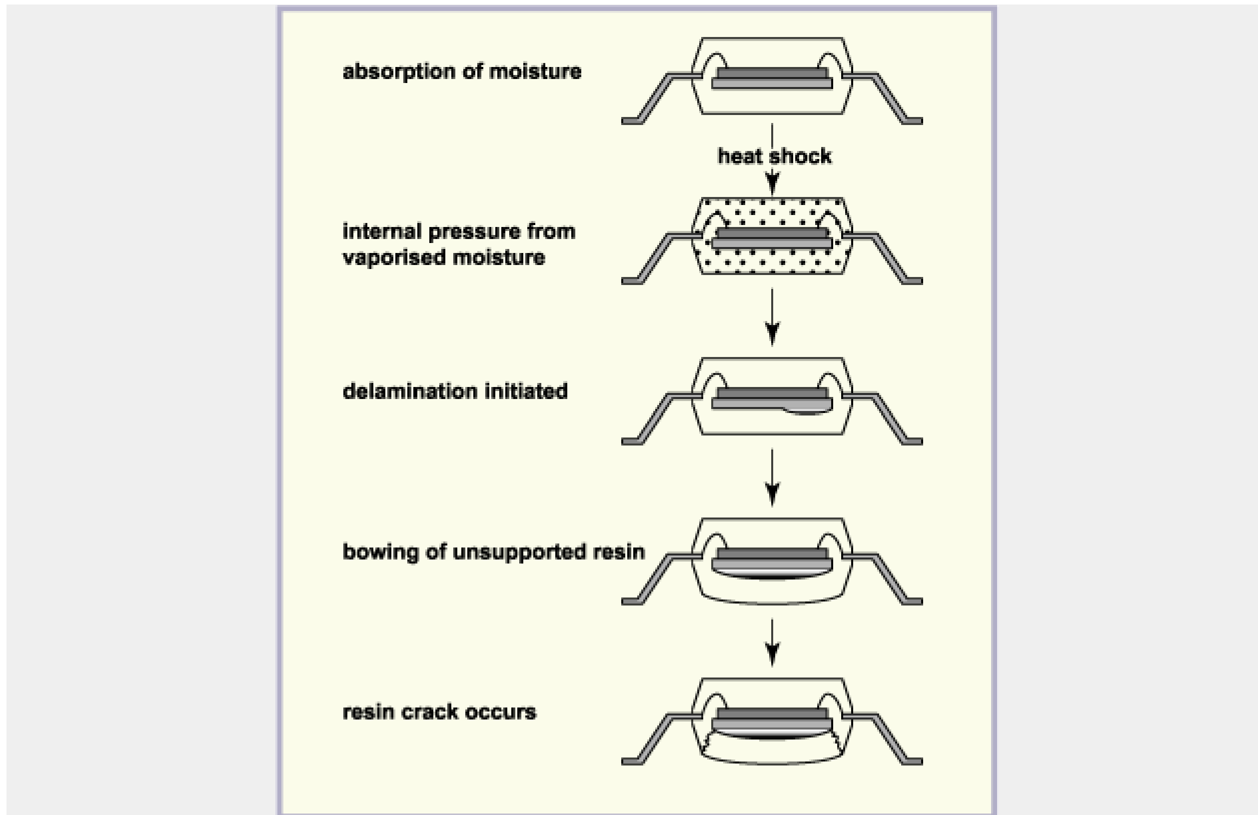


Figure 1: Moisture-induced crack generation and delamination model



The sensitivity to moisture will depend on the construction: at the device level, delamination effects can be reduced by perforating lead-frames to improve adhesion, decreasing the particle size of fillers, and stamping lead-frames to eliminate burr formation sites that contribute to stress concentration.

The popcorn problem is most commonly seen with large flat devices, and has been a particular problem with Ball Grid Arrays. The effect can, however, be largely eliminated by ensuring that the components are manufactured and stored in a strictly dry environment, and only exposed to factory conditions for a very short period prior to solder assembly.

J-STD-020, a joint EIA/IPC standard, defines six levels of susceptibility to moisture in terms of the maximum allowable assembly floor life. The levels given in Table 3 are related to specific test conditions which are applied before reflow soldering and evaluation.

Table 3: Floor life for components of different moisture sensitivity levels (J-STD-020)

Level	Conditions	Time
1	£30°C/90%RH	unlimited
2	£30°C/60%RH	1 year

3	£30°C/60%RH	168 hours
4	£30°C/60%RH	72 hours
5	£30°C/60%RH	24 or 48 hours
6	£30°C/60%RH	6 hours

Devices which pass the Level 1 test are classified as not moisture sensitive, and do not require dry packaging. All other parts should be fully dried by baking by the manufacturer and vacuum sealed in a moisture resistant bag, together with a packet of desiccant and a moisture indicator card. JEDEC specification JEP113B *Symbol and Labels for Moisture-Sensitive Devices* recommends a standard ID label, which incorporates the moisture-sensitive 'three raindrops' symbol.

After opening the bag, the moisture indicator card should always be checked to ensure the seal was not impaired. The parts then should be mounted within the floor life time given by the sensitivity level hours, depending on ambient conditions, or stored in an environment which prevents the total absorbed moisture from exceeding 0.1% of the total package weight.

A second 'caution' label on the bag should state the sensitivity level and the recommended heat treatment to be used to dry out packages suspected of having been stored in humid conditions. Typical conditions for re-baking are 192 hours at 40–45°C and <5%RH, or 24 hours at 120–130°C, the choice depending on the rated maximum temperature of the local packaging: reeled parts, for example, may not be able to withstand the higher temperature without the tape deteriorating.

Parts which will only pass Level 6 are regarded as extremely moisture-sensitive, with the dry pack providing inadequate protection. In such cases the customer must be advised of the classification at shipment, and a special warning label included to indicate that parts must be baked dry within the six hours preceding reflow. The minimum bake time and temperature for the device need to be determined from absorption studies.

Moisture and boards

The effects of moisture are not limited to the popcorning of active components; equivalent effects may be found with PCBs exposed to moisture and then soldered. Where damp boards are not thoroughly dried beforehand, they may delaminate during soldering, or at the very least there will be problems, such as solder balling on reflow and spitting and solder voids on wave soldering.

As with popcorning, most of the moisture-related issues are exposed during assembly. However, moisture can have an ongoing impact on circuit performance by affecting the electrical characteristics of the laminate. The higher the ambient relative humidity, the greater the moisture on the surface as well as in the bulk of the material. Ulbricht reported that the surface resistance expressed in ohms/square can vary as much as 4–5 orders of magnitude over a 30-90% relative humidity range. Dielectric losses also increase with increasing moisture content.

From this, one might suppose it better to keep parts dry, and assemble in a dry atmosphere. However, at humidities below 30%, static charging problems become

severe. As a compromise, most fabrication and assembly shops operate at a relative humidity of around 50%.

Moisture resistance of PEMs

We have seen already that moisture has an impact on plastic encapsulated micro circuits (PEMs) in the short term, before use, where absorbed moisture can result in failure. There is also a concern that moisture, in conjunction with sources of ions within the PEM, might result in unreliability. It was this concern that led to delays in the 1980s in converting from hermetic packages to PEMs for applications such as telephone exchange equipment.

Whilst hermetic packages can be assessed directly by leak testing, parts embedded in polymer have to be tested indirectly for moisture resistance by looking for the adverse effects of moisture penetration. This is done by subjecting parts simultaneously to high temperature and high humidity for an extended period, typically 1,000 hours, and is a destructive sample test to qualify the batch, rather than a 100% screen. Standard conditions start at 85°C/85% relative humidity (RH), but more severe tests are frequently specified, in order to test the limits of the latest encapsulating processes.

Device failure will generally be accelerated by voltage as well as by temperature and humidity, and tests with applied bias are sometimes specified. However, heat generated by the chip itself will reduce moisture concentration at the surface and thus has some protective effect.

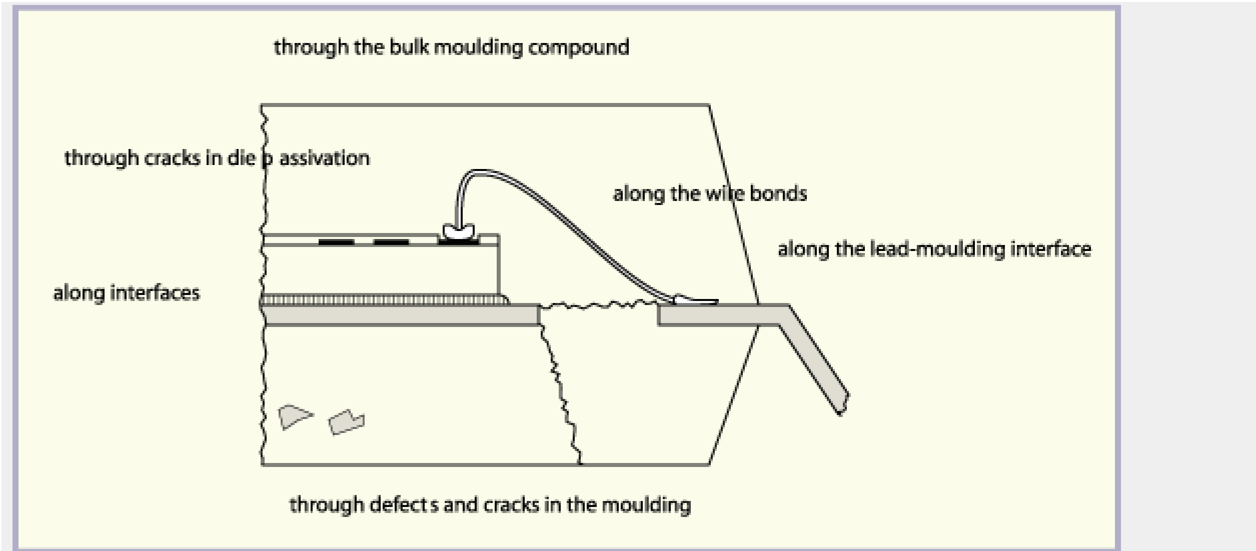
Special test chambers, often referred to as autoclaves because of their origin in medical sterilisation applications, apply elevated temperature and 100% RH simultaneously, but care has to be taken to ensure that moisture does not condense on the parts under test, especially when bias is applied to devices.

In hermetic packages, moisture can be excluded almost completely, but it can only be *minimised* in plastic packages. Not only are the intermolecular spaces of the plastic large enough to allow the diffusion of water, but additional paths for moisture penetration are found at the interfaces of different materials with badly optimised or weakened mutual adhesion. The most important interfaces are:

- moulding compound to lead-frame
- moulding compound to semiconductor die
- moulding compound to bond wires
- polymer to filler within the moulding compound.

Stress is built up during shrinkage after moulding and by CTE mismatch between the different package materials. Unless precautions are taken, this stress will lead to adhesion failure and delamination, enhancing the diffusion rate of moisture at the interfaces. Stress can also damage the chip surface and create micro-cracks in the package, all of which facilitate the penetration of moisture, as shown schematically in. Figure 2

Figure 2: Moisture penetration and structure of package



Important factors in minimising interface problems are:

- The design of the lead-frame, both to increase the path length for incoming moisture and to enhance the strength of the assembly. Strategies include mechanical locking with lead 'fishtails' and die pad perforations, and improving the overall package symmetry by using depressed pads.
- The compatibility, CTE mismatch, thermal resistance and adhesion of the materials used for lead-frame and encapsulation.
- The lead-frame cleaning and plating processes used after moulding.
- Reducing stresses in the lead-frame trim and form operation.

Source : http://www.ami.ac.uk/courses/topics/0125_fdh/index.html