Red Phosphorus Reliability Alert

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Déjà Vu?

I think that...

I have seen this all before!
Why Are We Talking About Red Phosphorus?

- Recent reports of corrosion, electrical shorts, and thermal events in connectors, sockets, and power cords

- All occurrences linked to the use of red phosphorus flame retardants

Recall – Linetek LS-15 Power Cord
Australia & New Zealand

Lenovo (Australia & New Zealand) Pty Ltd
Lenovo Recall

- Initiated in December 2014 for Australia/New Zealand and Brazil

- For notebooks sold from February 2011 to June 2012
  - Lenovo first started tracking incidents in September 2013
  - Suggests time to initial failures is 30 to 40 months

- Supplier of power cord is Linetek / Huachen
  - Linetek (Taiwan) is believed to be one of the largest manufacturers of power cords in the world
  - Linetek stopped production of power cords with red phosphorus in December 2011. Indication in production for several years

- Lenovo’s Brazilian recall notice claims that HP’s recall of power cords (August 2014) is due to the same issue
What Does Lenovo Claim?

**What are the product defects?:**

Inconsistent combining of flame retardant compounds in plug of power cord[]

**Details:**

Red Phosphorus has been used as a “green” flame retardant in mold compounds; it is known to cause certain failure modes if it is improperly processed:

- Red phosphorus is used as a charring-promoter flame retardant.
- It is normally coated with aluminum hydroxide and selected/screened for particle size.
- If the coating is incomplete or absent, the phosphorus particles oxidize to the highly hygroscopic phosphorus pentoxide (P2O5), which reacts with atmospheric moisture to form phosphoric acid (H3PO4). This acid breaks down overmold leading to cracking along mold stress lines and further moisture incursion. This acid is a corrosive electrolyte that in the presence of electric fields facilitates dissolution and migration of metal.
- Once a high impedance metal connection is made current will flow and localized heating will result. Metal migration will continue until a catastrophic event occurs.
- Higher voltage accelerates the failure mode, so countries with higher voltage, like China and others, would more likely see the failure first, and possibly in a higher number.
- Cracks in epoxy and red phosphorous crystal formation indicates red phosphorous – also noted throughout the material -- as source of failure in the Huachen housing.

- **Incomplete or absent coating around the red phosphorus particles**
- **Caused metal migration**
- **Is this True??**
Question of the Day

- How do you have metal migration when the voltage is alternating current (AC)?
  - The sum of the electric force on the metal ions will be ZERO
Agenda

- What is Red Phosphorus?
- What Happened the Last Time (Encapsulated Microcircuits)?
- What is the Root Cause This Time?
- How Can the Industry Avoid This?
What is Red Phosphorus?

- Selected as an alternative to traditional brominated flame retardants (BFRs)
  - UL certification requires polymeric material in electronic products to be flame resistant

- Epoxy encapsulants
  - TetrabromoBisphenol-A (TBBPA) dominates the market (~100%)
  - Reacted directly into the epoxy during polymerization
BFRs and Health Concerns

- Polychlorinated biphenyls (PCBs)
  - Banned in 1989 due health and environmental concerns
  - Thought to interfere with hormones
- Decabromodiphenyl ethers (DBDE)
  - Structure similar to PCB
  - Rising levels in environment
- Polybromodiphenyl ethers (polyBDE)
  - Includes pentabromodiphenyl ether (PBDE)
  - Banned by RoHS
- Environmental movement focused on all BFRs
  - Including TBBPA
- Most consumer electronic OEMs have eliminated BFRs at this point
Red Phosphorus

- Red phosphorus is physically added to the polymer blend

- Other phosphorus-based flame retardants, like phosphates and phosphinates, are chemically blended into the polymer structure
Limitations of Red Phosphorus

- Red phosphorus can be reactive
  - Can form phosphine gas and phosphoric acid when exposed to humidity at room temperature
- Manufacturers are well aware of this limitation
Limitations of Red Phosphorus (cont.)

Humidity resistance

Our red phosphorus products have also been improved in terms of phosphine emissions and degradation of electrical properties.

Phosphine emissions from red phosphorus fire retardants (in a nitrogen gas stream for three hours)

Conductivity of red phosphorus fire retardants soaked in water

These data are some representative figures, and they do not guarantee the quality of product.

Solutions to Red Phosphorus Challenges

- A two-layer coating
  - Inorganic controls phosphoric acid
  - Resin controls phosphine gas.

- Spherical particles
  - Created by halting heat treatment of white phosphorus before complete conversion to red phosphorus
  - Less reactive, more uniform coatings, smaller particle size (50mm) w/narrower distribution
Timeline of Red Phosphorus

- 1996: Sumitomo Bakelite introduces red phosphorus-based molding compound
  - Labeled as “green” molding compound or “bromide-free” molding compound (phosphorus content not always clearly stated)
  - Marketed as either environmentally friendly or improved resistance to Kirkendall voiding
- 1998: Large-scale ramp up
  - Use by numerous semiconductor device manufacturers and contract packagers
- Late 1999 / early 2000
  - First field failures reported
- Late 2001
  - First public acknowledgement of potential issues (Fairchild Semiconductor)
- 2002
  - Red phosphorus-based molding compounds pulled from the market
- 2006
  - Production of power cords with red phosphorus
Initial Failures
Failure Process

- **Step 1: Electrolyte Formation**
  - Particle degradation
  - Conversion to $\text{PO}_4^{3-}$ with moisture

- **Step 2: Attack of Ag, Cu**
  - Phosphoric acids can corrode silver and copper
  - Creates $\text{Ag}^+$, $\text{Cu}^{2+}$ cations
  - Can occur at the cathode or anode

- **Step 3: Migration**
  - Migration of cations to anode
  - Plate out and growth back to cathode
Initial Investigations and Response

- Focus on large particles

- Sumitomo reduced maximum particle size in May 2000
  - From 180 μm to 150 μm
  - Subsequent reductions to 75 μm

- Extensive efforts in predicting and modeling particle size distributions
  - Later failures occurred irrespective of particle size
Failure Analysis

- **Failure mode**
  - Elevated leakage currents between adjacent pins
  - Not always between power and ground (?)

- **Initial behavior highly intermittent**
  - Often misdiagnosed as no-fault-found (NFF)

- **Required additional exposure (40°C/93%RH) to reacquire failure behavior**
  - Intermittency became semi-permanent
  - May suggest transition
    - Conduction through electrolyte $\rightarrow$ conduction through dendrite
The diagram illustrates the relationship between relative humidity (% RH) and moisture content (%) over time. The graph shows different moisture content levels at specific time intervals:

- **4 kohms** after +4 hours
- **50 kohms** after +24 hours
- **120 kohms** after +75 hours

The data can be represented by the linear equation:

\[ y = 0.0024x + 0.0013 \]

where \( y \) is the moisture content and \( x \) is the relative humidity (% RH).
Environmental Conditions

- **Strong implication that min. 75%RH required to initiate reaction**
  - Higher than standard 40-60%RH in controlled environments (office, server farms, etc.)

- **Local conditions may exceed ambient settings**
  - Insufficient airflow
  - Outgassing from adjacent polymeric materials
SQUID Microscopy

- Extremely effective in site location
Wide Variation in Failure Morphology

- **Location**
  - Near the edge (moisture diffusion path)
  - Near the die (silver-plated fingers)
- **Evidence of corrosion, “mouse-bites”, on both anode and cathode (or both) (or none)**
  - Localized electrolytic conditions
  - Presence of larger red phosphorus particle
- **Evidence of dual migration paths**
  - Anode to cathode
  - Cathode to anode
- **Conductive path (pure Cu)**
  - Ribbons
  - Dendrites
Mouse-bites

- Cathode
- Anode
Mouse-bites (cont.)

- 111

* Both *

1-39

* None *
Growth Direction

- Anode to Cathode
- Cathode to Anode
Growth Direction (cont.)

- Both?
Conductive Path

- Dendrite
- Ribbon
Root-Cause (Phosphorus Particle Degradation)

- Initial theory
  - Damage due to physical contact
- Insufficient coating
  - Controlled using extractable phosphate levels
- Damage to coating
  - Packaging
  - Reflow
- Difficult to assess
  - Sub-micron coating
  - Not fail-safe
- Accelerated by poor adhesion between phosphorus and epoxy?
Root-Cause (Propagation Path)

- **Theory 1: Nominal Behavior**
  - Percolation threshold is reached
  - Silane-bonded interface is not fully dense
  - Provides pathways (similar to CAF)

- **Theory 2: Damaged**
  - Deflashing process can loosen interface
  - Excessive heat during reflow
  - “Micro-popcorning”
Red Phosphorus: Stage 2
Red Phosphorus in Connectors, Sockets, and Power Cords

- What can we say about the 2\textsuperscript{nd} round of red phosphorus failures?
All the cases of red phosphorus-induced failures consisted of Polybutylene Terephthalate (PBT).

What do we know about PBT?
- Semi-crystalline thermoplastic
- Closely rated to polyesters
- Very common as an insulator in electrical and electronic applications
Polybutylene Terephthalate (PBT)

- PBT is known to be susceptible to hydrolysis
  - Breakdown of polymer structure in the presence of moisture

- Hydrolysis is typically an autocatalytic reaction
  - Ester linkages are broken
  - Resulting end groups are hydrophilic (water-loving)

- Rate of hydrolysis is very temperature sensitive
  - Nothing below 40C, years at 60C, days at 120C

- Hydrolysis will cause a reduction in mechanical and electrical strength
Hydrolysis

- Decrease in breakdown strength over time at pressure cooker conditions
In the investigations performed by DfR, there was very limited evidence of metal migration

- One customer had failures without NO BIAS

- There was evidence of ‘water’ or ‘sweating’ on the materials
  - This is often a strong indication of hydrolysis reactions
  - Chemical analysis confirmed ester groups and carboxylic acids (breakdown products of esters)
Red Phosphorus (2): Hydrolysis (Again)

- Why is hydrolysis occurring at low temperatures?
- Red phosphorus seemed to play a critical role
  - Ambient humidity also seemed to have some effect
- However, the true root-cause is still uncertain
  - Several theories

The main reason for the reluctance of some processors to use this very efficient flame retardant is the disproportionation of the red phosphorus to phosphine and phosphoric acids that occurs in the presence of moisture at elevated temperatures. This means, however, that significant disproportionation can only take place in the injection molding process if the residual moisture content in the polyamide is too high. Efficient pre-drying is therefore a necessary and generally sufficient countermeasure.
Red Phosphorus (2): Root Cause

- **Theory 1**: There is an intrinsic incompatibility between PBT and red phosphorus as a flame retardant
  - Hydrolysis is accelerated by acids
  - Some phosphoric acid is always present, regardless of coating technology

Remember! Hydrolysis is Auto-Catalytic

- **Theory 2**: Issues with red phosphorus coating
  - Introduced an elevated level of phosphoric acid, which accelerated hydrolysis

- **Theory 3**: Issues with the molding process
  - Excessive molding forces, presence of voiding (which can result in condensation), or elevated residual moisture content
What Does This All Mean?

- Same material, different mechanism
- However, same over-arching root-cause
- Both were artifacts of an industry process that does not perform best practices in regards to new technology insertions
  - Heavy reliance on supply chain providing the new technology (fox guarding the hen house)
  - Test-to-spec (zero failures) heavily grounded in constant failure rate assumptions, which is not appropriate for new technologies
Understand Failures of New Technology (The Role of Outliers)

- Need to understand how technology can fail and the implement process control and design parameters to prevent failures
How Can the Industry Avoid This?

- After **twice** having comprehensive failures across the industry, it is clear red phosphorus can not be used where electrical bias exists?

- How to eliminate red phosphorus flame retardants from the supply chain?
  - **Thought 1**: Not possible. Supply chain is too complex and ever-changing
  - **Thought 2**: Standards Bodies (UL, CSA, CE, etc.)
Changes the Standards

- Standard Bodies should be lobbied to include the elimination of red phosphorus