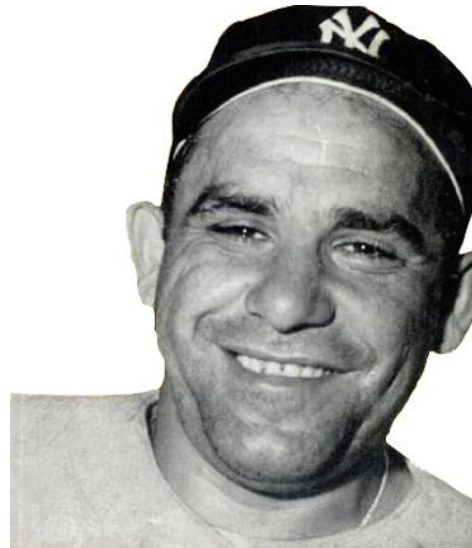


The Return of the Red Retardant

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A Little Homespun Wisdom:



- “It’s déjà vu all over again”
- “You can observe a lot by watching”

Red Phosphorus . . . Before

- Components: Semiconductors, Integrated Circuits
- Reports of: Electrical Shorts, Corrosion, Thermal Events, Recalls
- All Linked to: Red Phosphorus Flame Retardant

Red Phosphorus . . . Again

- Components: Connectors, Power Cords, Sockets
- Reports of: Electrical Shorts, Corrosion, Thermal Events, Recalls
- All Linked to: Red Phosphorus Flame Retardant

A Little Professional Wisdom:



- Commenting on the utility of models; he said,
- “Essentially all models are wrong; however, some are useful.”

Reliability Model – Conceptual Product Space

Product Use Conditions & Life Expectations

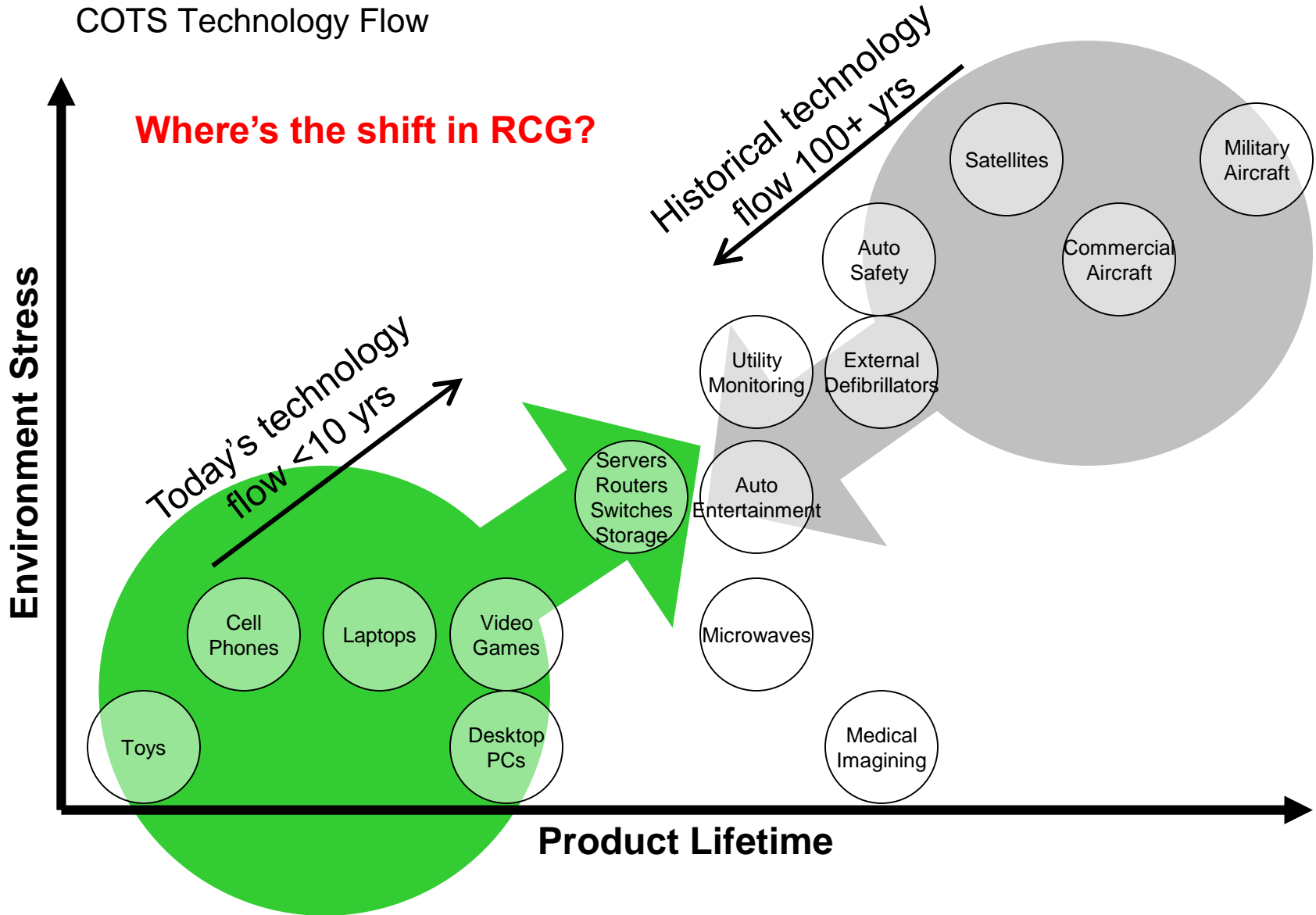
Environment Stress

							Satellites		Military Aircraft
						Auto Safety		Commercial Aircraft	
				Outdoor Signage	Utility Monitoring	Chemical & Petroleum Production	DHS Monitoring		
				Servers, Routers, Switches, Storage	Auto Entertainment	Telecom Cell Towers			
	Cell Phones	Laptops	Video Games		Microwaves		Washers		
Toys		iPods	Desktop PCs		Televisions	Medical Imaging	Dryers		

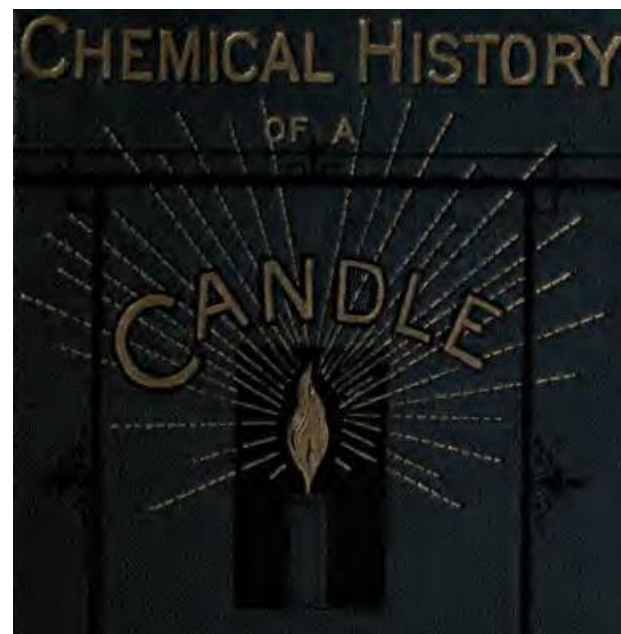
Product Lifetime

Reliability Model – Conceptual Product Space

COTS Technology Flow

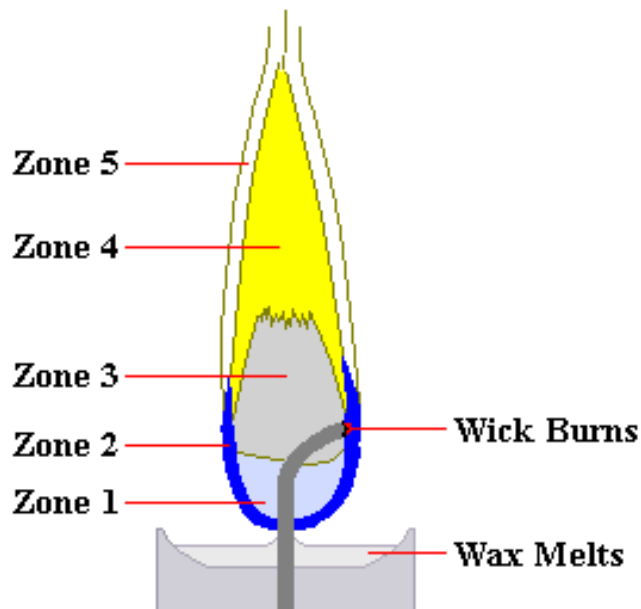


What's Happening in a Flame?



- Michael Faraday - 1860

Flame Zones

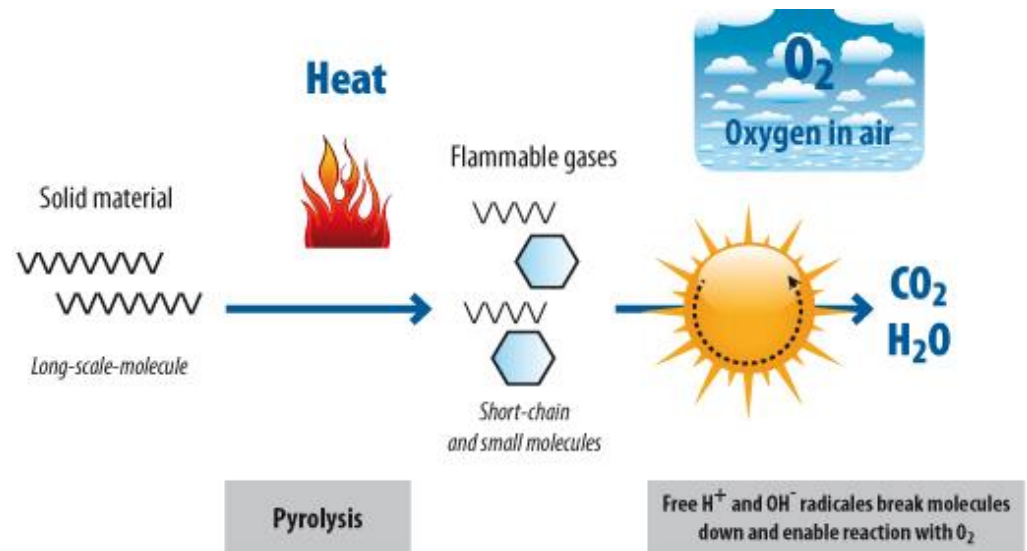
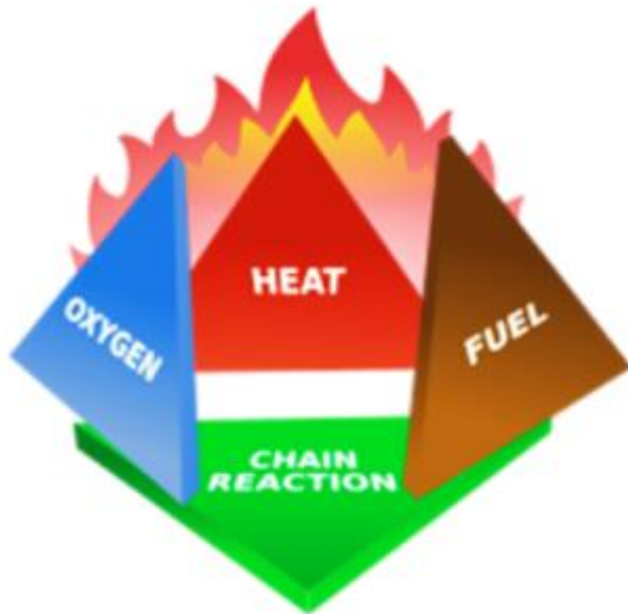


- Zone 1 – the non-luminous zone where fuel evaporates from the wick
- Zone 2 – the blue or oxidation zone where the fuel burns cleanly creating heat sufficient heat to melt the wax
- Zone 3 – the dark or reduction zone where pyrolysis and fuel decomposition begins
- Zone 4 – the luminous zone
- Zone 5 – the non-luminous veil zone where combustion is completed and is the hottest of the zones

Flame Properties:

- Organic materials in the solid state do not readily combust
- They first undergo pyrolytic decomposition
- Decomposition products include combustible gases
- Classic fire triangle: fuel, oxygen heat

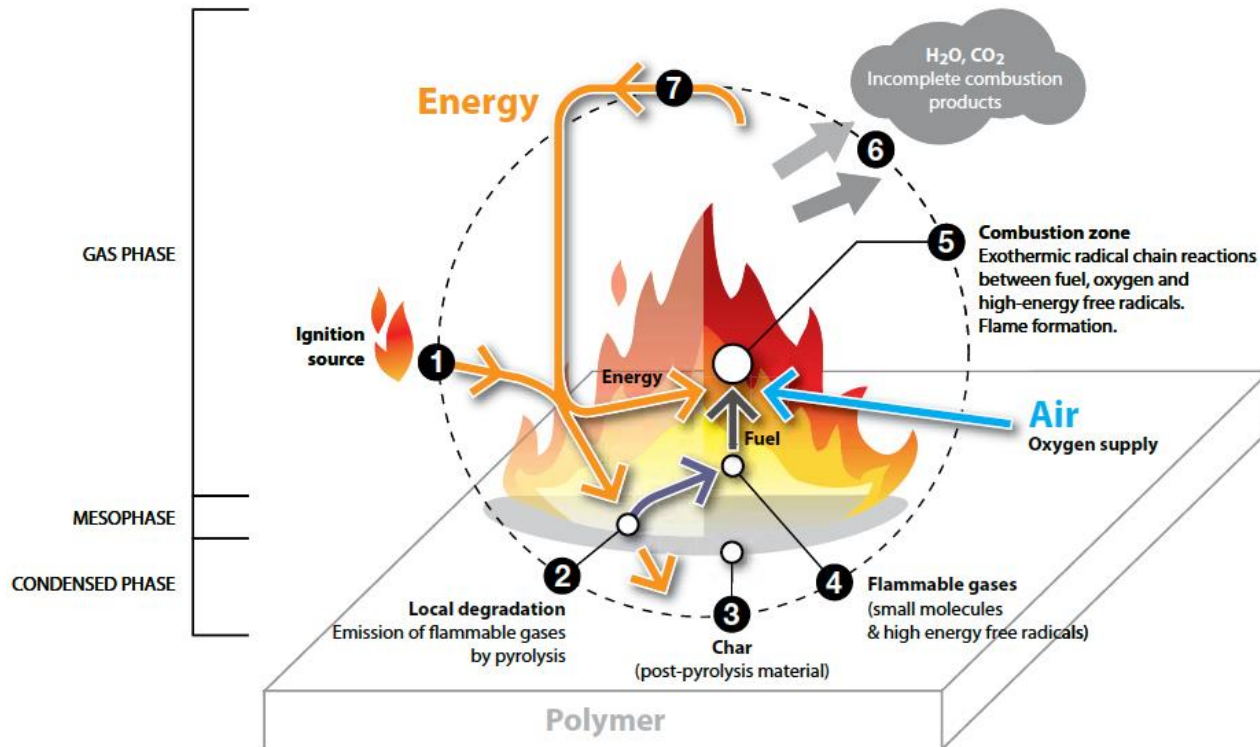
Flame Properties:



■ Fire Tetrahedron

■ Basic Polymer Chemistry

Polymer Flame Properties:

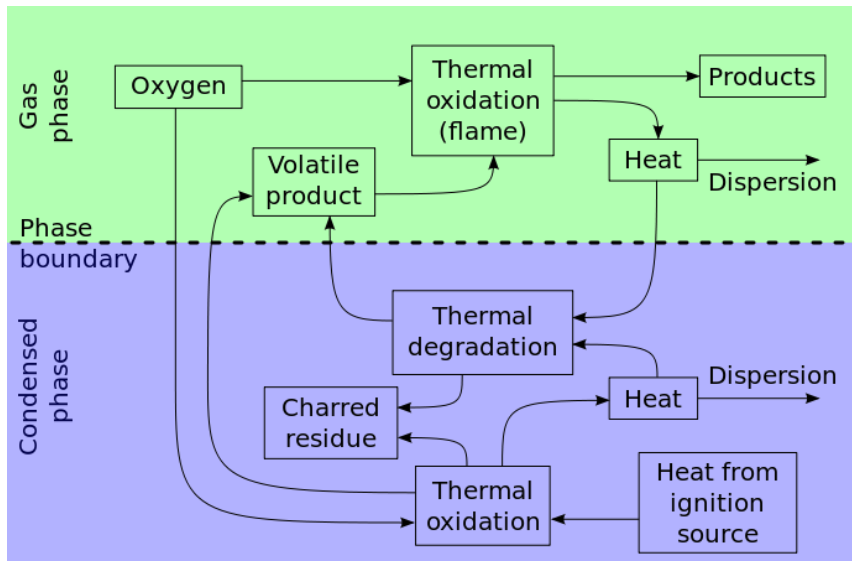


■ Phases

■ Char Formation

Red Phosphorus Retardancy Mechanisms

Phase Schematic



Phosphorus Retardancy

■ Gas Phase

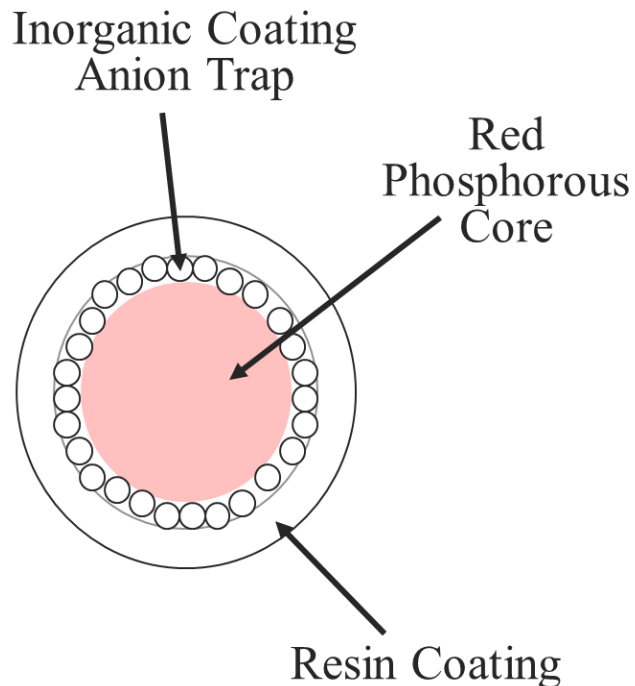
- Scavenging H^+ and OH^- free radicals
- Promoting gas phase recombination

■ Condensed Phase

- Promoting charring
- Intumescent foaming
- Organic glass formation

Red Phosphorus: Reactive ∴ Mitigate

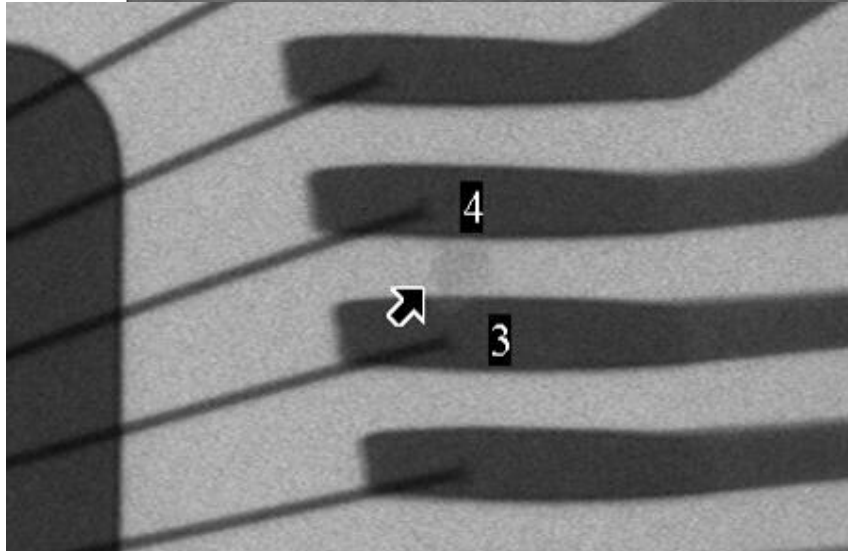
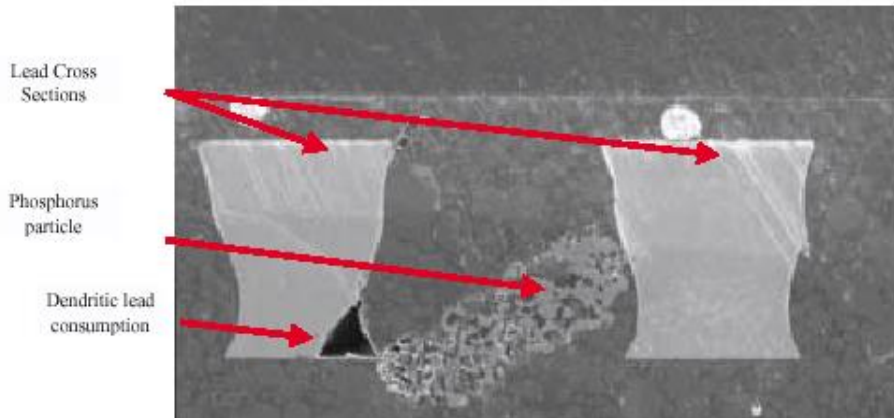
Particle Coatings



Particle Properties

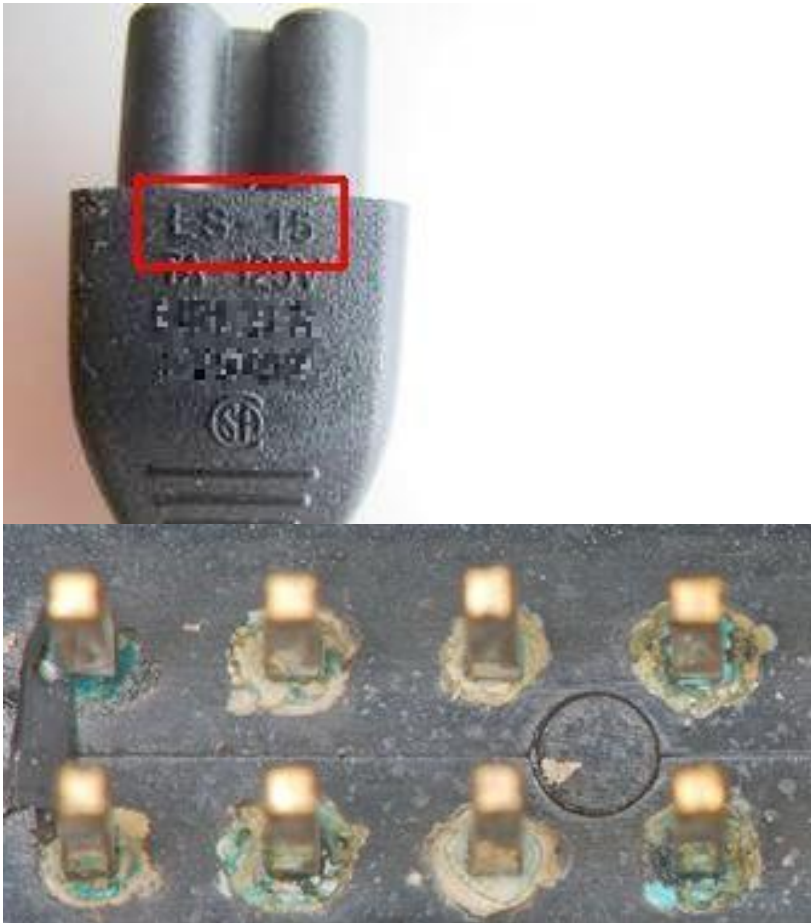
- Two Layer Coating
 - Inorganic
 - Typically metal oxide
 - Controls phosphoric acid
 - Organic
 - Resin
 - Controls phosphine gas
- Spherical Structure
 - Uniform size & shape
 - Tight distribution

Red Phosphorus . . . Before



- Components: Semiconductors, Integrated Circuits
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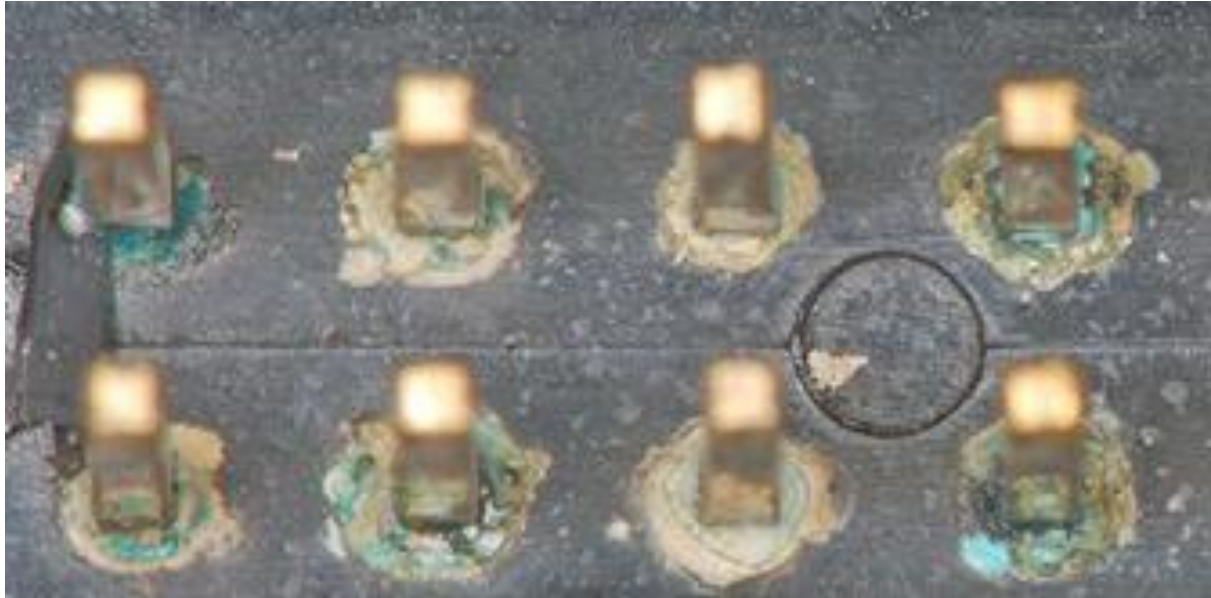
Red Phosphorus – Power Cord

■ Recall Notices

- Australian Competition and Consumer Commission
- US Consumer Product Safety Commission
- Product failures are due to incomplete or absent coating around the red phosphorus which led to the formation of highly hygroscopic P_2O_5 and subsequent creation of H_3PO_4 acid.
- The phosphoric acid promoted metal migration within the connector insulation which then led to current flow, heating and catastrophic failure.

■ However, Metal Migration is Largely DC

Red Phosphorus – Signal Connector



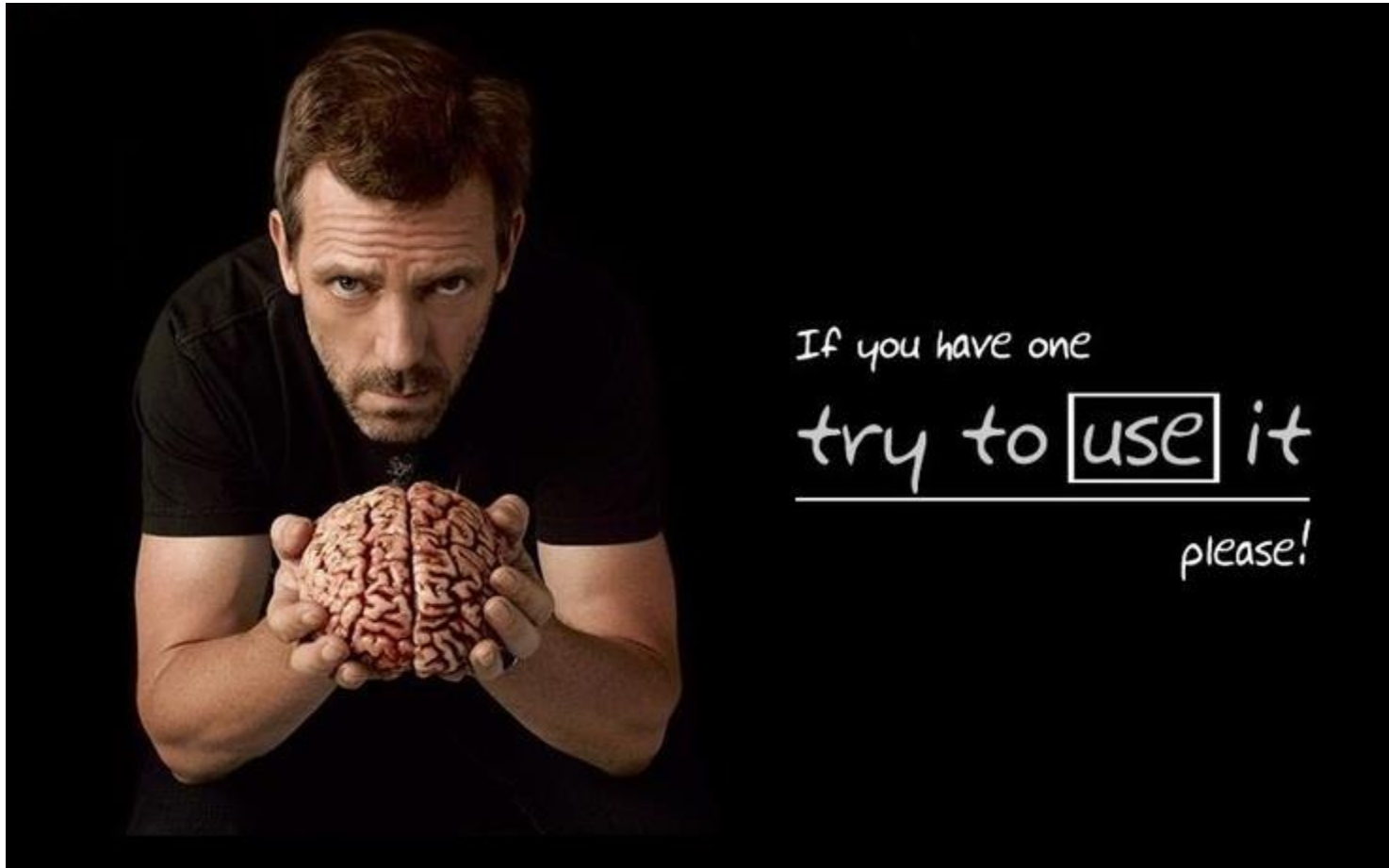
- Out of Box Electrical Failure
- Copper Patina Corrosion Discoloration

Red Phosphorus – Signal Connector



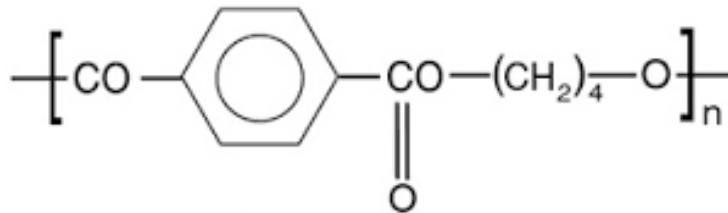
- Out of Box Electrical Failure
- Copper Patina Corrosion Discoloration
- What's the Sweating, Water?

Is There a Doctor in the House?



What's the Common Factor?

- For all the cases of red phosphorus-induced failures, the primary polymer was Polybutylene Terephthalate (PBT)



Polybutylene Terephthalate

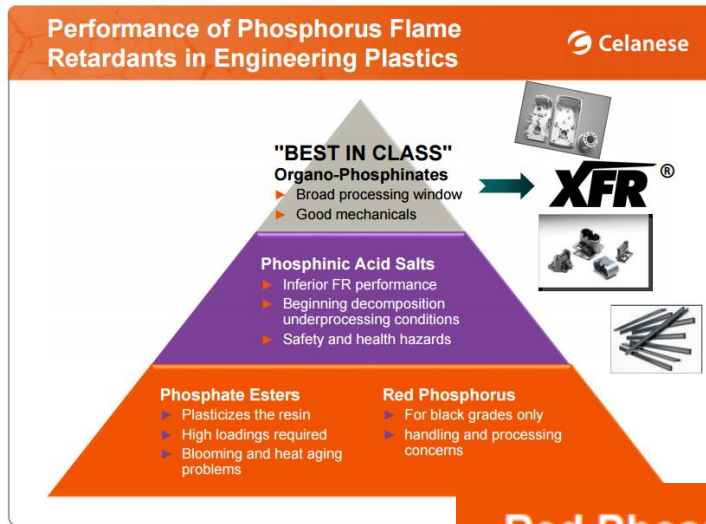
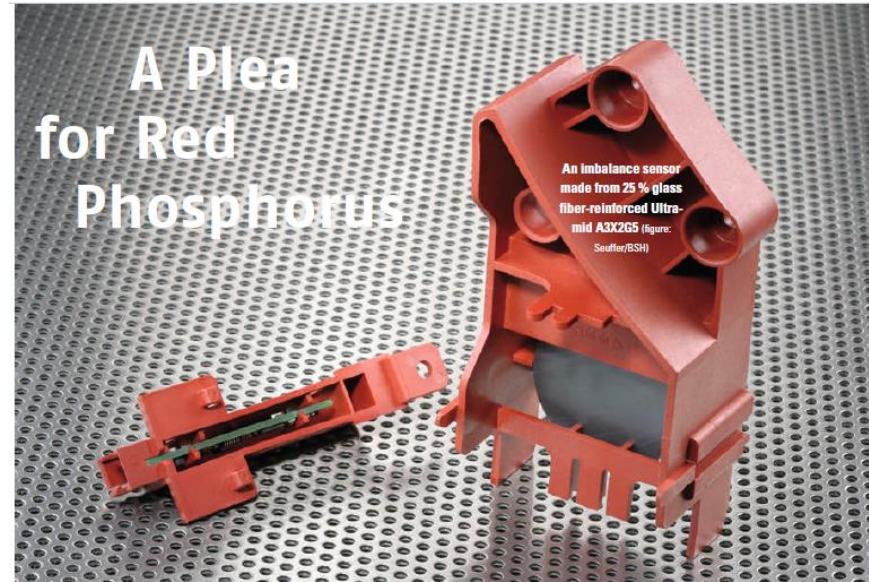
- What do we know about PBT?
 - Semi-crystalline thermoplastic
 - Closely related to polyesters
 - Very common as an insulator in electrical and electronic applications

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**

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



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Halogen-free Solutions

Red Phosphorus

- ▶ For black grades only
- ▶ handling and processing concerns

Limitations of Red Phosphorus

- “The main reason for the reluctance of some processors to use this very efficient flame retardant is the disproportionation of red phosphorus into phosphine and phosphoric acids
- This occurs in the presence of moisture at elevated temperatures
- Efficient pre-drying is therefore a necessary and generally sufficient countermeasure”

Red Phosphorus – Signal Connector



- **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)

Root Cause Theories

- 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
- 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



Thank You!

Questions?