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## Red Phosphorus Induced Failures in Encapsulated Circuits

By Craig Hillman, PhD

5110 Roanoke Place, Suite 101 College Park, Maryland 20740
Phone (301) 474-0607 Fax (240) 757-0053
www.DfRSolutions.com

# Red Phosphorus Induced Failures in Encapsulated Circuits

**ABSTRACT**

This paper discusses the reliability risks of using red phosphorus as a flame retardant material in encapsulated microcircuits. The focus is on chemical reactions, which can arise when red phosphorus is exposed to ambient humidity at high temperatures to form oxygen-containing phosphorus acids. These acids are corrosive and can alter the physical and electrical characteristics of the polymer composition and are root-cause candidates behind reported field failures in semiconductors encapsulated with epoxy resins containing red phosphorus flame-retardants.

## Background: Flame Retardants

Since the early 1990s, legislation and consumer demand has increased pressure on original equipment manufacturers (OEMs) to design and manufacture environmentally friendly electronic products. In response, companies throughout the electronic product supply-chain have begun to introduce "green" materials. The transition to "green" products has resulted in industry actively seeking alternatives to current electronic packaging materials while still ensuring adequate performance, cost, reliability and safety.

Flammability of electronics is one particular safety concern that can be mitigated by the appropriate selection of materials used to construct electronic products. Flammability is a concern since unforeseen shorts (unintended electrical connections) can lead to thermal runaways sufficient to ignite a fire. To mitigate this risk, flame-retardants are incorporated into materials such as plastic encapsulants and printed wiring board laminates used to package and construct electronic products.

In the most common plastic encapsulants, such as epoxy cresol novolac (ECN) and Tetrabromobisphenol A (TBBA) epoxy [1], flame retardancy is acquired through the addition of bromine-based aromatic[1] compounds. Brominated flame-retardants (BFR's) are highly valued

[1] The molecule is a benzene derivative, consisting of a six-sided (hexagon) bonding structure, primarily composed of hydrogen and carbon, with alternating single and double bonds.

for their effectiveness and low cost, especially in their ability to ensure compliance with the industry flammability standard, Underwriters Laboratories (UL) 94 V-0, and their low cost

**Brominated flame retardants**

Brominated flame-retardants (BFR) currently dominate the electronics and electrical equipment market and can be distinguished based on their chemical structure and how the BFR is incorporated into the encapsulant [2]. BFR's can have an aromatic, cycloaliphatic, or aliphatic[2] chemical bonding. Flame-retardants with aromatically bound bromine have the highest market-share, primarily because they tend to be resistant to breakdown over time or temperature. Examples of aromatic BFR's include polybromodiphenyl ethers (PBDE), polybrominated biphenyls (PBB), and tetrabromobisphenol–A (TBBA)-based compounds. The chemical structure is depicted in Figures 1 through 3. Hexabromocyclododecane (HBCD) and dibromoneopentyl glycol are examples of cycloaliphatic and aliphatic bound BFRs respectively.

BFR's can be incorporated into an epoxy encapsulant reactively or additively [3]. Reactive flame retardants are chemically reacted into the epoxy structure during the polymerization process. This is the most common approach for epoxy encapsulants, and includes tetrabromobisphenol–A (TBBPA), tetrabromophthalic anhydride, dibromoneopentyl glycol, and poly-di and tribromostyrene. Additive flame-retardants are physically added to the epoxy compound. They include tetrabromobisphenol–A (TBBPA), polybrominated diphenyl ethers (PBDE) and hexabromocyclododecane (HBCD). If they are compatible with the epoxy they act as plasticisers, otherwise they are considered fillers.

While there are over 30 different types of brominated chemicals used as flame retardants, almost 100% of the BFR's used to encapsulate electronic microcircuits are TBBPA-based compounds [3]. These TBBPA-based compounds tend to be reacted into the epoxy and form strong ether linkages to the polymer chain. TBBPA is also the most common flame retardant for epoxy laminates used to construct printed wiring boards (PWB)

***How do brominated flame retardants work?***

Epoxy encapsulants do not burn. However, when exposed to heat or open flame, the epoxy compounds breakdown through chain cleavage. This process releases free radicals, such as

[2] Open-chain, or non-cyclic hydrocarbons. The molecules that are not aromatic are aliphatic.

OH and H, in the form of flammable gases. Brominated flame-retardants work by chemically interfering with the gas phase of the combustion process [4]. First, the BFR breaks down and releases bromine ions ($Br^-$) that react with the surrounding polymeric material (RH). The resulting reaction releases hydrogen (H) from the functional group (R) to form hydrogen bromide (HBr),

$$Br^- + RH \rightarrow R + HBr$$

HBr in turn interferes with the radical chain mechanism by reacting with the high energy H and OH radicals,

$$HBr + H \rightarrow H_2 + Br^-$$
$$HBr + OH \rightarrow H_2O + Br^-$$

Bromine is effective because the active agent, HBr, is liberated over a narrow temperature range so that it is available at a high concentration in the flame zone. Once the reactions are initiated, they are self-sustaining because HBr is regenerated by continuous reaction with the hydrocarbons present in the epoxy. The exothermic processes are thus stopped, the system cools down, and the supply of flammable gases is reduced and eventually suppressed.

***Why remove bromine-based flame-retardants?***

The motivation for selecting a bromine replacement focuses primarily on environmental, health, and reliability concerns. Studies have measured rising levels of PBDE's in marine environments [5] and in human milk [6]. There are concerns because of PBDE's structural similarity to thyroid hormones [7], which could lead to abnormal behavior in animals and humans.

Bromine-containing compounds have also been found to form dioxins during the combustion process. The Environmental Protection Agency considers active dioxins carcinogens [9]. This can result in complications during clean up and disposal of fire-damaged electronics or during waste management through incineration. Because of these findings, and PBDE's chemical similarity to another environmental toxin, polychlorinated biphenyls (PCBs), the European Parliament had called for the ban of all PBDE's by 2006 [6].

At this time, TBBPA has not been conclusively been found to be a risk to the environment or human health. The World Health Organization (WHO), as part of its International Program on Chemical Safety, undertook a full scientific assessment of the environmental and human health impacts of TBBPA. It determined that TBBPA has little potential for bio-accumulation and therefore the environmental and health risks should be insignificant. The European Union's risk assessment of TBBPA is currently ongoing and will not be completed until 2003 [9]. However, there are still rising concerns about TBBPA. The levels of TBBPA in human milk have been found to be increasing over time. In addition, the results of some studies [10] suggest that TBBPA, just as PBDE's and PCB's, have the potential to replace thyroid hormones and detrimentally affect human health and behavior.

As a partial response to health concerns and concerns about the recycability of polymer-containing brominated flame retardants, the European Commission adopted two proposals for directives, one on Waste from Electrical and Electronic Equipment (WEEE) and one on the Restriction of the use of certain hazardous substances in Electrical and Electronic Equipment (ROHS). These waste-disposal regulations have proposed requiring separate and controlled disposal of halogen containing scrap [9], such as personal computers.

Bromine-containing epoxy resins can also be an issue in regards to electronic product reliability. The brominated resin often contains some concentration of unstable hydrolyzable bromides, which increases when the resin is exposed to high temperatures. The presence of hydrolysable bromides, in combination with chloride impurities, accelerates gold-aluminum intermetallic formation and can lead to premature failure of wire bonds [8]. BFR's also release hydrogen bromide, dibenzo-p-dioxin and dibenzofuran during combustion, which cause corrosion 0, reducing the probability of recovering electronics after exposure to a fire.

**Phosphorus-Based Flame Retardants**

Phosphorus-based flame-retardants have been considered as an appropriate replacement to TBBPA. Outside the electronics industry, the use of phosphorus and phosphorus-based compounds as flame-retardants is quite common, with phosphorus-based flame-retardants comprising a 24% share of the worldwide market [2].

Phosphorus-based flame-retardants impede the combustion process through multiple reaction steps. During exposure to the high temperature of ignition, the phosphorus-containing functional groups are converted to phosphoric acid by thermal decomposition [12]. The polyphosphoric acid esterifies, forming a protective carbonaceous layer. This protective layer is heat-resistant at higher temperatures and interferes with the transport of oxygen to the burning zone [13]. It is also believed that phosphorus can behave similar to bromine and react with radicals, such as H or OH, to reduce the energy of the flame in the gas phase.

Just as with bromine, phosphorus-based flame-retardants can be characterized by their chemical structure and how they are incorporated into the epoxy molding compounds. PFR's are primarily divided into organic and inorganic compounds.

***Organic Phosphorus Flame Retardants***

Organic phosphorus-based flame-retardants currently used in electronic applications consist of phosphates, phosphonates, phosphinates, and phosphine oxides. Examples include Triaryl Phosphates, Triphenyl Phosphates, Bisphenol A diphenylphosphate, and Resourcinol Diphosphate [14]. Organophosphates are usually mechanically blended, often in liquid form, into resin formulations. Additive organic phosphorus compounds can act as plasticizers and have been reported to have a deleterious effect on the thermomechanical properties of the epoxy resins [15]. In addition, the organic phosphorus compounds tend to increase the water absorbing property of the plastic encapsulant [16], increasing the probably of popcorning and moisture-related failure mechanisms.

Organic phosphorus compounds can be reacted directly into the polymer chain. Investigations have reported success in introducing phosphorus-containing functional groups into the backbones of epoxy. These functional groups include imide-epoxy resin [17], aryl phosphinate epoxyether [18]. Other examples include dihydrooxaphosphaphenanthrene oxide (DOPO), a hydrogen phospinate [15]. One of the advantages of organic phosphorus is that its reaction product with ambient humidity tends to be non-corrosive phosphorus compounds. This is not always the case with inorganic phosphorus.

***Red Phosphorus***

Inorganic phosphorus compounds include red phosphorus and ammonium polyphosphate (APP), with red phosphorus being most common in electronic applications. Red phosphorus is one of three allotropic[3] forms of elemental phosphorus, with the others being white (or yellow) and black (or violet). Red phosphorus can be formed by heating white phosphorus above 250$^{o}$C or by exposing white phosphorus to light. These processes cause the tetrahedral structures of white phosphorus to be chemically re-arranged into a chain of non-periodic five- and six-membered rings, with some additional cross-linking.

Red phosphorus has been used as a flame retardant in polymeric material for almost thirty years [19][20]. Red phosphorus generally exhibits a very high flame-retarding ability. In typical applications, the molding compositions contained approximately 5 to 40 weight % red phosphorus particles[4]. The maximum diameter of the red phosphorus particles ranges between 75 to 200 microns. The actual distribution of the particle sizes is dependent on the processing technique, but the preferred range is between 10 to 40 microns in diameter [21].

Early users found red phosphorus to be too reactive to be used in industrial processes due to concerns over the evolution of toxic hydrogen phosphide, $PH_3$ (phosphine gas) during exposure to elevated temperatures. The release of such a toxic gas could be a threat to the health and safety of manufacturing employees or personnel present during the combustion process. Additional reactions were found to occur when red phosphorus was exposed to ambient humidity. At sufficient temperatures, red phosphorus will react with water to form various oxygen-containing, phosphorus-based acids, such as phosphoric acid, phosphorous acid, and hypophosphorus acid [21]. These phosphorus-based acids are corrosive and can alter the physical and electrical characteristics of the polymer composition.

It was determined that these reactive processes could be retarded by the incorporation of stabilizers. One of the first such proposed stabilizers consisted of silicon oil or a combination of ammonium bisulfate, paraffin oil, and pentaerythritol [20]. These stabilizers were blended with red phosphorus powders before mechanical incorporation into the polymer composition.

[3] An element that is found in nature with different physical structures, but with similar chemical properties.
[4] Less then 5, reduced effect of PFR's; More then 40, detrimental effect on epoxy resin.

As the application of red phosphorus migrated to epoxy, other methods to ensure a more stable red phosphorus were developed. The principal approach consisted of coating red phosphorus particles with a thermosetting resin, such as formaldehyde-based 0, melamine-based [23] or phenol-based [24] compositions. Thermosetting resin coatings provided a number of advantages, including improved coverage, superior wettability and increased resistance of the melt-proof coatings to industrial processes.

The primary coating process consisted of adding the thermoset resin, as a raw material or a precondensation product, to an aqueous dispersion of red phosphorus particles. The mixture was agitated and then polymerized. Upon the coating treatment, a dispersion stabilizer and a stabilizer for red phosphorus such as magnesium hydroxide may be added to the aqueous dispersion. After the polymerization procedure, the treated red phosphorus particles were filtered, washed with water and dried 0. Additional stabilization methods included the use of aluminium hydroxide ($Al(OH)_3$) [25][26][27].

These methods noticeably reduced the formation of phosphine and of phosphorus oxygen-containing acids, but were not considered completely sufficient. Additional improvements in making red phosphorus safe and efficacious were initiated through the development of a dual coating process [21][28], consisting of an initial coat of aluminium hydroxide and/or zinc hydroxide, followed by an additional coat of thermoset resin. The initial coat was applied by mixing red phosphorus powder with aluminum sulfate in an aqueous solution. The composition is adjusted to a pH value of approximately 8-9 so that $Al(OH)_3$ precipitates on the individual particles of the red phosphorus powder. The second coat is applied when the encapsulated powder is dispersed into an aqueous solution of ammonium chloride and a pre-condensed resin. The resin then precipitates on the pre-encapsulated red phosphorus particles when the temperature of the solution is increased to approximately 100$^{o}$C.

While these inventions greatly retarded the reaction of red phosphorus, consistent concerns about the long-term stability of red-phosphorus based fire retardants limited their use in microelectronic applications. It was known that electronic components encapsulated in epoxy resins with red phosphorus flame-retardants were subjected to degradation of the insulation and corrosion of the metallic leads due to the deterioration of the red phosphorus flame retardant and the eventual formation of phosphine and corrosive oxidation products. Rinkagaku

Kogyo, one of the world's largest producers of red phosphorus for flame retardant applications, stated in its patent application [16] that the dual coating method "can not meet the requirements for resinous materials intended to use in high performance electronic components in which an extremely high resistance to moisture and corrosion is required." Rinkagaku Kogyo determined that the reason for this inadequate performance was that the pulverization process used to create a fine powder was a primary driver for red phosphorus reactivity.

***Spherical Red Phosphorus***

After the heat-treatment of white phosphorus, the resulting red phosphorus is a coagulated cake-like solid. Creation of a fine powder, necessary for use in epoxy resins, requires a pulverizing step. This pulverizing step creates particles having a complicated polyhedral configuration consisting of acute ridgelines and sharp-edged angular facets. These surface structures create active sites where moisture and oxygen tend to adhere and react to form phosphine and oxidation products. Further, these irregular particles also tend to be difficult to coat, with either thermosetting resin or aluminum hydroxide, and some portions of the unstable faces tend to be left uncoated.

Rinkagaku Kogyo developed a process for the manufacturing of fine red phosphorus powder that did not require a pulverization step. One of the key differences was to halt the heat treatment[5] of white phosphorus before complete conversion to red phosphorus. When conversion is greater then 70%, the resulting red phosphorus becomes a lump and pulverization is required. When heat treatment is held at 280C for four hours, conversion is only 40% and the resulting red phosphorus powder is spherical, approximately 50 microns in diameter with a very narrow distribution.

It was found that coated spherical red phosphorus had negligible reactivity with moisture in comparison with the reactivity of known pulverized red phosphorus similarly coated. It is considered that the unusual stability of the flame retardant of the present invention is ascribable to the absence of active sites, such as ridgelines and facets. This leads to improvements in moisture and corrosion resistance without losing the advantages of the red phosphorus flame retardant.

[5] Traditionally between 250 to 600$^{o}$C

**Red Phosphorus in Epoxy Molding Compounds (EMCs)**

These improvements in red phosphorus led to their incorporation into plastic encapsulants for integrated circuits (IC's). This application required that the flame retardant chemistry be very stable over long periods of time when exposed to humidity and elevated temperatures.

Sumitomo Bakelite initiated mass production of red phosphorus containing epoxy-molding compounds around 1996 [29]. Sumitomo Bakelite selected phosphorus because of its superior properties and cost, especially in comparison to other halide replacements (see Table 1). The Sumitomo Bakelite formulations containing red phosphorus, 6730UC [30], 7351UT, 7351UL, and 7351UQ [31], were composed primarily of [32]

| | |
|---|---|
| Epoxy Compounds (Biphenyl, O-Cresol Novolac, Phenol) | 12 – 25% |
| Fused Silica | 70 – 85% |
| Carbon Black | ~0.5% |
| Red Phosphorus Flame Retardant | 0.3 – 5% (avg 1.5%) |

The red phosphorus-based flame-retardant was coated with a primary coat of aluminum hydroxide and a secondary coat of phenol resin. The content of red phosphorus in the coated flame-retardant is preferably 60 to 95% by weight. When the red phosphorus content is less than 60% by weight, it becomes necessary to incorporate a large amount of the flame-retardant into the epoxy resin composition and the addition of a large amount of the flame-retardant decreases the moisture resistance of the encapsulant. When the content of red phosphorus exceeds 95% by weight based on the weight of the flame-retardant, there is a problem in respect to the stability of the red phosphorus [32].

The average diameter of the red phosphorus-based flame-retardant particles ranged from 10 to 70 microns, with the maximum diameter not exceeding 150 microns. These limits to particle size are due primarily to their effect on the resin manufacturing process. The fluidity of the epoxy resin formulation is diminished when the average particle diameter drops below 10 microns or when the maximum particle diameter exceeds 150 microns [32].

By 1999, Sumitomo Bakelite was producing 50 tons/month of "green" encapsulant material using red phosphorus as a flame retardant [29]. The fine size of the red phosphorus particles, their double layer coating, and a direct mention in ref. [32] suggests that the red phosphorus-based flame-retardant used in Sumitomo Bakelite encapsulant material was NOVA RED or NOVA EXCEL, which are formulations manufactured by the Rinkagaku Kogyo Company (subsidiary of Tosoh Corporation).

The other major manufacturers of molding compounds seemed to take a different approach to halogen replacements. Dexter's statements on red phosphorus-containing compounds suggest concerns about undesirable properties such as high moisture absorption [33]. Instead, Dexter has focused on the development of molding compounds based on metal oxides and hydrates. Dexter believes that these flame-retardants show good high temperature reliability as measured by the high temperature storage life test (HTSL) and good retention of gold wire bond strength at high temperatures 0.

Nitto Denko and Shin-Etsu Chemical have used red-phosphorus, but in a synergistic effect with another flame retardant[6]. This allows for a much smaller amount of red-phosphorus to be used. Nitto Denko has developed metal hydroxide / metal oxide blends, primarily focusing on magnesium hydroxide [35][36] ($Mg(OH)_2$). The use of red phosphorus reduces the amount of metal hydroxide required, therefore increasing the encapsulant's moisture resistance [37]. Shin-Etsu has developed a compound consisting of red phosphorus and zinc molybdate.

In past patent filings, Sumitomo has identified limitations in using red phosphorus flame-retardants in epoxy resins used to encapsulate semiconductors. In a patent application filed in November of 1998, Sumitomo Bakelite stated that “red phosphorus reacts with a very small amount of water to generate phosphine or corrosive phosphoric acid and has a problem in moisture resistance, making impossible its use in an epoxy resin composition for encapsulating a semiconductor which has a severe requirement for moisture resistance. Hence, it was tried to coat red phosphorus particles with aluminum hydroxide, a metal oxide, an inorganic compound or an organic compound (e.g. a thermosetting resin) to stabilize red phosphorus; however, such an approach still has a problem in moisture resistance. Thus, no epoxy resin composition for

[6] Note: In the description of the formulations, the weight percent of red phosphorus was comparable to formulations containing red phosphorus alone.

encapsulating a semiconductor has been developed yet which uses neither halogen-based flame retardant nor antimony trioxide but which has both flame retardancy and moisture resistance" [38]. In a patent filed in September of 2000, Sumitomo Bakelite stated [sic] “there has been proposed a red phosphorus-based flame retardant obtained by covering the surface of red phosphorus with a metal hydroxide such as aluminum hydroxide or magnesium hydroxide and further covering the surface of the metal hydroxide with a phenolic resin. However, phosphate ion and phosphite ion eluting from this flame retardant adversely affect moldability and curability of the resin composition and moisture resistance and electric characteristics of the resulting semiconductors, and, thus, none of the resin compositions containing red phosphorus-based flame retardants have satisfied the moldability, the curability, the moisture resistance and the electric characteristics” [39].

**Potential Red Phosphorus-Based Failure Mechanisms**

On August 16, 2001, Fairchild Semiconductor released a "High Pin Count TSSOP Product Alert Notice" [40]. Based on feedback from customers, Fairchild determined that 48, 56, and 64 lead TSSOP packages packaged between December 1998 and September 2000 with Sumitomo Bakelite EME-7351UT mold compound were susceptible to elevated failure rates[7]. The failure mode was elevated current leakage and intermittent electrical shorts between adjacent leads.

Root-cause analysis performed by Fairchild implied that were interacting root-causes. At the failure sites, large red phosphorus particles, diameter unknown, were sited between adjacent leads. An image of a suspected red phosphorus particle bridging adjacent leads is displayed in Figure 4. This could create the potential for a conductive path. The report then suggests that the aluminum hydroxide coating experienced breakdown, exposing red phosphorus flame-retardants to moisture absorbed by the epoxy resin and allowing for the creation of phosphoric acid. The actual physical mechanism that initiates the increase in current leakage is unclear. Phosphoric acid is a conductive electrolyte [41], and therefore could cause current to travel

[7] The full statement: “We have noted a slightly elevated field failure rate on high pin count TSSOP packages with older date codes (part number suffix MTD and MTDX) at some customers. Most customers have not reported any such cases. Our analysis indicates that the devices have a common failure mode (leakage & shorts), and detailed analysis indicates phosphorous particles between adjacent leads.”

between adjacent conductors subjected to an electrical potential (e.g., bond pads, wirebonds, and lead fingers). Phosphoric acid is also corrosive and can react with packaging material, including aluminum bond pads, silver-plated bond fingers and copper leadframes, resulting in the formation of conductive filaments or dendrites that can migrate between biased adjacent leads. This process is known as electrochemical migration (ECM).

In May 2000, Sumitomo Bakelite's supplier changed the sieve mesh from 180 microns to 150 microns. More recently, Sumitomo Bakelite's supplier has reduced the sieve mesh even further, to 75 microns. These process changes have reduced the occurrence of large phosphorus particles [31][40]. However, this corrective action was unexpected since reference [32], which was originally filed in December 1996, stated that the maximum red phosphorus particle size in a Sumitomo Bakelite formulation was 150-micron diameter. Sumitomo Bakelite has also attempted to reduce the level of extractable phosphorus by adding additional metal hydroxide and phenolic resin to the coated red phosphorus mixture [39].

Cirrus Logic has filed a complaint against Amkor in the Northern District Court of California [42]. In its filing with the court, Cirrus Logic alleged that the Sumitomo Bakelite EME-7351UL molding compound that Amkor used to package Himalaya 2.0 and Numbur micro-processors was defective. Amkor has since filed a complaint against Sumitomo Bakelite under the same case number [43]. In addition, IDT has stated that a particular mold compound with a high amount of phosphorus flame-retardants was found to cause electrical shorts between adjacent pins [44]. IDT alleged that the phosphorus particles can become slightly conductive when they react with the copper lead frame in the presence of moisture, heat or electrical biasing. EME-6730UC is a phosphorus-containing mold compound that has been used by IDT [30]. No other phosphorus-containing molding compounds were identified. On August 1, 2002, Maxim Integrated Products released a "Notification to Maxim Customers and Industry" [45]. Maxim stated the potential for degradation in electronic components packaged with the Sumitomo Bakelite EMExxxxU Series phosphorus-based molding compound. The degradation mechanisms seemed to be growth of silver dendrites between adjacent pins, but the document states that the exact cause of the dendritic growth has not yet been determined.

Red phosphorus formulations manufactured by Sumitomo Bakelite include 6730UC [30], 7351UT, 7351UL, and 7351UQ [31]. A review of publicly available documents, such as process/product change notifications (PCN's), part manufacturers, part numbers, and contract packaging house show that the Sumitomo Bakelite molding compound formulations are being use (see **Table 2**).

**Discussion and Conclusions**

It is the intrinsic behavior of red phosphorus to react with ambient moisture to form phosphorus-based acids and phosphine gas. While hydroxide and resin coatings may slow this process, there is no indication that these coatings are hermetic [51]. In addition, the high temperatures and pressures used in the component molding process could generate high enough stresses to cause shearing or some other type of damage to the dual coating. Phosphorus-based acids can then form within the exposed red phosphorus particle and eventually leach out [51]. Phosphine gas can also be released and redeposit as a film of phosphorus-based acid. In particular, phosphoric acid is a known electrolyte and can conduct current. It is also corrosive and is known to attack both copper [52] and aluminum [53].

The effect of particle size is currently under investigation. The field failure rate has been reported to drop from approximately 5000ppm to 500ppm when the maximum particle diameter is reduced from 180 to 150 microns. However, the minimum internal spacing between wire bonds will soon reach 30 microns [54]. Therefore, the diameter of the red phosphorus particle is still much larger then the minimum pitch between electrical chip-to-package interconnects.

Red phosphorus-based flame-retardants are also currently being used in the production of "green" printed wiring boards [55]. The concerns over the corrosive behavior of exposed red phosphorus holds true for printed boards. In addition, the average particle size in some formulations [55] can be as large as 200 microns diameter, which is four times larger then the 50 micron dielectric thickness between power and ground in some high technology printed wiring boards. Other technologies that may see red phosphorus include flip chip underfills, where interconnect spacing will soon be 50 microns [56], and film capacitors [57]. The effect on the long-term reliability of these components is currently under investigation.

Sumitomo has stated that they no longer market encapsulating mold compounds containing red phosphorus flame retardants [31]. Alternatives to red phosphorus have been developed and are already in the marketplace. Some encapsulant manufacturers are marketing organic phosphorus flame-retardants. Sumitomo Bakelite currently manufactures a Multi Aromatic Resin (MAR) system that contains no phosphorus-based flame retardants [32]0. However, there are also concerns over the long-term reliability of these alternative flame-retardants in uncontrolled environments. Sumitomo Bakelite has previously indicated they found unacceptable reliability for components encapsulated with resin using phosphate ester flame-retardants (see Table 1). Mitsubishi has also suggested that the use of phosphate-based flame-retardants can lead to lower reliability in high humidity environments [59]. Reliability performance of other formulations, such as Dexter's metal oxides / metal hydrates blends and Nitto Denko's metal hydroxide / metal oxide blends, are not widely available.

During the transition to environmentally friendly electronics, designers, manufacturers and users of equipment requiring long-term reliability must practice due diligence. The market has still not selected the replacement for bromine-based flame-retardants. As a result, a large number of "green" encapsulant systems are being manufactured, some which may not have been tested to the extent required to meet long-term, high reliability requirements.

Unfortunately, due to insufficient communication between component manufacturer supply chain and OEMs, important reliability information is still not available. These include:

1. What is the effect of voltage, temperature, humidity, lead spacing, soldering temperatures, and environmental temperature cycling on the reliability of components encapsulated in resin systems using alternative flame-retardants?
2. What is the actual physical mechanism of failure? Can electrolytic conduction or electrochemical migration occur? What is the magnitude of the current leakage and how does it increase over time?
3. Are certain conductor materials (copper, silver, aluminum, tin, palladium) more or less susceptible to electrolytic conduction, electrochemical migration, or other failure mechanisms resulting from the introduction of alternative flame-retardants?
4. Is there the potential for developing a screening program for identification and removal of components susceptible to premature failure?

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| Flame Retardant | Flammability | Moisture Sensitivity | Reliability (HAST) | Moldability | Cost |
|---|---|---|---|---|---|
| **Red Phosphorus** | Excellent | Good | Good | Good | Same[8] |
| **Phosphate Ester** | Fair | Bad | Bad | Fair | High |
| **Magnesium Oxide** | Good | Fair | Good | Fair | Higher |
| **Metal Oxide** | Fair | Good | Good | Fair | High |
| **Metal Borate** | Fair | Bad | Good | Fair | Low |

Table 1: Benchmarking of halogen replacements (performed by Sumitomo Bakelite) [29]

[8] Indicates that the phosphorus was not selected on a cost basis so much as on the basis of its performance (communication from Sumitomo Bakelite, June 27, 2002)

| Molding Compound | Part Manufacturer | Package Style | Start Date | Stop Date | Contract Packager | Ref. |
|---|---|---|---|---|---|---|
| EME-6730UC | IDT | PB32 | 02/2000 | 01/2001 | Unknown | PCN G9911-05<br>PCN G0110-06 |
| EME-7351UL | Cirrus Logic | Unknown | 10/1999 | 08/2001 | Amkor | Civil Complaint |
| EME-7351UL | Conexant Systems | Exposed-Pad Thin Quad Flat Package (eTQFP) | Unknown | Q2/2002 | Amkor | CN 031902 |
| EME-7351UT | Fairchild | Thin Shrink Small Outline Package (TSSOP) 8L (48, 56, and 64 lead) | 12/1998 | 03/2002 | Amkor | PCN 20011901-A |
| EME-7351UT | Motorola | Unknown | Unknown | 07/2002 | Amkor | PCN 7317 |
| N/A | Atmel Corporation | Unknown | 4/1999 | Unknown | Amkor and ChipPac | Civil Complaint |
| N/A | Philips Semiconductors | Unknown | Fall 1999 | Unknown | Philips | Civil Complaint |
| EME-XXXXU | LSI | L64733 | 11/1999 | 7/2001 | Maxim/Amkor | Notification to Customers |
| EME-7351UL | STMicroelectronics | QFN (Quad Flat No Lead) Plastic Package | Unknown | 11/2002 | Amkor | PCN DSG20023436 |
| EME-7351U | Intersil | QFN, TSSOP, LQFP, MQFP, and TQFP | Unknown | 7/2002 | Amkor and ChipPac | PCN 02015<br>PCN 02026 |
| N/A | Agere Systems | Unknown | Unknown | Unknown | Amkor | Nikkei Electronics |
| N/A | Mitsubishi Electric | Unknown | Unknown | Unknown | Unknown | Nikkei Electronics |
| N/A | Cypress Semiconductor | Unknown | Unknown | Unknown | Amkor | Nikkei Electronics |
| EME-7351UL | Unknown | MicroLeadFrame (MLF) | Unknown | Unknown | Amkor | Website |
| EME-7351UL | Unknown | Exposed-Pad Thin Quad Flat Package (eTQFP) | Unknown | Unknown | ASE Korea | Website |

Table 2: A listing of part manufacturers and part numbers that are encapsulated with epoxy compounds containing red phosphorus flame retardants

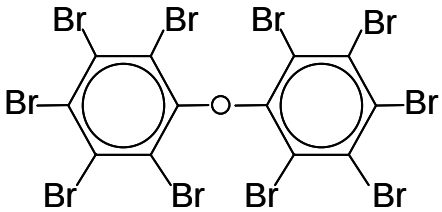


**Figure 1:** Chemical structure of Decabromodiphenyl ether (Deca-BDE)

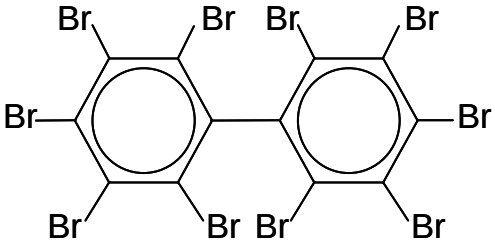


**Figure 2:** Chemical structure of Decabrominated biphenyl (Deca-BB)

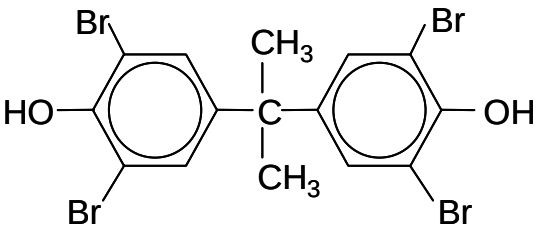


**Figure 3:** Chemical structure of Tetrabromobisphenol–A (TBBPA)

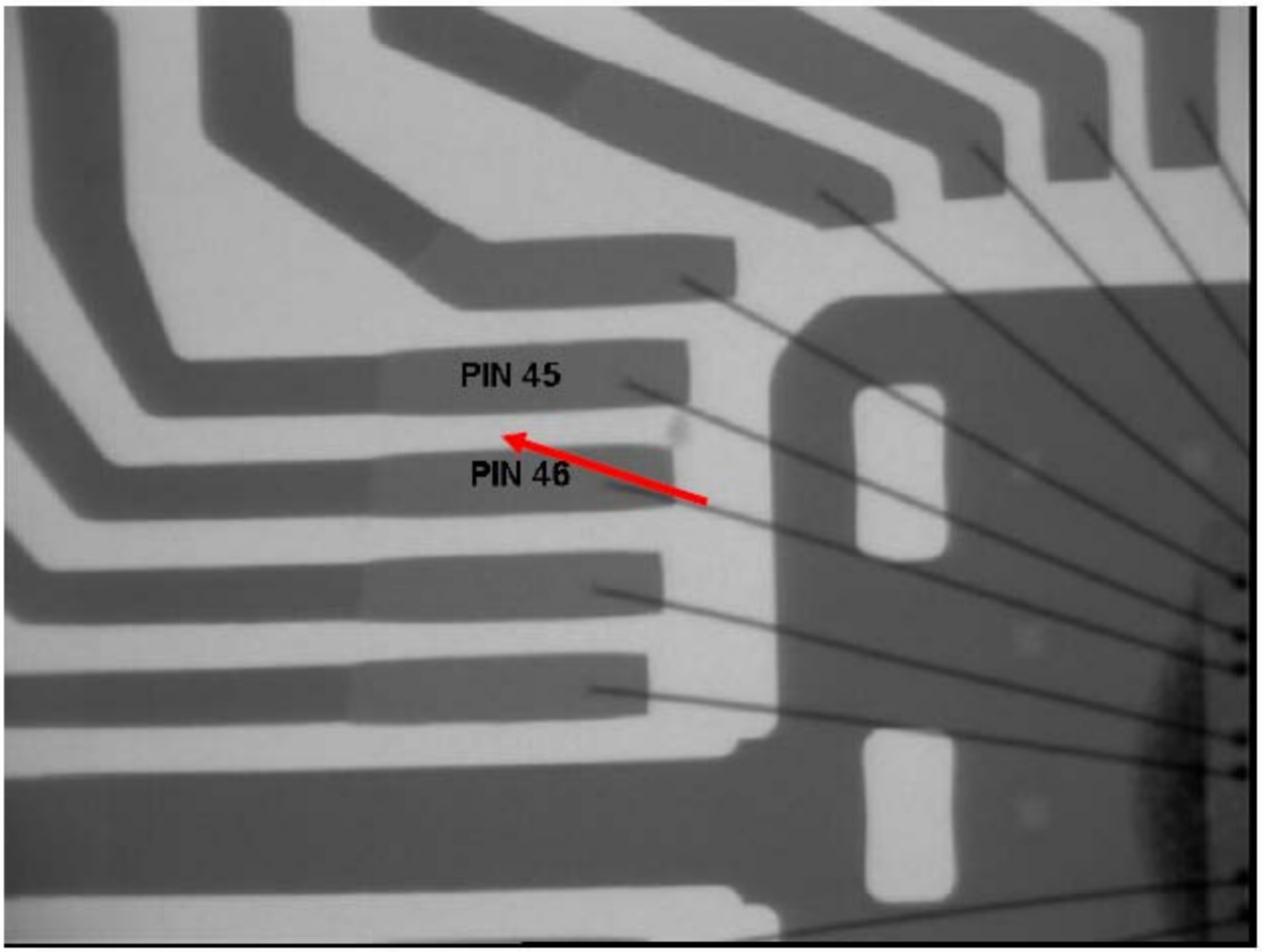


**Figure 4:** Suspected phosphorus particle bridging adjacent leads (marked by the arrow).