



## An Overview of Flame Retardants in Printed Circuit Boards for LEDs and other Electronic Devices

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*Received 10 Feb 2023,*

*Revised 28 Mar 2023,*

*Accepted 01 Apr 2023*

### Keywords:

- ✓ PCBs;
- ✓ Flame retardants
- ✓ epoxy;
- ✓ fibre glass
- ✓ LEDs

*Citation: Ike-Eze I.C.E., Ucheji O.N., Ubi P.A., Oji E.O., Aigbodion V.S., Omah A.D. and Ogbuefi C.C. (2023). An Overview of Flame Retardants in Printed Circuit Boards for LEDs and other Electronic Devices, J. Mater. Environ. Sci., 14(4), 410-420.*

**Abstract:** Printed circuit boards (PCBs) are commonly found in domestic and industrial electronic products, such as LEDs, computers and mobile phones. Most PCBs are often made of layers of dielectric glass fiber reinforced epoxy resin laminated with particles of copper for improved electrical conductivity and flame-retardant (FR) additives to improve fire safety. All PCBs produced is expected to meet the fire requirements as specified by Underwriters laboratory (UL-94) standards. The PCB fire safety compliant boards referred to as FR4 boards are usually laminated using brominated epoxy resins, with which tetra-bromo-bisphenol-A (TBBPA) form part of the polymeric backbone of the resin. This is very harmful to human life during soldering of parts or fire outbreaks. However, there is a trend going on now, emphasis recently is on non-halogenated FRs in order to reduce the toxicity of the FRs. This safety requirements therefore makes it imperative for more alternatives flame-retardant additives and laminate materials alternatives to be developed for PCBs. Currently, the trend is towards bio flame retardants and their synergetic effects. This paper captured the various types of PCB laminate materials, FRs in use, and developments being advocated for FRs additives.

## 1. Introduction

Printed circuit board (PCB) is a non-conductive circuit board made of glass fiber reinforced polymer board with traces of copper particles. PCBs are important parts of electrical and electronic (EE) equipment and presents about 3-6% of overall amount in every electronic equipment/device (Ravi, 2018). They provide both electrical connectivity and mechanical support between the components (Seyed *et-al.*, 2019). Effective selection of flame retardants (FRs) during PCB manufacture of polymer-based PCBs is crucial for health and safety of humans during device repair works and fire outbreaks.

Electronic connections have always been a thing made from past ages, but before the development of PCBs all the components are connected with a wire which increases complexity and decreases reliability of the circuit. This simply made it impossible to make a very large circuit connection like we have in our today's motherboards. In PCBs, all components are connected internally

without wires thereby reduces the complexity of the overall circuit design and making miniaturization of circuit boards now possible which enables down-scaling of the printed circuit board (PCB) real to reduce the space, weight, and manufacturing cost and time (Seyed *et-al.*, 2019). PCBs are in our everyday domestic and industrial devices such as in motherboard, medical devices, industrial machinery, televisions, radio panels, children's toys, mobile phones, digital camera, graphic cards, robotics, automotive industries, airplanes, lighting systems, power system devices and military equipment and electric bulbs among others.

There are three major types of PCBs substrates based on its base materials used (Wang *et-al.*, 2012; Nassifar *et-al.*, 2021; de Souza *et al.* 2022) and they include

(1) *Reinforced polymer composite base substrate* – This type PCB is called FR4 and its main components include (i) a glass fiber epoxy composite laminates substrate for the dielectric properties (ii) copper particles to provide the conductive part and (iii) flame retardant for fire protection and safety (2) *Teflon or polyimide base materials substrate* – This type PCBs are made of flexible or rigid-flex designs depending on its thickness. Polyimide and Polytetrafluoroethylene (PTFE) commonly called Teflon are used. Teflon is extremely flexible, lightweight, good flame resistant, high physical strength and thermally stable making it useful for high speed, high frequency applications (3) *Aluminum/metal base material substrate* - In this type PCBs, copper and other good conducting metallic materials of aluminum, iron, etc are also used which gives a longer product life than FR4, however they are more expensive. All polymer substrate-based PCBs can be customized for any specifications to user requirements but of real time problem is the toxicity of the flame retardant additives used.

A review by (Wabeeke, 2022) on flame-retardant plastics reported that the safe use of halogen containing flame retardant materials in plastics is been discouraged due to its toxicity and environmental incompatibility such that reputable manufacturers of brominated flame retardants are making serious efforts to develop safer products. For this reason, alternative flame-retardant materials are now being used in many other applications but only in a small percentage in FR4 boards, about 3-5% were reported in 2008 with aluminum phosphonate FR, (Anna, 2017).

In this survey, we x-rayed types of PCBs based on flexibility/rigidity and substrate types. It reviewed briefly the various flame retardants used in PCBs manufacture and projected current advances being made for alternative flame retardants subject to all controlling parameters in FR materials selections.

## **2. Classification of PCBs and Laminate Substrates**

### **2.1 Classification of PCBs**

PCB can be group under three broad types. These are rigid PCBs; Flex-rigid PCBs (semi-flex) and flexible PCBs. Each of the above can have a single layer, double layer or multiple layer structure. Modern-day electronic systems are characterized by high functionality and relatively compact construction. The amount of space that device designers make available for the electronic equipment is always limited and therefore needs to be utilized in the best way possible. The conventional interconnection systems with volumes of wire take up a considerable amount of the limited space available in every electronic packaging and therefore solution to it is being sort continually.

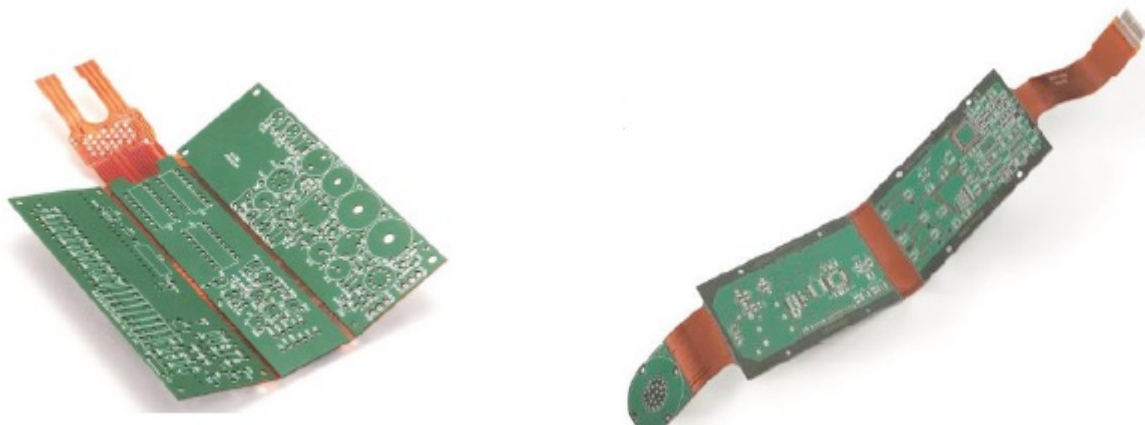
A review article by (Hamed *et-al.*, 2020) reported that many applications in real life require cyclic movement or stretching while still maintaining an electrical connection. To achieve this need, flexible circuit boards are one possibility and the right choice to consider. They are used in laptops to ensure the connection between the computer and monitor remains intact, as a laptop may be folded thousands of times in its lifetime. However, the most reliable technology is offered by the flex-rigid circuit board that can be assembled three-dimensionally.

### 2.1.1 Rigid PCB

Just as the name implies, these are shift boards that cannot be bent, folded or twisted to any other shape after manufacture. Rigid PCBs are made out of solid materials which don't allow PCBs for folding or twisting. It can also consist of different layer configuration just like flex PCBs, such as single layer, double layer and multi-layer rigid PCB. The shape after installation remains in position as fixed. The major advantage of this type of PCBs is that their lifespan is very high. It is used in many computer parts assemblies like mother board, RAM, CPU and other electronic devices. The single sided rigid PCBs are simple in design and easy to manufacture and hence one of the most used PCBs, although where space is limited, multi-layer rigid PCBs that can have about 9-10 layers will be the preferred choice.

### 2.1.2 Flex-rigid PCB

Flex-rigid boards as the name implies is a combination of two types in one in form of hybrid designs, as they are made up of both rigid and flexible substrates. Flex-rigid boards consist of multiple layers of flexible PCB attached to a number of rigid PCB layers. Flex-rigid board is as shown in Figure 1. It is a very important PCBs model because of its flexibility in design and versatility in application. It is believed that even though rigid-flex PCBs are more expensive than rigid boards, its advantages of weight and volume reduction, 3D design, cost saving on materials and labour for connectors & wires and compactness with high reliability is a real gain (Albert, 2017)



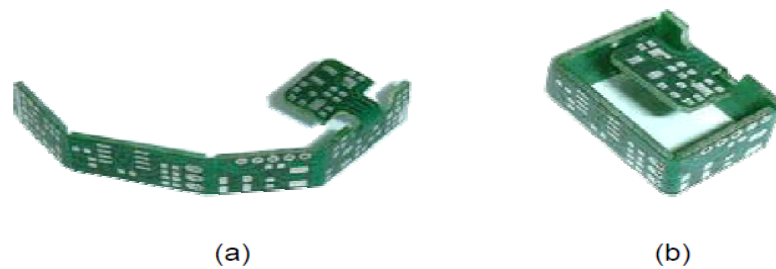
**Figure 1.** Example of rigid-flex PCB [9], source: Albert Schweitzer

(Ruwel *et-al.*, 2006) reported that flex-rigid boards consist of two or more rigid areas that are electrically interconnected by flexible areas. This feature allows integrated interconnection between several rigid boards without wires and plug-in connections and thus reduces the number of wires soldered joints and cables. It ensures assembly of the electronic component with minimal waste of space thereby improving quality and reliability of the board. Reliability because many plug-and-socket connections and soldered joints - a well-known source of faults – have been removed reasonably. The flex-rigid board is no long new in the industry as many PCB manufacturers have firmly established its application in many sectors of the electronic industry and are used in cell phones, digital cameras, photocopiers, printers and automobiles among others.

### 2.1.3 Flexible PCB

Flexible PCB is simply called and known as flex circuit. These type of PCBs uses flexible plastic material like *polyimide*, *Polytetrafluoroethylene (PTFE)*, *Polyether ether ketone (PEEK)* or transparent conductive *polyester film* as substrate materials which provides the dielectric protection against

ambient conditions and environment, (Gazit, 1986) This is an interesting but complex type of PCB that can be folded or twisted and may consist of different range of layers like single sided flex circuit, double sided flex circuit and multisided flex circuit as shown in Figure 2.



**Figure 2.** A single-sided flexible circuit for generating a 3D interconnection to minimize space requirements. (a) as product and (b) after assembly. (Courtesy of Lyncolec Ltd).

The basic material elements that constitute a flexible circuit include: a dielectric substrate film (base material), electrical conductors (usually copper foils), a protective additives (FRs) and adhesives to bond the various materials together. Flex circuit PCBs are used in automotive industries, laptops and desktop computers, light emitting diode (LCD) fabrication, cell phones, flex solar cell panels, camera and other complex electronics devices. The very major advantages of flex circuit over rigid PCBs are in line with those listed in the rigid- flex type such as smaller in size (miniature), increase in the reliability of the system since few connections (wires) are needed, elimination of wire routing errors which are major failure points and reduced assembly production time. Above all weight and volume are reduced and 3D design can be done easily with higher design freedom. Depending on the number of build-up layers, flex circuits can be very thin, or very robust enough to carry a few million cycle bend loadings without damage (Prime, 2002).

## 2.2 Types of Laminate Substrates for PCBs

There are many types of PCBs based on the substrate materials. The main elements of the PCB are dielectric substrate (rigid or flexible) with copper conductors on it. It may have holes and may be plated or non-plated. The common names to PCBs substrate classifications are FR4, FR5 (FR4 High Tg), FR1, FR2, CEM3, CEM1, Polyimide, PTFE and metal substrate. Most printed circuit boards are made of FR4 type with standard glass-epoxy laminate, with dielectric constant  $D_k$  range from 3.8 to 4.6, depending on the supplier. Its operating temperature can be from  $-50$  to  $+110^\circ\text{C}$  and glass transition temperature  $T_g$  of  $135^\circ\text{C}$ . Polyimide substrates are best materials for high temperature operations and high temperature stresses. It has a good electric strength and often used for military products or in high endurance applications. However, the cost of the polyimide materials is higher than the basic material for FR4. The details of each substrate type are given below ((Prime, 2002).

### (i) FR4

Many printed circuit boards and substrates in use today are composed of a material called FR4 (Hamed *et-al.*, 2020). The term “FR” in FR4 stands for fire retardant. The 4 in FR4 is a particular composition that is a glass fiber epoxy laminate. 1.60mm FR4 uses 8 layers of (7628) glass fiber material. The 7628 is a common glass fabric that has a particular weight, thickness, warp and weft”. The FR4 material can be made for the single sided, double sided and multilayer printed circuit boards with strict specified mechanical strength and flammability rating of UL-94 standard. It has a glass transition temperature ( $T_g$ ) and dielectric constant ( $D_k$ ) of  $135^\circ\text{C}$  and 3.8-4.7 respectively. The most common used flame

retardant in FR4 substrate is bromine, however legislation is of recent advocating for halogen free flame retardants.

**(ii) FR4 –halogen free**

In a work done by (Kellyn, 2008, Sylvia 2002), he reported that due to environmental impacts many of these electronics companies have pledged to remove brominated and/or halogenated flame retardants from some or all of their products. This laminate type therefore does not contain halogenate materials such as bromine or chlorine. The FR4 halogen free does not emit hazardous substances when burning like brominated FR4. It has a dielectric constant in the range 4.5-4.9 and T<sub>g</sub> of about 140°C.

**(iii) FR1/FR2/FR3**

FR1 is basically the same as FR2 except that FR1 has a higher T<sub>g</sub> of 130°C against the 105°C for FR2. Most laminate manufacturers who produce FR1 may not produce FR2 since the cost and usage are similar and it is not cost effective for having both. FR3 is mainly a European product that is basically FR2, but an epoxy resin binder in place of phenolic resin. The FR1 and FR2 are paper material with phenolic binder and are used only for the production of single side printed circuit boards. The major difference between the FR1 and FR2 is that FR1 has a higher glass transition temperature T<sub>g</sub>. FR1 Laminates have a good mechanical processing potential such as milling and punching. Flammability rating is UL94-VO and is mostly produced in the industry than FR2.

**(iv) FR5**

This grade is very similar to FR4 substrate and it is sometimes called FR4 High T<sub>g</sub>. It has excellent performance in Pb-free soldering with a dielectric constant in the range 3.8-4.6 and a glass transition temperature (T<sub>g</sub>) of about 170°C.

**(v) CEM-1 and CEM -3**

CEM stands for composite epoxy material. CEM-1 composite material is composed of woven glass fabric surfaces and paper core combined with epoxy resin. It is not suitable for creating plated through holes. Plated through holes can be made on FR4 and CEM-3 boards, but not on the other types. CEM-3 is a new printed circuit substrate material developed based on FR4 model. In recent years, CEM-3 is being developed very similar to FR4 however instead of woven glass fabric a ‘flies’ type is used. CEM-3 has a milky white color and is very smooth. It will be a complete replacement for FR4 and has a very large market share in Asia especially in Japan. It is a kind of flame-retardant epoxy copper-clad plate glass material that is generally used in electronics with double sided and multilayer printed circuit boards.

**(vi) Polyimide**

In this substrate type, Polyimide resin - a flexible polymeric film is reinforced with aramid fibers for the production of flexible and rigid-flex PCB. It has a good working temperature from -200°C to + 300°C with high glass transition temperature in the range (195-260°C), a dielectric constant of 4.4 and good coefficient of thermal expansion. Its major drawback is high water absorption (up to 3% by weight) and relatively high price. The polyimide film thickness can vary widely over a narrow range from 12 to 125 μm as used in practice. As a rule of the thumb when designing the flexible printed circuit boards; the stiffness of the flexible materials must be proportional to the third power of their thickness. That means if the material thickness is doubled, it becomes eight times tougher but will bend eight times less with the same load.

**(vii) Polytetrafluoroethylene (PTFE)**

The PTFE also called Teflon is a flexible substrate for high frequency laminates with a T<sub>g</sub> of about 240-280°C and a wide range in dielectric constant of 2.2 – 10.2. It is used in PCBs that require a low dissipation factor and very stable dielectric constant. PTFE laminates are commonly used for radio frequency /microwave circuits due to their excellent electrical performance at higher frequencies, (Sylvia 2002). PTFE circuit materials typically exhibit a dissipation factor of around 0.002, signifying very low dielectric loss, whereas FR4 materials typically have a dissipation factor of around 0.020 with much higher dielectric losses. However, polytetrafluoroethylene (PTFE) has high coefficient of thermal expansion (CTE) values and can suffer from excessive material expansion when subjected to the elevated temperatures.

**(viii) Metal Base Substrate PCBs**

Aluminum is a non-ferrous metal with combination of properties that makes it an attractive choice as a substrate material for PCBs. These properties include, low cost (aluminum is roughly \$2 per kilogram while FR4 is about \$6 per kilogram, a good coefficient of thermal expansion which is close to that of copper, dimensional stability which exceeds that of FR4, relative lightweight, although aluminum is admittedly denser than FR4 laminate, (2.8 g/cm<sup>3</sup> aluminum versus 1.8 g/cm<sup>3</sup> for FR4) the amount of aluminum required can be very cost competitive in the long run, (Fjelstad, 2015). There are many advantages of metal core PCBs over FR4 PCBs in thermally sensitive applications. In a similar work (William *et-al.*, 2013) reported that metal core and insulated metal substrate PCBs are categories of PCB technologies which provide enhanced thermal management and current carrying capability. The paper stated that 15 different types of metal core and metal backed PCB technologies are available to handle thermal dissipation in power electronics to suit almost every application.

### **3. Application of PCBs in Electronic Devices**

Printed circuit boards, or PCBs, are key components of electronic components and they are critical to a wide variety of industries. Most people use them every day without even thinking about it. There are a massive number of applications for PCBs, one of which is light emitting diodes LEDs, used for residential and commercial lighting and across numerous industries including the automotive, medical, aerospace and computer technology, telecommunication, maritime, energy /power sectors among others because of their energy saving efficiency, long life and compactness. One role that PCBs play in LEDs is the transfer of heat away from the device and therefore most PCBs used for LEDs are typically made with aluminum, which can transfer heat better than other metals. This eliminates the need for an additional heat sink to a design. For instance, in the aerospace, PCBs are key components in the power supplies equipment, monitoring equipment and communication equipment (EMSG, 2023).

There are various kinds of FRs incorporated in the PCBs. The choice of a particular FR depends on the target application and their compatibility with other materials fire safety standards of the product as well as reliability, and cost considerations. The health effects of flame retardant chemicals include carcinogenicity, endocrine and reproductive effects. The neurological and developmental disorders are of concern to the global community too. Most of the flame retardants used in PCBs are halogen based, (Elmar and Margot, 2008).

Beside PCBs, flame retardants are used in a wide variety of other products including foam, furniture, plastics, textiles, children's toys, car seats, changing table pads, sleep positioners, portable mattresses, nursing pillows, baby carriers, high chairs, and infant bath mats and slings among others. Flame retardants are added to products to slow the spread of a fire and provide additional escape time for occupants, (Souware *et-al.*, 2017). Flame retardants typically function by separating into free radicals that absorb energy, thereby slowing combustion and propagation of fire.

### 3.1 Types of Flame Retardants in PCBs

Flame retardants used in PCBs can be broadly categorized into two based on how they are incorporated into the material (1) additive and (2) reactive flame retardants. There is also another classification based on their level of toxicity such as (i) halogen-based retardants, (ii) non halogen based (iii) inorganic retardants and (iv) organic or bio-based flame retardants.

#### 3.1.1 Additive flame retardants

These are FRs not chemically bonded to the polymers or chemical materials during its initial synthesis but are added and mixed with other components during the batch manufacture of a product. These flame retardants maintain their distinctive chemical structure and are evenly dispersed throughout the product. They can easily escape from their matrix through release to the air and accumulate in dust (Stapleton *et-al.*, 2008). The additive flame retardant alternatives include aluminum diethylphosphinate, aluminum hydroxide, magnesium hydroxide, melamine polyphosphate, and silicon dioxide. They also have varied hazard designations for human health effects but certainly less harmful than halogenated FR. Aluminum diethylphosphinate has moderate aquatic toxicity hazard whereas silicon dioxide because of its inhalation of particles less than 10µm in size has high dose of toxicity. while the other flame retardants have low toxicity designations.

#### 3.1.2 Reactive flame retardants

These are chemically bonded to the polymers during initial polymerization syntheses, coupling or grafting processes. and become an integral part of the product structure. For this reason, they are much less likely to be released and therefore have less threat to human health and the environment during consumer use. However, reactive flame retardants may still be released from products, either because they are liberated from the polymer during soldering processes in repair works or outright fire outbreak. Reactive and additive forms of the same chemical have different physical and chemical properties and so are not interchangeable. Tetrabromobisphenol-A (TBBPA), can be used in either form depending on the target application while most other flame retardants are only used in either the additive or reactive form (Saskia *et-al.*, 2015, EPA, 2014).

## 4.0 Next generation PCBs research and development

(i) **Laminate Materials** - Halogenated flame retardants are in use for PCBs over many years and they are rated very effective but due to health and environmental impacts of halogenated flame retardants especially Tetrabromobisphenol-A (TBBPA) which generates dioxins and furans during combustion (Hong *et-al.*, 2023), the development of non-halogen flame retardants has been a priority of manufacturers. However, in seeking alternatives to the halogenated flame retardants, the human health and environmental impact as well as the cost implications and actual performance of laminates containing these non-halogen flame retardants are also a very serious issues being studied.

Another alternative to epoxy resin is polyimide resin and polytetrafluoroethane (PTFE) commonly known as Teflon resin. Polyimide are being used for flex parts and for high temperature applications but it is very expensive compared to epoxy resin (Liu *et-al.*, 2023). Another new trend in replacing halogenated flame retardants partially or wholly is by using phosphorus-based flame retardants for casings and circuit boards, and using minerals such as nanoclays in combination with aluminum hydroxide and magnesium hydroxide for the wiring and cabling. However, there are concerns that these phosphorus-based retardants are suspected to be neurotoxicants when they break down in the environment. Anyway, research is ongoing to see if this effect will be reduced by incorporating it as reactive phosphorus-based retardants instead of its active status for printed circuit boards. Certainly, the real breakthrough will be to develop inherently nontoxic and non-flammable plastics for commodity-type applications in the aerospace, electronics and building/home furniture applications. At the forefront of this research effort is a team at the University of Massachusetts Amherst, where researchers have developed a new plastic polymer based on bishydroxydeoxybenzoin (BHDB) that releases water vapor rather than hazardous gases when it breaks down in a fire (Melissa *et-al.*, 2015, Kenneth *et-al.*, 2006).

(ii) **Production Process**- Improvements in the production (lamination) process are also being developed such as the formation and multi-layering at room temperature of ceramic film on resin circuit boards, allowing for further multi-functionality, miniaturization, and cost reduction of electronic devices (EPA, 2014). Laser drilling techniques can be used for direct copper ablation, as they can quickly vaporize copper without damaging the epoxy and glass substrate (Wang and Zheng, 2009, Wang *et-al.*, 2008, Ciszewski and Sochacki 2020). This will allow for the production of smaller microvias which may allow for the creation of smaller circuit boards (Barclay, 2004).

#### 4.1 Advances towards bio-based flame retardants and synergetic effects

The production of FRs has increased rapidly during the last two decades and R&D on it is oriented around improving the performance of FR4 laminates. For example, manufacturers are seeking to improve the glass Tg of FR4 laminates in order to produce laminates better able to withstand heat. A higher Tg is generally compatible with the use of lead-free solder, which often requires a higher soldering temperature. A review by (Chukwunweike *et-al.*, 2019) reported that, most abundant elements including C, H, N, Ca, K, Si, Mg, Al, S, Fe, P, Cl, Na, Mn, Ti, have been established as possessing good flame retardant effects, however, emphasis of recent is on the use of biobased modified polymers (Yang *et-al.*, 2020, Muhammad and Gunnar, 2020) which can be used as in either intrinsically alone or in combination with traditional phosphorus or nitrogen flame retardants. It can be chemical modified and grafting into the polymer chain. Biobased compounds that have been used intrinsically include lignin, tannin, starch, chitosan and proteins and DNA (Prime, 2002, Muhammad and Gunnar, 2020, Jacob *et-al.*, 2019) while their combinations have always been with either phosphorus and/or nitrogen.

#### Conclusion

A survey of classification, substrate materials and types of flame retardants used in PCBs were carried out with a highlight on the regulation against use of halogenated flame retardants in PCBs. The trend towards the synergetic effect of biobased flame retardants modified phosphorus or nitrogen was briefly put forward as a good alternative and substitute to halogenated flame retardants (HFR). However, these



biobased FR though less toxic than that of halogenated flame retardants has not been proved to be 100% toxic free. Again, the biobased FRs are also less effective in efficiency compared to HFRs but its assumed safety and biofriendly disposition during soldering repairs and fire outbreaks is outstanding. It is therefore most likely that best results will be achieved under a synergetic formulation between a little quantity halogen and bigger weight percent of other non-halogen flame retardants and modified biobased flame retardants for both PCBs and other polymeric products. This shall form a justification for our next research.

### Acknowledgement

The authors wish to acknowledge the African Centre of Excellence for Sustainable Power and Energy Development, (ACE-SPED) University of Nigeria, Nsukka and Tertiary Education Trust Fund (TET Fund) IBR 2022 grant.

**Disclosure statement:** *Conflict of Interest:* The authors declare that there are no conflicts of interest.

*Compliance with Ethical Standards:* This article does not contain any studies involving human or animal subjects.

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