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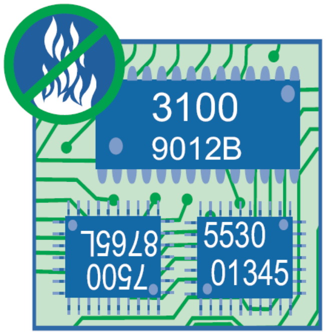
# FLAME RETARDANTS IN PRINTED CIRCUIT BOARDS

## Chapter 3



## FINAL REPORT

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# 3 Chemical Flame Retardants for FR-4 Laminates

This chapter summarizes the general characteristics of flame retardants and associated mechanisms of flame retardancy. The flame-retardant chemicals currently used in printed circuit boards (PCBs) are also briefly introduced, with more detailed information about their potential exposure pathways, toxicity, and life-cycle considerations presented in later chapters.

## 3.1 General Characteristics of Flame-Retardant Chemicals

Fire occurs in three stages: (a) thermal decomposition, where the solid, or condensed phase, breaks down into gaseous decomposition products as a result of heat, (b) combustion chain reactions in the gas phase, where thermal decomposition products react with an oxidant (usually air) and generate more combustion products, which can then propagate the fire and release heat, and (c) transfer of the heat generated from the combustion process back to the condensed phase to continue the thermal decomposition process (Hirschler, 1992; Beyler and Hirschler, 2002).

In general, flame retardants decrease the likelihood of a fire occurring and/or decrease the undesirable consequences of a fire (Lyons, 1970; Cullis and Hirschler, 1981). The simplest way, in theory, of preventing polymer combustion is to design the polymer so that it is thermally very stable. Thermally stable polymers are less likely to thermally degrade, which prevents combustion from initiating. However, thermally stable polymers are not typically used due to cost and/or other performance issues such as mechanical and electrical properties incompatible with end-use needs for the finished part/item. As a result, manufacturers use other methods, such as using flame-retardant chemicals, to impart flame-retardant properties to polymers.

Flame retardants typically function by decreasing the release rate of heat (Hirschler, 1994), thus reducing the burning rate or flame spread of a fire, or by reducing smoke generation (Morose, 2006). In the gas phase, flame retardants can interfere with free radical chain reactions, thereby reducing the tendency of the fire to propagate and spread. Flame retardants can also act in the gas phase by cooling reactants and thereby decrease the rate of combustion. In the condensed phase, flame retardants can act by forming a solid char (or a glassy layer), which interferes with the transfer of heat back from the gas phase to the condensed phase. This inhibits or prevents further thermal decomposition.

Typically, flame retardants contain one of the following seven elements: chlorine, bromine, aluminum, boron, nitrogen, phosphorus, or antimony (Lyons, 1970; Cullis and Hirschler, 1981; Hirschler, 1982). There are, however, a number of replacements and synergists that are also effective. For example, aluminum (which is most often used as an oxide or hydroxide) can be replaced with magnesium hydroxide or by a magnesium salt. In addition, some elements, such as zinc (often used as zinc borate or zinc stannate) and molybdenum (often used as ammonium molybdates), are effective primarily as smoke suppressants in mixtures of flame retardants.

### 3.1.1 Flame Retardant Classification

Flame retardants are generally incorporated throughout the polymeric material, although they can also be coated on the external surface of the polymer to form a suitable protective barrier. Flame retardants can be classified, broadly speaking, into two types according to the method of incorporation:

- *Reactive:* Reactive flame retardants are incorporated into polymers via chemical reactions. The production of existing polymers is modified so that one or more unsubstituted reactant monomers is replaced with a substituted monomer containing flame-retardant heteroelements. The substituted monomers and their heteroelement components become an integral part of the resulting polymer structure. Reactive flame retardants must be incorporated at an early stage of manufacturing, but once introduced they become a permanent part of the polymer structure. Once they are chemically bound, reactive flame-retardant chemicals cease to exist as separate chemical entities. Reactive flame retardants have a greater effect than additive flame retardants on the chemical and physical properties of the polymer into which they are incorporated.

- *Additive:* Additive flame retardants are incorporated into the compounds via physical mixing. Compounds containing flame-retardant elements are mixed with existing polymers without undergoing any chemical reactions. As a result, the polymer/additive mixture is less susceptible to combustion than the polymer alone. Since additive flame retardants can be incorporated into the product up until the final stages of manufacturing, it is typically simpler for manufacturers to use additive flame retardants than reactive flame retardants.

Due to the differing physical and chemical properties of flame-retardant chemicals, most are used exclusively as either reactive or additive flame retardants. Both reactive and additive flame retardants can significantly change the properties of the polymers into which they are incorporated. For example, they may change the viscosity, flexibility, density, and electrical properties, and may also increase the susceptibility of the polymers to photochemical and thermal degradation.

Flame retardants can also be classified into four main categories according to chemical composition (IPC, 2003; and Morose, 2006):

- *Inorganic*: This category includes silicon dioxide, metal hydroxides (e.g., aluminum hydroxide and magnesium hydroxide), antimony compounds (e.g., antimony trioxide), boron compounds (e.g., zinc borate), and other metal compounds (molybdenum trioxide). As a group, these flame retardants represent the largest fraction of total flame retardants in use.

- *Halogenated*: These flame retardants are primarily based on chlorine and bromine. Typical halogenated flame retardants are halogenated paraffins, halogenated alicyclic and aromatic compounds, and halogenated polymeric materials. Some halogenated flame retardants also contain other heteroelements, such as phosphorus or nitrogen. When antimony oxide is used, it is almost invariably used as a synergist for halogenated flame retardants. The effectiveness of halogenated additives, as discussed below, is due to their interference with the radical chain mechanism in the combustion process of the gas phase. Brominated compounds represent approximately 25 percent by volume of the global flame retardant production (Morose, 2006). Chemically, they can be further divided into three classes:

  - Aromatic, including tetrabromobisphenol A (TBBPA), polybrominated diphenyl ethers, and polybrominated biphenyls;
  - Aliphatic; and
  - Cycloaliphatic, including hexabromocyclododecane.

- *Phosphorus-based*: When this partnership was convened, the current information showed that this category represented about 20 percent by volume of the global production of flame retardants and includes organic and inorganic phosphates, phosphonates, and phosphinates as well as red phosphorus, thus covering a wide range of phosphorus compounds with different oxidation states. There are also halogenated phosphate esters, often used as flame retardants for polyurethane foams or as flame-retardant plasticizers but not commonly used in electronics applications (Hirschler, 1998; Green, 2000; Weil, 2004).

- *Nitrogen-based*: These flame retardants include melamine and melamine derivatives (e.g., melamine cyanurate, melamine polyphosphate). It is rare for flame retardants to contain no heteroatom other than nitrogen and to be used on their own. Nitrogen-containing flame retardants are often used in combination with phosphorus-based flame retardants, often with both elements in the same molecule.

### 3.1.2 Flame Retardant Modes of Action

The burning of polymers is a complex process involving a number of interrelated and interdependent stages. It is possible to decrease the overall rate of polymer combustion by interfering with one or more of these stages. The basic mechanisms of flame retardancy will vary depending on the flame retardant and polymer system.

#### Flaming Combustion

***Chemical Inhibitors*** – Some flame retardants interfere with the first stage of burning, in which the polymer undergoes thermal decomposition and releases combustible gases. Interference during this stage alters polymer breakdown in such a way as to change either the nature of released gases or the rate at which they are released. The resulting gas/oxidant mixture may no longer be flammable.

***Fillers*** – A completely different mode of action is that exerted by inert solids incorporated into polymers. Such materials, known as fillers, absorb heat and conduct heat away by virtue of their heat capacity and thermal conductivity, respectively. As a result, fillers keep polymers cool and prevent them from thermally decomposing. The temperature is kept down even more effectively if the fillers decompose endothermically. Since fillers act predominantly via a physical rather than a chemical process, large levels of fillers are needed.

***Protective Barriers*** – Some flame retardants cover the flammable polymer surface with a non-flammable protective coating. The coating helps insulate the flammable polymer from the source of heat, thus preventing the formation of combustible breakdown products and their escape into the gas phase. The non-flammable coating may also prevent gaseous oxidants (normally air or oxygen) from contacting the polymer surface. Intumescent compounds, which swell as a result of heat exposure, lead to the formation of a protective barrier in which the gaseous products of polymer decomposition are trapped. Alternatively, a non-flammable layer can be directly applied to the surface of the polymer to form a non-intumescent barrier coating. Many phosphorus-containing compounds form such non-intumescent surface chars.

***Gaseous Phase Mechanisms*** – Flame-retardant chemicals can also inhibit combustion of the gaseous products of polymer decomposition. These reactions are known as the gaseous flame reactions. As for condensed phase inhibition, there are several rather distinct possible modes of action.

In some cases, flame retardants lead to the release of reactive gaseous compounds into the combustion zone, which can replace highly active free radicals with less reactive free radicals. The less reactive free radicals slow the combustion process and reduce flame speed. In other cases, flame retardants can cause the evolution of a small particle "mist" during combustion. These small particles act as "third bodies" that catalyze free-radical recombination and hence chain termination. This mode of action is typical of halogenated flame retardants, which usually act by decomposing at high temperature to generate hydrogen chloride or hydrogen bromide. These compounds react with oxygenated radicals and inhibit gas phase combustion reactions (Cullis and Hirschler, 1981; Hirschler, 1982; Georlette et al., 2000).

Flame-retardant chemicals can also operate by releasing relatively large quantities of inert gas during decomposition, which can change the composition and temperature of gaseous polymer decomposition products. The resulting mixture of gaseous products and surrounding gaseous oxidants are no longer capable of propagating flame. In some systems, when the polymer burns the flame-retardant chemical is released chemically unchanged as a heavy vapor, which effectively "smothers" the flame by interfering with the normal interchange of combustible gaseous polymer decomposition products and combustion air or oxygen. This mode of action is typical of metal hydroxides, such as aluminum or magnesium hydroxide (Horn, 2000).

***Melting and Dripping*** – Some flame-retardant chemicals inhibit combustion by interfering with the transfer of heat from combustion back to the polymer. Certain chemicals may promote depolymerization, which lowers the molecular weight of the polymer and facilitates melting. As the burning melt drips away from the bulk of the polymer it carries with it a proportion of the heat that would otherwise contribute to polymer decomposition and volatilization. By reducing the release of volatile decomposition products into the gas phase, these flame retardants reduce the amount of gaseous decomposition products available to feed the flame. While enhanced melting should decrease flammability in theory, in practice droplets of burning molten polymer may help spread a fire to other combustible materials.

***Ablation*** – Combustion can also be retarded by coating or constructing the polymer in such a way that, when it burns, incandescent sections disintegrate from the original polymer and remove with them heat from the combustion zone. This mechanism of action, known as ablation, is in a sense the solid phase parallel of liquid phase melting and dripping. A surface char layer is frequently formed, which isolates the bulk of the polymer material from the high temperature environment. This charry layer remains attached to the substrate for at least a short period while a degradation zone is formed underneath it. In this zone, the organic polymer undergoes melting, vaporization, oxidation, or pyrolysis. The ablative performance of polymeric materials is influenced by polymeric composition and structure, as well as environmental factors, such as atmospheric oxygen content. Higher hydrogen, nitrogen, and oxygen content of the polymer increases the char oxidation rate; higher carbon content decreases the char oxidation rate (Levchik and Wilkie, 2000).

### Smoldering (Non-Flaming) Combustion

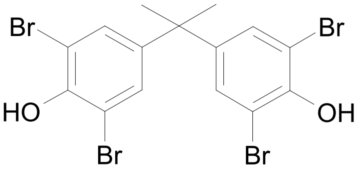
Smoldering (non-flaming) combustion and the closely related phenomenon of glowing combustion occur primarily with high-surface area polymeric materials that break down during combustion to form a residual carbonaceous char (typically cellulosic materials). In general, it is possible to inhibit non-flaming combustion either by retarding or preventing the initial breakdown of the polymer to form a char, or by interfering with the further combustion of this char. Boric acid and phosphates are the primary flame retardants used for preventing non-flaming combustion of organic polymers.

## 3.2 Flame-Retardant Chemicals Currently Used in FR-4 Laminates

Over the last several years, the electronics industry has been increasingly focused on researching and developing halogen-free alternatives to TBBPA, due in large part to environmental concerns and the anticipation of possible regulatory actions in the European Union. Several flame-retardant chemicals are commercially available to meet fire safety standards for Flame Resistant 4 (FR-4) laminates. As of 2008, the halogenated flame retardant TBBPA is used in approximately 90 percent of FR-4 PCBs. The majority of halogen-free alternatives to TBBPA are based on phosphorus compounds that are directly reacted into the epoxy resin or combined with aluminum trioxide or other fillers (De Boysère and Dietz, 2005). This section briefly discusses TBBPA, dihydrooxaphosphaphenanthrene (DOPO), Fyrol PMP, and four commonly used halogen-free fillers: aluminum hydroxide, melamine polyphosphate, metal phosphinate, and silica. In this report, these four fillers are also referred to as additive flame retardants.

### Reactive Flame-Retardant Chemicals

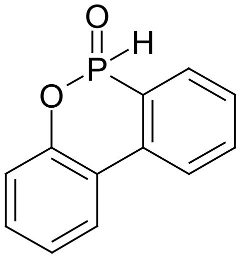
#### *TBBPA*



TBBPA is a crystalline solid with the chemical formula $C_{15}H_{12}Br_4O_2$. TBBPA increases the glass transition temperature ($T_g$) of the epoxy resins and enables the resin to achieve a UL (Underwriters Laboratories) 94 V0 flammability rating. TBBPA is most commonly reacted into the epoxy resin through "chain extension," meaning TBBPA is reacted with a molar excess of diglycidyl ether of bisphenol A, or other similar epoxy. Once the TBBPA is chemically bound, the finished epoxy resin typically contains about 18 to 21 percent bromine (Weil and Levchik, 2004).

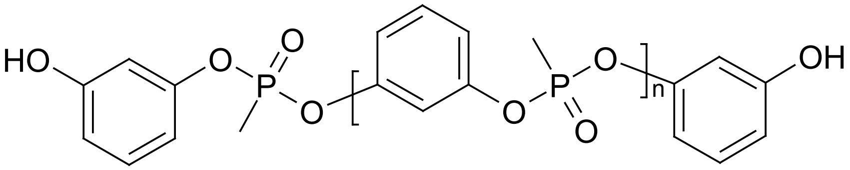
TBBPA is produced by several flame retardant manufacturers. According to High Density Packaging User Group International (2004) and Morose (2006), TBBPA's market dominance is due primarily to its moisture resistance, thermal stability, cost-effectiveness, compatibility with the other components of PCBs, and ability to preserve the board's physical properties. Aside from PCBs, another primary application of TBBPA is its use as an additive flame retardant in the acrylonitrile-butadiene-styrene resins found in electronic enclosures of televisions and other products.

### *DOPO*



DOPO is a hydrogenphosphinate made from *o*-phenyphenol and phosphorus trichloride. Similar to TBBPA, it can be chemically reacted to become part of the epoxy resin backbone. DOPO was originally developed as a flame retardant for polyester textile fibers and also has applications as an antioxidant-type stabilizer (Weil and Levchik, 2004). Due to DOPO's higher cost (nearly four times as much as TBBPA at the time this partnership was convened), its use has been limited by laminate manufacturers. To decrease the cost of their formulations, some laminate manufacturers are using DOPO in combination with less expensive materials such as alumina trihydrate (ATH) and/or silica (Thomas et al., 2005) or along with more cost-effective compounds like metal phosphinates (De Boysère and Dietz, 2005).

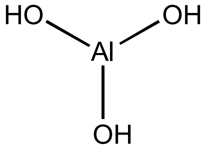
### *Fyrol PMP*



Fyrol PMP is an aromatic phosphonate oligomer with high phosphorus content (17 to 18 percent). Similar to TBBPA and DOPO, Fyrol PMP can be chemically reacted to become part of the epoxy resin backbone. When reacted into a phenol-formaldehyde novolak epoxy, Fyrol PMP provides good flame retardancy at loadings as low as 20 percent (Weil, 2004).

## Flame-Retardant Fillers

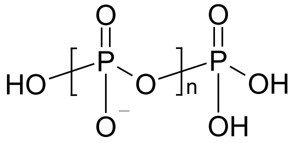
### *Aluminum Hydroxide*

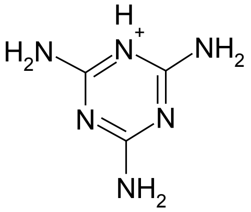


While the use of aluminum hydroxide ($Al(OH)_3$) in FR-4 PCBs was relatively low several years ago, it was the largest volume flame retardant used worldwide, with an estimated 42 percent volume market share in 2006 (BCC, 2006). Aluminum hydroxide is commonly referred to as ATH and has been used to impart flame retardancy and smoke suppression in carpet backing, rubber products, fiberglass-reinforced polyesters, cables, and other products. It is also used in the manufacture of a variety of items – antiperspirants, toothpaste, detergents, paper, and printing inks – and is used as an antacid.

ATH is difficult to use alone to achieve the FR-4 rating of laminates, and as a result, high loadings relative to the epoxy resin, typically up to 60 to 70 percent by weight, are needed (Morose, 2006). ATH is most commonly used in FR-4 PCBs as a flame-retardant filler, in combination with DOPO or other phosphorus-based compounds. When heated to 200-220°C, ATH begins to undergo an endothermic decomposition to 66 percent alumina and 34 percent water (Morose, 2006). It retards the combustion of polymers by acting as a “heat sink” – i.e., by absorbing a large portion of the heat of combustion (HDPUG, 2004).

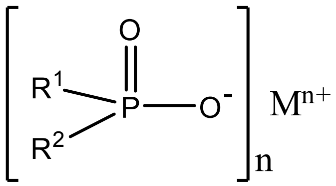
### *Melamine Polyphosphate*





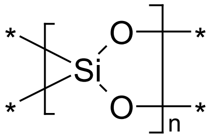
Melamine polyphosphate, an additive-type flame retardant based on a combination of phosphorus and nitrogen chemistries, is typically used as crystalline powder and in combination with phosphorus-based compounds. Its volume market share in 2006 was slightly more than 1 percent (BCC, 2006) but is expected to increase as the demand for halogen-free alternatives increases. Similar to ATH, melamine polyphosphate undergoes endothermic decomposition but at a higher temperature (350°C). It retards combustion when the released phosphoric acid coats and therefore forms a char around the polymer, thus reducing the amount of oxygen present at the combustion source (Special Chem, 2007). Melamine polyphosphate does not negatively impact the performance characteristics of standard epoxy laminates, and functions best when blended with other non-halogen flame retardants (Kaprinidis, 2008). Melamine polyphosphate dissociates in water to form melamine cations and phosphate anions.

***Metal Phosphinates***



Flame retardants based on phosphinate chemistry were a relatively new class of halogen-free flame retardants on the market at the time this partnership was convened. One such phosphinate-based flame retardant – aluminum diethylphosphinate – is a fine-grained powder with high phosphorus content (23 to 24 percent) used as a filler in FR-4 laminates (De Boysère and Dietz, 2005). It is designed primarily for use in FR-4 laminate materials with $T_g$ greater than 150°C (mid-range and high $T_g$ applications). Like most phosphorus-based compounds, metal phosphinates achieve flame retardancy by forming a char barrier upon heating, thereby cutting off access to the oxygen needed for the combustion process. Due to its low density and high surface area, aluminum diethylphosphinate cannot be used alone. It is typically used as a powerful synergist in combination with modified resins and sometimes other filler-type flame retardants.

***Silica***



Also known as silicon dioxide ($SiO_2$), silica is characterized by its abrasion resistance, electrical insulation, and high thermal stability. Silica is not a flame retardant in the traditional sense. It dilutes the mass of combustible components, thus reducing the amount of flame retardant necessary to pass the flammability test. Silica is most commonly used in combination with novolak-type epoxy resins. For example, silica clusters can be reacted with phenolic novolak resins (the resin bonds to hydroxyl groups on the silica cluster) to form a silica-novolak hybrid resin (Patent Storm, 2002). It can be used as an inert, low expansion material in both the epoxy resin and electronic circuit. One drawback is its abrasiveness, which affects drilling operation during the PCB manufacturing process.

***Magnesium Hydroxide***

HO−Mg−OH

Magnesium hydroxide is functionally similar to ATH, in that it endothermically decomposes at high temperatures to produce an oxide (MgO) and water. The absorption of heat retards the combustion of polymers, and the release of water may create a barrier that prevents oxygen from supporting the flame (Huber, 2007). However, whereas ATH undergoes thermal decomposition at 200-220°C, magnesium hydroxide decomposes at approximately 330°C. This allows manufacturers to use magnesium hydroxide when processing temperatures are too high for ATH (Morose, 2006). Similar to ATH, high loadings of magnesium hydroxide are required to achieve the FR-4 rating. In many polymer systems, in order to reduce loadings, magnesium hydroxide is sometimes combined with more effective flame retardants, such as phosphorus (Morose, 2006).

## Other Chemicals

Following is a brief description of other chemicals that can be used as flame retardants in FR-4 PCBs but are not evaluated in this paper.

### *Ammonium Polyphosphate*

Ammonium polyphosphate is an intumescent flame retardant, meaning that it swells when exposed to heat, and can be used in epoxies. However, it is not commonly used in electronic applications. At high temperatures (>250°C), ammonium polyphosphate decomposes into ammonia and polyphosphoric acid. When exposed to water, polyphosphate reacts to form monoammonium phosphate, a fertilizer (Chemische Fabrik Budenheim, 2007).

### *Red Phosphorus*

Red phosphorus is produced from white phosphorus by heating white phosphorus in its own vapor to 250°C in an inert atmosphere. It is fairly stable and is used in the manufacture of several products, such as matches, pesticides, and flame retardants (Lide, 1993; Diskowski and Hofmann, 2005). Its main use as a flame retardant is in fiberglass-reinforced polyamides. Although it does function in epoxy resins, it is not recommended for electronic applications, because red phosphorus can form phosphine ($PH_3$) and acidic oxides under hot and humid conditions (Clariant, 2002). The oxides can lead to metal corrosion, and hence electric defects can occur (Clariant, personal communication 2007).

### *Antimony Oxide*

Antimony oxide, typically antimony trioxide ($Sb_2O_3$), can be used as a flame retardant in a wide range of plastics, rubbers, paper, and textiles. Antimony trioxide does not usually act directly as a flame retardant, but as a synergist for halogenated flame retardants. Antimony trioxide enhances the activity of halogenated flame retardants by releasing the halogenated radicals in a stepwise manner. This retards gas phase chain reactions associated with combustion, which slows fire spread (Hastie and McBee, 1975; Hirschler, 1982; Chemical Land 21, 2007).

### *Melamine Cyanurate*

Melamine cyanurate is relatively cheap and highly available. However, it is a poor flame retardant and requires high dosage (>40 percent weight) (Albemarle, 2007).

## 3.3 Next Generation Research and Development of Flame-Retardant Chemicals

Some companies are already offering halogen-free alternatives to TBBPA. In 2008, JJI Technologies, for example, is developing new activated, non-halogen flame-retardant formulations for PCBs – both additive and reactive. An activated flame retardant is one that provides enhanced flame retardancy through the incorporation of an activator, which may consist of either a char-forming catalyst or phase-transfer catalyst or both. Activated flame retardants may improve flame-retardant features, including faster generation of char, higher char yield, denser char, self-extinguishing performance, thermal insulation, and lower smoke emissions (JJI Technologies, 2007).

In addition to halogen-free alternatives to TBBPA, flame retardant manufacturers have beenexploring ways to achieve a V0 rating in the UL 94 fire test result through the redesign of flame-retardant chemicals and epoxy resin systems. One of the largest areas of research and development involves the use of nanotechnology to impart flame retardancy and increased functionality to PCBs and other electronics products. However, their technical and commercial viability is still limited, and their future use in commercial settings remains unknown. So far, only combinations of nano flame retardants with traditional flame retardants have met performance requirements. In addition, these new nano-traditional flame-retardant combinations are only usable in certain polymer systems.

One type of halogen-free nano flame retardant is being developed through the synthesis of ethylene-vinyl acetate copolymers with nanofillers (or nanocomposites) made of modified layered silicates (Beyer, 2005). Nanofillers are incorporated into the olefin polymer during the polymerization process by treating the surface of the nanofiller to induce hydrophobic tendencies. The hydrophobic nanofiller disperses in the olefin monomers, which then undergo polymerization and trap the nanofillers (Nanocor, 2007). Nanocomposites can also incorporate aluminum into their structures, and can be combined with additive flame retardants, such as ATH, leading to a reduction of the total ATH content and a corresponding improvement in mechanical properties (Beyer, 2005).

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