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CHEMICAL STRATEGIES FOR FIREPROOFING POROUS FLAMMABLE MATERIALS: ADVANCES, APPLICATIONS, AND ENVIRONMENTAL CONSIDERATIONS

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Purpose. This paper provides a comprehensive overview of the chemical strategies used for fireproofing porous flammable materials. It aims to synthesize recent advances, outline key mechanisms of action, and evaluate the environmental and health implications of different flame retardant classes. The work addresses the urgent need for balancing fire safety with sustainability and regulatory compliance.

Methods. A systematic review of peer-reviewed research, standards, and technical reports from 2018 to 2024 was conducted. Data sources included scientific journals, regulatory documents, and industry guidelines. The analysis covered halogenated and halogen-free flame retardants, nanostructured systems, bio-based chemicals, and hybrid approaches. Special focus was given to studies employing advanced characterization techniques, cone calorimetry, thermal analysis, and life cycle assessment.

Findings. Halogenated flame retardants remain effective but are increasingly restricted due to toxicity and environmental persistence. Halogen-free alternatives, such as ammonium polyphosphate, aluminum diethyl phosphinate, DOPO[1] derivatives, and bio-based systems, show promising performance, especially when combined with nanomaterials or reactive chemistries to enhance stability. Innovative solutions, including metal-organic frameworks, graphene derivatives, and phytic acid-based coatings, are emerging for improved efficacy and lower ecological footprint. However, scalability, cost, and long-term durability remain challenges. The porosity of materials introduces specific issues such as leaching and off-gassing, necessitating careful selection and application methods. Regulatory frameworks like REACH[2] and the Stockholm Convention[3] play a decisive role in guiding safer chemical adoption.

Application field of research. Developing safer and more sustainable fire protection strategies in the age of advanced materials and growing ecological awareness.

Keywords: fire retardants, porous materials, halogen-free flame retardants, nanomaterials, environmental safety.

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1. Introduction

Porous flammable materials play a central role in modern industrial applications due to their unique combination of lightweight structure, insulation capabilities, and design flexibility. Found in products ranging from furniture foams, packaging materials, and insulation boards to wearable fabrics, natural wood, paper, and high-performance polymeric aerogels, these materials are often selected for their functionality and efficiency. However, one of the most critical vulnerabilities of porous materials is their susceptibility to fire. The very features that make them desirable – high porosity, low thermal conductivity, and high surface area – also make them inherently more combustible and capable of propagating flames rapidly once ignited [1].

The behavior of porous materials under fire conditions is distinct from that of dense or compact materials. Their interconnected pore structures allow for the easy diffusion of air (oxygen), volatile gases, and heat, which accelerates ignition and combustion. Once initiated, fire spreads quickly within the porous network, releasing smoke, toxic gases, and potentially lethal heat [1]. This presents a considerable risk not only in domestic and commercial environments but also in

[1] 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (*DOPO*) is an organophosphorus compound that is used to produce fire retardants.

[2] Registration, Evaluation, Authorisation and Restriction of Chemicals (*REACH*) – Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006.

[3] *Stockholm Convention* on Persistent Organic Pollutants is an international environmental treaty, signed on 22 May 2001 and effective from 17 May 2004, that aims to eliminate or restrict the production and use of persistent organic pollutants.

critical sectors such as transportation, aerospace, defense, and construction. For instance, in residential buildings, upholstered furniture and insulation foams are often involved in early fire development stages due to their porous and flammable nature. In aircraft interiors, composite foams must meet strong fire safety regulations to prevent disaster in the event of electrical faults or engine overheating [2].

Given these risks, substantial efforts have been invested in enhancing the fire resistance of porous flammable materials. While physical barriers such as metal cladding or fire-resistant fabrics can offer some protection, these methods are often limited in effectiveness, flexibility, and cost-efficiency. In contrast, chemical fireproofing – using substances that interrupt the combustion process through thermal, physical, or chemical means – provides a versatile and effective solution. Chemical fire retardants can be tailored to operate through various mechanisms, such as absorbing heat, releasing water or inert gases, promoting char formation, or interfering with flame-propagating radicals [1]. Moreover, they can be applied through multiple techniques including impregnation, surface coating, and chemical bonding, making them compatible with different types of porous substrates.

The challenge, however, lies in balancing fire performance with environmental and mechanical considerations. Traditional flame retardants, particularly halogenated compounds, have come under increasing scrutiny due to their toxicity, persistence in the environment, and potential for bioaccumulation [3; 4]. These concerns have led to regulatory restrictions and the development of safer, halogen-free alternatives. Furthermore, many flame retardants affect the mechanical properties, processability, and durability of the materials to which they are added. For example, mineral-based retardants require high loading levels that can compromise structural integrity, while some reactive phosphorus-based compounds may cause discoloration or surface degradation over time [5].

As a result, the field of chemical fireproofing is evolving rapidly, with a growing focus on multifunctional systems that not only resist combustion but also preserve or enhance the performance of the host material. Nanotechnology and material science innovations have introduced a new generation of flame retardants, including layered silicates, carbon-based nanostructures like graphene, and hybrid materials such as metal-organic frameworks (MOFs) [3]. These substances offer the potential for improved dispersion, greater efficiency at lower loadings, and added functionalities such as thermal conductivity, mechanical reinforcement, and even antimicrobial properties. Biobased flame retardants derived from natural polymers, DNA, and other renewable sources are also being explored as eco-friendly alternatives [6; 7].

This review aims to provide a comprehensive, critical analysis of chemical fireproofing methods applicable to porous flammable materials. In the sections that follow, we delve into the classification of fire retardants by their chemical mechanism and mode of action, examine application techniques specific to porous structures, and discuss the latest research developments including nanomaterial-enhanced and biobased systems. We also evaluate the environmental and regulatory landscape shaping the adoption and development of these technologies. Our goal is to offer insights that inform both academic research and industrial implementation, contributing to safer, more sustainable fire protection strategies in the age of advanced materials and growing ecological awareness.

2. Classification of fire-retardant chemicals and mechanisms

Fire retardants can be broadly categorized based on their chemical composition and mechanisms of action. Their ability to inhibit, suppress, or delay combustion varies depending on their interactions with the thermal degradation pathways of the host material. The six major groups discussed here are mineral-based additives, organophosphorus compounds, halogenated substances, intumescent systems, graphene-based nanomaterials, and MOFs [8–11].

2.1. Mineral-based endothermic additives. Mineral fillers are inorganic particulate materials added to polymers or composites to improve mechanical and thermal properties, reduce cost, and enhance flame retardancy. They such as aluminum hydroxide and magnesium hydroxide are among the most widely used fire retardants. Their primary function is to undergo endothermic decomposition upon heating, releasing water vapor that dilutes combustible gases and absorbs heat from the system [12]. The resulting residue forms a protective barrier that limits further pyrolysis.The flame-retardant mechanism of Mineral fillers have shown in Figure 1. The flame-retardant mechanism of aluminum hydroxide starts decomposing around 180 °C, while magnesium hydroxide functions at slightly higher temperatures (~300 °C), making each suitable for different polymer systems. For porous foams and insulation materials, these mineral fillers are often integrated into the polymer matrix at high loadings (typically 40–60 % by weight), which can compromise mechanical properties like flexibility and tensile strength [13]. Despite this drawback, mineral-based fire retardants are favored for their non-toxicity, low smoke emission, and environmental friendliness. They are commonly used in rigid polyurethane (PU) foams, ethylene-vinyl acetate composites, and wood-plastic composites [14].

2.2. Organophosphorus compounds. Organophosphorus flame retardants (OPFRs) are widely used in both halogen-free and intumescent systems due to their dual action in the condensed and gas phases, this has been demonstrated by both experimental and theoretical calculations [15]. In the condensed phase, they promote char formation by catalyzing dehydration reactions, whereas in the gas phase, they scavenge flame-propagating radicals (e.g., OH· and H·) [1]. The flame-retardant mechanism of OPFRs is presented in Figure 2*a*. Ammonium polyphosphate (APP), triphenyl phosphate, and aluminum diethyl phosphinate (AlPi) are notable examples. APP is especially popular in intumescent coatings used for porous wooden substrates, where it supports foamed char development under heat [3; 4]. AlPi is often used in thermoplastics and foamed polyamides due to its thermal stability and low volatility. A significant advantage of OPFRs is their relatively low environmental toxicity compared to halogenated systems. However, their potential for migration from porous matrices and their interaction with humidity can reduce long-term durability. Encapsulation and grafting techniques are being explored to mitigate these issues [4].

2.3. Halogenated flame retardants (HFRs), particularly brominated and chlorinated compounds, function by releasing halogen radicals during combustion. These radicals intercept the combustion chain reaction by neutralizing high-energy flame radicals. The flame-retardant mechanism of HFRs is presented in Figure 2*b*. Tetrabromobisphenol A and decabromodiphenyl ether have historically been used in foamed insulation and upholstered furniture [3]. While HFRs are highly effective at low loadings, their environmental impact has led to widespread regulatory scrutiny. They have been associated with endocrine disruption, persistent organic pollutants behavior, and bioaccumulation [16]. The European Union and U.S. Environmental Protection Agency have listed several HFRs under restriction due to these concerns. Their use in porous materials is declining in favor of halogen-free alternatives, but legacy applications and recycling challenges continue to pose risks. Moreover, combustion of HFR-treated materials often leads to the formation of toxic gases like hydrogen bromide, posing serious risks during fires [17].

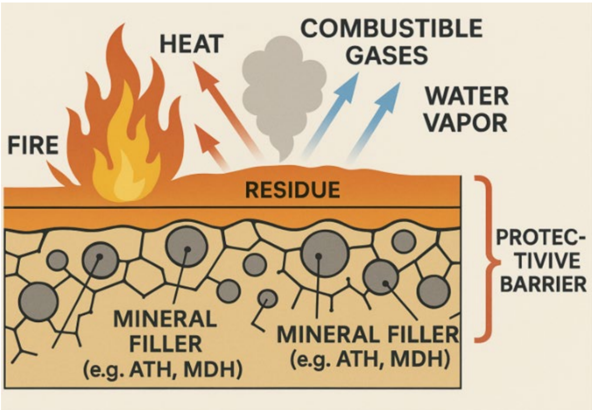
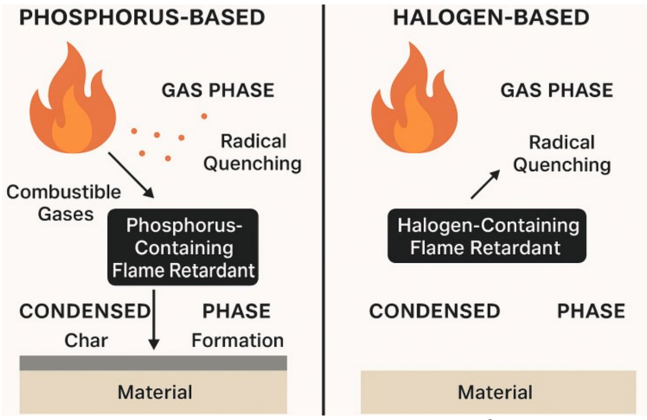


Figure 1. – The flame-retardant mechanism of Mineral fillers



a *b*

Figure 2. – The flame-retardant mechanism of OPFRs (*a*) and HFRs (*b*)

2.4. Intumescent flame retardants (IFRs) form a swollen, thermally insulating char layer when exposed to fire. Typically comprising an acid source (e.g., APP), a carbon source (e.g., pentaerythritol), and a blowing agent (e.g., melamine), these systems are particularly effective for porous wood and cellulose-based materials [4]. The mechanism involves the acid catalyzing dehydration of the carbon source while the blowing agent generates inert gases, expanding the matrix into a foamed char. This barrier protects the underlying material from heat and oxygen. The flame-retardant mechanism of IFRs have shown in Figure 3. IFRs can be applied as surface coatings or embedded within porous foams using impregnation techniques. Recent advancements have focused on enhancing the mechanical durability and water resistance of IFR coatings through cross-linking agents and hybrid nanofillers such as layered double hydroxides and graphene oxide [18].

2.5. Graphene-based fire retardants. Graphene and its oxidized form, graphene oxide, offer promising fire retardant properties due to their high aspect ratio, mechanical strength, and ability to form dense, impermeable layers that hinder heat and gas transfer [1]. When incorporated into porous polymeric systems via spray coating or layer-by-layer (LBL) assembly, graphene acts as a barrier to volatile degradation products and external oxygen. It also promotes graphitization of the char, increasing thermal stability [3]. The flame-retardant mechanism of graphene is illustrated in Figure 4. Graphene-based systems are often used in synergy with conventional flame retardants to lower overall loading levels. However, dispersion challenges and high production costs remain barriers to widespread adoption. Ongoing research is exploring functionalized graphene and eco-friendly exfoliation methods to overcome these limitations [6].

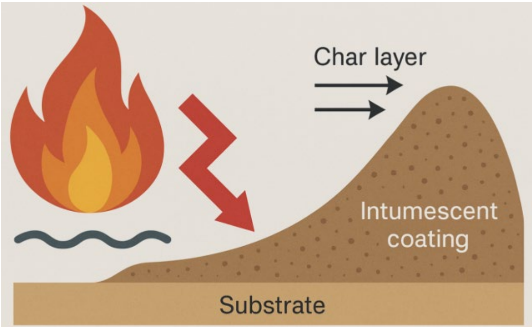


Figure 3. – The flame-retardant mechanism of IFRs

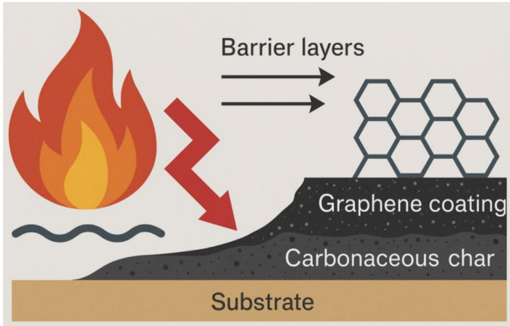


Figure 4. – The flame-retardant mechanism of Graphene

2.6. Metal-organic frameworks (MOFs) are crystalline hybrid materials composed of metal ions and organic ligands that form porous networks. Their tunable structure allows for the integration of fire retardant functionality via gas-phase radical capture, catalytic charring, or synergistic action with other retardants [2]. Recent studies have shown that incorporating MOFs into PU foams can reduce the peak heat release rate and delay ignition. Zeolitic imidazolate frameworks (ZIFs) and MIL-series MOFs are particularly promising due to their high thermal stability and ability to adsorb decomposition gases [19]. The flame-retardant mechanism of MOFs is illustrated in Figure 5. Challenges remain regarding the moisture sensitivity and scale-up of MOF production. However, their unique architecture and multifunctional performance have positioned MOFs as a frontier in next-generation flame retardancy for porous materials.

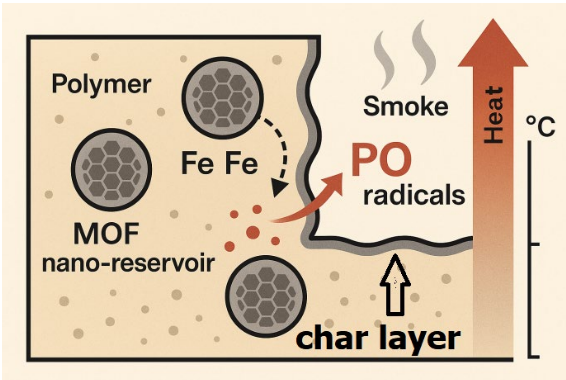


Figure 5. – The flame-retardant mechanism of MOFs

3. Application techniques for fire-retardant chemicals in porous materials

The performance of fire-retardant chemicals depends not only on their chemical structure and decomposition mechanism but also on the method of application to the porous material. Application techniques determine the depth of penetration, adhesion, long-term stability, and overall efficiency of the fire-retardant treatment. In porous flammable materials – such as foamed polymers, wood, textiles, and composite laminates – three major strategies are commonly used: impregnation, surface coating, and reactive incorporation. Each of these techniques presents its own set of advantages, limitations, and technological opportunities.

3.1. Impregnation methods. Impregnation involves the diffusion or forced penetration of fire-retardant solutions into the internal pore structure of the substrate. In wood products, this method is widely used in pressure-treatment processes, where chemicals such as borates or phosphate salts are driven deep into the wood under vacuum and pressure cycles [20]. This ensures long-lasting flame retardancy even when the surface is abraded or subject to mechanical wear. The effectiveness of impregnation depends heavily on the porosity, permeability, and hygroscopic nature of the substrate. Wood species with open grain structures, such as southern yellow pine, absorb treatment chemicals more uniformly compared to denser hardwoods. Cellulose-rich substrates, including paper insulation and cotton fabrics, also allow moderate penetration without significant structural degradation.

However, water-soluble fire retardants impregnated into porous structures often face challenges of leaching, especially in outdoor or high-humidity environments. Fire retardants based on ammonium salts, for instance, tend to migrate over time and lose effectiveness unless they are stabilized through polymeric encapsulation, sol-gel chemistry, or post-treatment curing [21]. As a result, current research is focused on hybrid impregnation systems that include both inorganic and organic binders to improve retention. In some advanced applications, supercritical CO_2 has been explored as a carrier for impregnating fire-retardant nanoparticles deep into porous foams and natural fibers. This approach offers excellent penetration while avoiding water-based swelling or distortion of the substrate. Moreover, it can be used to introduce multifunctional additives – such as UV absorbers and antimicrobial agents – alongside fire-retardant agents.

Table 1. – Summary of impregnation-based fire retardant treatments

Material type	Common chemicals used	Depth of penetration	Advantages	Limitations
Wood	Ammonium phosphate, boric acid	High	Uniform protection, deep reach	Susceptible to leaching
Cotton fabrics	Diammonium phosphate, urea mixes	Medium	Low cost, effective for textiles	Wash durability is low
Cellulose foams	Inorganic salts, silicates	Medium to high	Preserves texture	Moisture sensitivity, migration risk
Paper insulation	Borates, organophosphates	High	Lightweight, low-cost fire barrier	Requires lamination
Bio-based fibers	Modified starch + phytic acid	Medium	Sustainable, compostable	Durability under testing

3.2. Surface coatings. Surface coatings offer a straightforward method to apply flame-retardant chemicals directly onto porous substrates. They are especially suitable when the bulk properties of the material must remain unchanged or when high production throughput is required. Coatings may be applied via spraying, dipping, roll-to-roll processing, or brushing, depending on the scale and nature of the application [3]. The most widely used coatings are intumescent formulations that expand under heat to form insulating carbonaceous foams. These coatings are frequently applied to building insulation boards, wooden claddings, and foam-based insulation panels. However, the performance of such coatings is closely linked to the uniformity of coverage and thickness. Thin or poorly adhered coatings can crack or delaminate under fire exposure, compromising protection.

Recent developments have focused on the use of nanomaterials and hybrid coatings to improve fire resistance at the microscale. LBL assemblies, consisting of alternating polyelectrolyte and nanoplatelet layers, provide an exceptionally thin yet robust flame barrier. These are particularly beneficial for soft, flexible porous substrates like foams and textiles where bulk loading of flame retardants is impractical [3]. In addition to intumescent and LBL coatings, sol-gel techniques are also gaining attention. In these systems, a silica or alumina matrix is formed in situ to encapsulate the substrate in a ceramic-like layer. These coatings are advantageous for porous composite laminates or thermoset structures requiring long-term durability and resistance to weathering.

Table 2. – Comparison of coating types for porous substrates

Coating type	Mechanism	Suitable substrates	Fire performance	Durability factors
Intumescent coatings	Expand to form char barrier	Wood, textiles, polymers	Very good, depends on thickness	Susceptible to weathering
LBL nanocoatings	Barrier + radical scavenging	Foams, aerogels, fabrics	Excellent at nanoscale	Requires precision application
Sol-gel derived hybrids	Ceramic-like barrier formation	Thermoset composites	Moderate to high	High thermal stability
Silicone-elastomer films	Thermal shielding, flexibility	Flexible foams, wiring ducts	Good for mechanical stress	UV and aging resistance varies

A notable challenge in coating porous substrates lies in maintaining breathability and mechanical compliance. Overly rigid coatings may crack when the substrate is compressed or flexed. Researchers are investigating smart coatings that respond to stimuli such as heat or humidity by modifying their properties – such as softening to absorb impact or expanding more aggressively under thermal flux.

3.3. Reactive incorporation. In reactive incorporation, the flame-retardant chemical is covalently bonded to the polymer matrix during its synthesis. This method is highly desirable for porous polymeric foams, epoxy composites, and thermoset materials where additive migration would undermine long-term performance [5]. DOPO-based phosphonates and phosphinates are among the most commonly used reactive retardants. Their introduction during ring-opening or polyaddition polymerization allows them to become integral to the polymer backbone. This confers excellent thermal and mechanical stability, reduced smoke toxicity, and minimal impact on transparency or surface finish [5].

The use of reactive fire retardants is also being explored in combination with 3D printing and additive manufacturing of porous scaffolds. By embedding flame-retardant monomers in photocurable resins, researchers have fabricated lightweight, porous lattices with built-in flame resistance suitable for aerospace and biomedical applications [22–24]. Reactive systems, however, are typically more expensive and complex to formulate. They often require rigorous control of stoichiometry, pH, curing time, and catalyst presence. Additionally, once cured, these systems are difficult to recycle or reprocess, which may present a barrier in sustainability-conscious industries. In applications such as porous ceiling tiles, thermal insulation foam panels, and automotive interiors, hybrid strategies are emerging. These include combining reactive incorporation with outer coatings to provide both intrinsic and surface-level flame resistance. Multi-functional additives like silicon-phosphorus hybrids or phosphorus-nitrogen-silica networks are showing promise in this regard [23; 25]. In summary, the application technique for flame retardants in porous materials must be chosen with careful consideration of the target performance, substrate characteristics, environmental exposure, and manufacturing constraints. Table 3 below provides a consolidated summary of the techniques discussed in this section.

Table 3. – Summary of application methods for fire-retardant chemicals in porous materials

Method	Penetration depth, mm	Fire performance indicators*	Cost efficiency	Durability	Typical use cases
Impregnation	2–10 mm (medium to deep)	Flammability group: G2–G3; Ignition ability: B2; Independent combustion time: 30–60 s	Medium	Moderate	Wood panels, textiles, paper products
Surface coating	0.1–1 mm (shallow)	Flammability group: G2–G3; Ignition ability: B2; Independent combustion time: 20–40 s	High	Variable	Foam panels, fabrics, composite laminates
Reactive incorporation	Uniform through matrix	Flammability group: G1; Ignition ability: B1; Independent combustion time: ≤ 10 s	Low to medium	Very high	PU foams, epoxy boards, electronics

Note. * – Fire performance indicators are aligned with classifications from Russian GOST 30244-94[4], GOST 30402-96[5] and GOST 12.1.044-89[6]. In this context, the flammability group is referenced according to GOST 30244-94, the ignitability is referenced according to GOST 30402-96, and the independent combustion time is referenced according to GOST 12.1.044-89.

– «Flammability group» (G1–G4) ranks materials from low to high combustibility; «Ignition ability» (B1–B3) indicates ease of ignition; «Independent combustion time» measures self-sustained burning duration after flame removal.

– Values shown are typical ranges and may vary depending on substrate porosity, chemical formulation, and curing process.

By combining and customizing these methods, modern fire-retardant systems are achieving better integration with porous materials, higher multifunctionality, and longer service life – marking a significant advance in the field of passive fire protection [1; 26; 27].

4. Emerging technologies in fire retardancy for porous materials

As the demand for environmentally friendly, multifunctional, and high-performance fireproofing solutions grows, the field of flame retardancy is shifting toward the integration of advanced materials and new chemical architectures. Porous flammable substrates – due to their complexity and variety – benefit significantly from innovations that extend beyond traditional additive systems.

[4] GOST 30244-94. Building materials. Methods for combustibility test. – Ministry of Construction of Russia, 1996.

[5] GOST 30402-96. Building materials. Ignitability test method. – Ministry of Construction of Russia, 1996.

[6] GOST 12.1.044-89. Occupational safety standards system. Fire and explosion hazard of substances and materials. Nomenclature of indices and methods of their determination. – USSR, 1991.

This section examines some of the most promising emerging technologies, with a focus on nanotechnology, hybrid composites, biobased retardants, and intelligent flame-resistant systems. We also present comparative data in two comprehensive tables to clarify the properties, functions, and future potential of these innovations.

4.1. Graphene-based and 2D nanomaterial composites. Graphene and related two-dimensional nanomaterials such as boron nitride, graphene oxide, montmorillonite clays and MXenes[7] are at the forefront of nanotechnology-driven flame retardancy. These nanostructures possess exceptional thermal stability, high surface area, and the ability to form continuous barrier layers that impede heat, oxygen, and volatile products during combustion [1; 13]. A representative example is graphene oxide and its modified derivatives. When integrated into porous polymer foams, they forms compact networks that reduce flammability and thermal conductivity while also enhancing mechanical [28]. These materials are ideal for aerospace, automotive, and construction foams that require both strength and fire protection [1; 29].

Table 4. – Properties of selected 2D nanomaterials for flame retardancy

Material	Key properties	Flame retardant role	Compatibility
Graphene	High surface area, conductive, barrier-forming	Physical shield, char reinforcement	PU foams, epoxy
MXene	Thermal conductive, tunable chemistry	Heat dissipation, synergist	Thermoplastics, PU
Montmorillonite clay	High aspect ratio, ionic exchange capacity	Smoke suppression, intumescence	Fabrics, composites
Boron nitride nanosheets	Thermal insulation, oxidation resistance	Delay degradation, suppress heat	Electronic foams

Incorporating 2D materials requires dispersion strategies to avoid aggregation. Surface functionalization (e.g., silane or carboxylation) improves compatibility with polymer matrices. Several recent studies show that even 1–3 wt% of functionalized graphene or MXene can dramatically reduce peak heat release rates and increase time to ignition [3].

4.2. MOFs and hybrid metal–organic networks. MOFs represent a class of crystalline materials formed by coordinating metal ions with organic ligands. Their highly porous structures and tunable chemistry make them effective for catalyzing char formation, scavenging radicals, and enhancing thermal resistance [2]. When embedded in porous polymers such as PU, MOFs enhance flame retardancy through multiple pathways: 1) promoting early char formation; 2) releasing inert gases; 3) acting as sacrificial shields during decomposition [8]. Recent innovations include integrating MOFs with phosphorus or nitrogen elements to improve their compatibility and performance in foamed matrices [30]. Table 5 illustrates that different MOFs exhibit various flame-retardant effects in porous polymers, such as catalyzing char formation, releasing inert gases, scavenging radicals, and delaying heat release. These MOFs demonstrate strong synergistic interactions with complementary additives like APP, graphene oxide, or phytic acid, thereby enhancing flame-retardant performance across a range of substrate materials including polyurethane foams, epoxy resins, and polyesters.

Table 5. – MOFs for flame retardancy in porous polymers

MOF type	Flame retardant effect	Synergistic components	Target material
ZIF-8	Char catalyst, gas release	APP, AlPi	PU foams
MIL-101(Fe)	Smoke suppression, heat delay	Graphene oxide, DOPO	Epoxy/PU composites
UiO-66-NH2	Radical scavenger, crosslinking	Phytic acid, nitrogen polymers	Polyesters, PU coatings

Though highly effective, MOFs often face issues of moisture sensitivity and high synthesis costs. Researchers are now working on scalable synthesis and hybridizing MOFs with biopolymers to mitigate environmental concerns [12].

4.3. Biobased and Eco-Friendly Flame Retardants. Environmental regulations and increasing awareness of chemical toxicity have accelerated the development of bio-based flame retardants derived from renewable natural resources. These materials aim to replace halogenated or

[7] *MXenes* are a class of two-dimensional inorganic compounds, that consist of atomically thin layers of transition metal carbides, nitrides, or carbonitrides.

petroleum-based flame retardants, which often pose environmental persistence and toxicity concerns. Representative examples include phytic acid, commonly extracted from rice bran or other plant seeds, DNA obtained from marine biomass such as fish sperm, lignin sourced from cellulosic biomass and pulping residues, and casein, a milk-derived protein [31]. These biopolymers and biomolecules are intrinsically rich in phosphorus, nitrogen, and sometimes sulfur, allowing them to act as multi-functional flame retardants [32; 33]. During combustion, they can promote char formation, release non-flammable gases such as water vapor and ammonia, and dilute flammable volatiles, thereby reducing heat and smoke generation [6]. Moreover, their biodegradability and low toxicity align well with the principles of green chemistry and circular materials engineering. For porous substrates such as cotton fabrics, wood, and bio-based polymer foams, these natural flame retardants can be integrated through impregnation (soaking), LbL self-assembly, or covalent reactive grafting to form protective, intumescent coatings. However, despite their environmental advantages, challenges remain in achieving long-term durability, washing resistance, and mechanical integrity, particularly under humid or high-temperature conditions. Ongoing research is therefore focused on crosslinking strategies, hybridization with inorganic nanoparticles, and surface modification techniques to enhance the stability and practical applicability of these promising green flame-retardant systems.

4.4. Smart and stimuli-responsive flame retardants. Next-generation flame retardants are being designed with intelligent response behaviors. These systems undergo structural or phase changes when triggered by heat, UV light, or pH [34; 35]. One emerging class is the polymer-particle hydrogel that expands into a porous flame-retardant dome when heated, offering temporary but robust insulation during wildfires [20]. These systems hold promise for protecting structures in extreme conditions – such as aerospace re-entry, battery fires, or wildland-urban interfaces. Some experimental approaches are also exploring shape-memory intumescent coatings and phase-changing protective foams [36–38]. In summary, the landscape of flame retardants for porous materials is rapidly advancing through nanotechnology, green chemistry, and intelligent design. Each of these emerging systems introduces new functionalities beyond mere flame suppression, such as structural reinforcement, environmental safety, or fire sensing.

5. Environmental and health considerations of fire retardant chemicals

The application of chemical fire retardants has indisputably contributed to fire safety across a vast range of industrial and domestic settings. However, their deployment, especially in porous flammable materials, raises complex environmental and health challenges that are increasingly difficult to ignore. Porous materials, by virtue of their microstructure, not only absorb flame retardants deeply but also provide pathways for the long-term emission, degradation, and migration of these chemicals into surrounding environments [39; 40]. This has led to growing concerns about toxicity, persistence, bioaccumulation, and unintended human and ecological exposure.

One of the most pressing concerns in the use of fire retardants involves halogenated compounds, particularly polybrominated diphenyl ethers (PBDEs) and tetrabromobisphenol A. These compounds have been widely used for decades due to their high flame-retardant efficiency, particularly in polyurethane foams, electronics, and textiles [21; 41–43]. However, extensive toxicological studies have linked PBDEs to a range of adverse health outcomes, including neurotoxicity, endocrine disruption, reproductive disorders, and developmental issues in children [13; 43]. Their lipophilicity and environmental persistence make them prone to bioaccumulation, allowing them to travel through the food chain and persist in human tissues over extended periods. In indoor environments where porous materials are used – such as mattresses, upholstered furniture, and acoustic panels – PBDEs can gradually escape as vapor or attach to airborne particles and dust, leading to chronic low-dose exposure through inhalation or ingestion, particularly among infants and children [18].

Compared to their halogenated counterparts, halogen-free flame retardants like AlPi, APP, and DOPO-based derivatives offer a more favorable environmental and health profile. These compounds typically break down into less toxic byproducts and are not prone to bioaccumulation. For example, APP, widely used in intumescent coatings, decomposes into polyphosphoric acid and water [44], forming a stable char that insulates the material beneath while avoiding the release of toxic gases or smoke [45]. Similarly, DOPO-based reactive agents, when integrated into epoxy or polyester matrices, have shown minimal migration potential due to their covalent bonding within the polymer backbone [5; 6]. Still, the classification of halogen-free retardants as «safe» can be misleading. Several organophosphorus-based compounds exhibit aquatic toxicity at certain concentrations or may form undesirable degradation products under high heat, particularly when used in open, porous structures exposed to humidity or mechanical wear.

To support this analysis, Table 6 presents a comparative evaluation of several commonly used flame retardants across key environmental and toxicological parameters, including human toxicity, environmental persistence, bioaccumulation potential, and their relative safety profiles when applied to porous substrates.

Table 6. – Comparative environmental and health profiles of selected flame retardants

Flame retardant	Classification	Human toxicity	Environmental persistence	Bioaccumulative	Remarks
PBDEs	Halogenated	High	High	Yes	Banned in EU; still found in old foams
Tetrabromobisphenol A	Halogenated	Moderate	Medium	Possible	Still used in electronics
APP	Halogen-free	Low	Low	No	Common in intumescent systems
AlPi	Halogen-free	Low to moderate	Low	No	Used in thermoplastics
DOPO derivatives	Halogen-free	Low	Low	No	Chemically bonded to matrix
Phytic acid (biobased)	Halogen-free	Very low	Biodegradable	No	Sustainable alternative

The porosity of a material significantly influences the behavior of fire retardants in environmental contexts. Unlike nonporous materials, porous substrates such as foams, wood composites, nonwoven fabrics, and cellulose-based insulation have larger surface-to-volume ratios and open channels that promote capillary movement [1; 46]. When these materials are treated with water-soluble fire retardants like borates or phosphate salts, the chemicals are at risk of leaching due to exposure to rain, cleaning processes, or even ambient humidity. Over time, this not only reduces fire resistance but also facilitates the transport of chemicals into soil and water systems, potentially contaminating local ecosystems [30]. On the other hand, more hydrophobic or encapsulated formulations have been developed to mitigate such issues. For instance, microencapsulation techniques now allow for embedding fire retardants in polymeric shells, releasing the active agents only under elevated temperatures. This controlled-release strategy helps to minimize environmental release during normal use and ensures functionality only in the event of fire [47; 48].

Despite these technological advances, the need for comprehensive lifecycle assessments of fire retardant-treated porous products is greater than ever. Lifecycle assessments consider the environmental impacts of a product from raw material extraction to disposal. For fire retardants, this includes emissions during production, potential release during product use, end-of-life treatment (e.g., incineration or landfilling), and recycling constraints [49]. For instance, brominated retardants in foamed plastics create major barriers to recycling because they contaminate melt streams and can lead to toxic byproducts during thermal processing [50; 51]. Furthermore, materials that incorporate chemically reactive or crosslinked retardants are often non-recyclable, prompting concerns about long-term sustainability [52].

In response to these concerns, regulatory frameworks across the globe have become increasingly strict. The European Union's REACH regulation mandates rigorous evaluation of chemical safety, resulting in the banning or phase-out of several high-risk flame retardants such as decabromodiphenyl ether and hexabromocyclododecane (HBCD) [53; 54]. Meanwhile, the Stockholm Convention – a global environmental treaty – has classified PBDEs and HBCD as persistent organic pollutants, leading to their elimination or severe restriction in many signatory countries [55; 56]. In the California's TB117-2013[8] regulation marked a major shift by eliminating the requirement for furniture to pass an open flame test, thereby enabling manufacturers to reduce or eliminate HFR use without compromising fire safety [16; 17].

Alongside regulatory restrictions, green certification programs have emerged as influential drivers for the adoption of safer fire retardant technologies. Programs such as *GREENGUARD*, *Blue Angel*, and *Cradle to Cradle Certified* assess the chemical emissions of materials and their potential

[8] Technical Bulletin 117-2013. Requirements, test procedure and apparatus for testing the smolder resistance of materials used in upholstered furniture. – United States, California, Department of Consumer Affairs, 2013.

impacts on indoor air quality, resource safety, and material reuse [57–59]. Products incorporating halogen-free or reactive flame retardants that demonstrate low emissions and safe end-of-life processing are more likely to meet these standards, thus gaining broader market acceptance in sustainability-driven industries such as green building and consumer products.

Table 7. – Summary of regulatory and certification frameworks related to flame retardants

Framework/Standard	Region	Focus area	Impact on flame retardant use
REACH	European Union	Chemical safety, registration	Bans many halogenated flame retardants
Stockholm Convention	Global	Persistent organic pollutants	Restricts PBDEs, HBCD, promotes safe alternatives
TB117-2013	California, USA	Flammability standard	Supports halogen-free compliance for furniture
GREENGUARD	Global	Indoor air quality	Encourages low-emission flame retardants
Cradle to Cradle Certified™	Global	Product lifecycle safety	Rewards safer chemistry and recyclability
Blue Angel (Der Blaue Engel)	Germany	Eco-label for products	Restricts toxic additives in consumer goods

Table 7 demonstrates that regulatory frameworks and certification programs play a crucial role in guiding the development and adoption of safer and more environmentally friendly flame retardants. These frameworks not only impose regulatory pressure but also shape innovation trends in flame-retardant materials toward safer, low-emission, and more sustainable solutions, thereby promoting the transition toward green chemistry and a circular economy within the materials industry.

6. Conclusion

The fireproofing of porous flammable materials using chemical flame retardants is a critical field of study that blends chemistry, materials engineering, toxicology, and environmental science. Throughout this review, we have explored a wide range of chemical classes – from halogenated and halogen-free systems to advanced nanostructured and bio-based flame retardants – and analyzed their modes of action, application methods, performance profiles, and environmental implications.

In particular, halogenated flame retardants, while historically effective, are now under global scrutiny for their toxicological effects and persistence in ecosystems. In contrast, halogen-free compounds such as ammonium polyphosphate, aluminum diethyl phosphinate, and DOPO derivatives show promise as safer alternatives, particularly when used in synergy with nanomaterials or reactive polymers that reduce their migration and leaching. Moreover, surface treatments, impregnations, and chemical grafting tailored to porous structures are proving essential to enhance adhesion and long-term retention of flame retardants.

Recent innovations, including the integration of metal-organic frameworks, two-dimensional materials (e.g., graphene oxide, MXenes), and phytic acid-based biopolymers, offer exciting new directions. These systems promise not only superior flame retardancy but also lower ecological footprints. However, their industrial scalability, long-term durability, and regulatory acceptance remain challenges to be addressed.

Environmental and health concerns must remain at the center of flame retardant development. The porosity of materials amplifies issues like leaching, off-gassing, and human exposure, particularly in indoor applications. Regulatory frameworks like REACH and the Stockholm Convention, along with green certification programs, play an increasingly influential role in shaping safer chemical use. Lifecycle assessments should be routinely applied to ensure that materials remain safe not only during fire incidents but throughout production, use, and disposal.

As the industry moves toward circularity and carbon neutrality, future flame retardants must be inherently safe, high-performance, and sustainable. The path forward will depend on collaborative efforts between researchers, manufacturers, and regulators to ensure that porous materials can be effectively and responsibly protected against fire.

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Chemical strategies for fireproofing porous flammable materials: advances, applications, and environmental considerations

Химические стратегии огнезащиты пористых огнеопасных материалов: достижения, применение и экологические соображения

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ХИМИЧЕСКИЕ СТРАТЕГИИ ОГНЕЗАЩИТЫ ПОРИСТЫХ ОГНЕОПАСНЫХ МАТЕРИАЛОВ: ДОСТИЖЕНИЯ, ПРИМЕНЕНИЕ И ЭКОЛОГИЧЕСКИЕ СООБРАЖЕНИЯ

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Цель. Обобщение последних достижений в области огнезащиты пористых горючих материалов, описание ключевых механизмов действия и оценка воздействия различных классов антипиренов на окружающую среду и здоровье. Работа посвящена насущной необходимости достижения баланса между пожарной безопасностью, устойчивым развитием и соблюдением нормативных требований.

Методы. Проведен систематический обзор рецензируемых исследований, нормативных документов, технических отчетов и отраслевых руководств за период с 2018 по 2024 г. Анализ охватывал галогенированные и безгалогеновые антипирены, наноструктурированные системы, биохимические вещества и гибридные подходы. Особое внимание уделялось исследованиям, в которых применялись передовые методы характеризации, конусная калориметрия, термический анализ и оценка жизненного цикла.

Результаты. Галогенированные антипирены остаются эффективными, но их применение все больше ограничивается из-за токсичности и воздействия на окружающую среду. Безгалогеновые альтернативы, такие как полифосфат аммония, диэтилфосфинат алюминия, производные DOPO и системы на основе биологического сырья, демонстрируют многообещающие результаты, особенно в сочетании с наноматериалами или реактивными химическими веществами, для повышения стабильности. Появляются инновационные решения, включая металлорганические каркасы, производные графена и покрытия на основе фитиновой кислоты, для повышения эффективности и снижения экологического следа. Однако масштабируемость, стоимость и долговечность остаются проблемами. Пористость материалов создает определенные проблемы, такие как выщелачивание и газовыделение, что требует тщательного выбора и применения методов. Такие нормативные акты, как регламент REACH Европейского союза и Стокгольмская конвенция о стойких органических загрязнителях, играют решающую роль в обеспечении более безопасного внедрения химических веществ.

Область применения исследований. Разработка более безопасных и устойчивых стратегий противопожарной защиты в эпоху современных материалов и растущей экологической сознательности.

Ключевые слова: антипирены, пористые материалы, безгалогенные антипирены, наноматериалы, экологическая безопасность.

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