Flame retardant coatings: a review of issues lowering down attraction of private venture investment

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Abstract: The increasing complexities in the development of new fire-protective coatings hinder the attraction of private investments and impede the progress of innovation.
The review provides an overall picture of the research and specifically illustrates the extraordinary diversity of their directions and explains the inherent reason for such diversity.
The goal of this review is to establish an information foundation for a critical analysis of the feasibility of private investments in developments in this field and to show some possible ways.
The wide range of choices for specific components in fire-protective coatings and the diversity of mechanisms they employ result in a factorial number of possible combinations. The variety of properties of these components and the complexity of their interactions make it difficult to assess the outcomes of their selection unequivocally without conducting experiments during the development of new materials. Therefore, confident prediction of the results of new research is extremely challenging. As a consequence, there is a broad spectrum of directions and sub-directions in ongoing developments. Summing up the results of these investigations is further complicated by the difficulty of testing materials for aging parameters and resistance to external influences.
The wide range of choices for specific components in fire-protective coatings and the diversity of mechanisms they employ result in a factorial number of possible combinations. The diverse properties of these components and the complexity of their interactions prevent a definitive evaluation of the results of their inclusion in the composition prior to conducting experiments in the development of new materials. Therefore, confident forecasting of the results of new research is extremely challenging. As a consequence, there is a broad range of directions and sub-directions in ongoing developments. Summing up the results of these investigations is further complicated by the difficulty of testing materials for aging parameters and resistance to external influences.
The high uncertainty in forecasting the prospects of specific developments stimulates the advancement of simulation methods for compositions and coating manufacturing technologies, as well as the prediction of their effectiveness, etc. However, these methods only provide a partial increase in the reliability of expectations.
A more thorough execution of a feasibility study is recommended to substantiate venture investments. One of the additional approaches capable of enhancing its credibility is the utilization of non-traditional specialized methods for researching patent information.
Keywords: fire-protective coatings, specifically illustrates the extraordinary diversity, prospects of specific developments stimulates; simulation methods for compositions and coating manufacturing technologies.

Introduction

In the field of fire-protective coatings, numerous research efforts worldwide have yielded significant achievements and demonstrated promising ideas, approaches, compositions, and structures. However, when evaluating the feasibility of investing in a specific project or research, objective doubts inevitably arise in space where reliable prognostic answers are lacking. These uncertainties ultimately raise the question of whether a particular development has a competitive future or not.

This challenge is particularly pronounced in any area where extensive research is supported by government funding through universities, and qualified scientific papers showcase the potential of such research.

This situation is particularly relevant in the field of providing fire-protective properties to polymers, including the development of flame retardant coating properties.

Modern fire-protective coatings need to meet a complex set of functional and environmental requirements [1]. This leads to significant challenges in the development of new coatings. On one hand, there are numerous publications on new developments, each providing certain achievements and aiming to meet regulatory requirements such as environmental safety, while also demonstrating potential for further advancement. On the other hand, progress in coatings that have found widespread application has been relatively slow in recent years.

Therefore, it is not surprising that experts have expressed the opinion that the industry as a whole develops at a slow pace, and it may be challenging to accelerate this development.

The acceleration of development in any innovative technology is closely tied to private investment. How should one approach the selection of directions and developments capable of ensuring a financial return? Are there methods or approaches that can be employed to identify the most promising directions for focusing efforts and allocating funding with a higher degree of reliability than the commonly accepted practices? Some approaches capable of enhancing credibility of a venture project feasibility study, including unconventional specialized methods for researching patent information, are presented in [2,3].

The high demand for advancements in fire-protective coatings holds significant potential for accelerating their development. However, to achieve this, it is essential to increase private capital investment by enhancing the reliability of investment object selection.

This review can provide guidelines to be used as foundational or supplementary information when analyzing the feasibility of investments in specific projects within the field of fire-protective coatings. The examples provided primarily focus on the protection of solid materials, but the approaches and compositions for protecting soft materials (such as woven and non-woven fabrics, foams, etc.) are similar.

Several published reviews have outlined directions and sub-directions that the authors consider to be priorities, and their assessments are valid. However, these proposals generally encompass a broad range of developments within each direction, making them less instrumental, that is less specific and actionable. Furthermore, despite the long-standing recognition of these priorities, progress is still lagging. Therefore, it may not always be advisable to solely rely on previously established viewpoints.

The specific features of requirements for fire-protective coatings

The main trends in the development of innovations in the coatings industry are generally aimed at meeting the following common requirements, combined with improving specific functionality [1]:

- **Increase in Durability**
  Enhancing the durability of coatings is crucial to ensure that products maintain their quality over an extended period, even when exposed to adverse environmental conditions.
  Factors such as moisture, UV radiation, heat, cold, and weathering can potentially degrade the surface of coatings, leading to issues like swelling and cracking.

- **Regulatory requirements: health and wellness considerations**
  The matter of substituting chemicals that present health and wellness challenges, encompassing the reduction of volatile organic compound (VOC) emissions and other eco- and health-related concerns.

- **Sustainability: increasing ecological demands**
  There is a growing emphasis on the ability to recycle materials and minimize harmful emissions throughout the process.

- **Growth in demands for antimicrobial, anti-mold, and antiviral properties**.
  This demand is of utmost importance in healthcare and food packaging industries.
  Moreover, these properties also play a crucial role in long-term used construction components, where preventing microbial growth and mitigating viral transmission are essential considerations.

The combination of required properties poses significant challenges in the development of new coatings: often, one of these requirements contradicts the others. Enhancing such characteristics involves overcoming multiple contradictions simultaneously, ensuring that improvements in one aspect do not compromise the others.

Moreover, each of the key requirements encompasses several qualitative features, leading to additional conflicts in innovation development. For instance, the antimicrobial properties of protective coatings for hospitals must also satisfy the demands for non-toxicity, non-carcinogenicity, and non-teratogenicity under normal conditions.

The simultaneous increase in requirements for reducing volatile organic compounds (VOCs), energy and resource efficiency, use of renewable materials, non-toxicity during application and recycling poses significant challenges. These challenges also lead to a slowdown in the development of practical advancements in protective coatings for widespread use.

As a result, a proper assessment of the feasibility of funding innovations in this field is complex and highly pertinent.

Flame retardant coatings are required to possess a range of properties [4,5,6]:

- Ability to slow down flame propagation and high temperatures, and prevent the ignition of underlying substrates. This primarily involves low thermal conductivity, low flame spread, and preventing access of gas fuels and oxygen to the protected substrate.

- Resistance against ignition, melting, and nonflammability.

- Safety during combustion, with low or no emission of toxic VOCs and smoke.

- Ability to actively extinguish flames.

- Additionally, they should exhibit nearly all the properties expected from other types of coatings, such as mechanical resistance, high adhesion, durability, non-toxicity, environmental compatibility, and the ability to be recycled.

Frequently, meeting the essential fire-protective requirements can be at odds with other desired properties. Finding a balance between the conflicting demands is a challenging task for researchers and developers. It requires innovative approaches and careful selection of materials and formulations to achieve the desired fire protection performance without compromising other important characteristics.

For these reasons, the development of flame retardant coatings, like protective coatings in general, has not witnessed significant breakthroughs in recent times. The main directions of flame retardant coating development align with the overall trends in protective coatings. In recent years, the dominant focus has been on recyclability, the use of recycled materials, and the absence of harmful emissions during use and processing. Researchers strive to enhance the fire resistance performance against this backdrop.

In achieving these objectives, various challenges are addressed, including:

- Adding flame retardant properties to other functional characteristics of polymer materials. For instance, providing flame retardancy to scratch-resistant, self-healing, antimicrobial, or anti-corrosion coatings, as well as imparting scratch-resistant, self-healing, antimicrobial, or anti-corrosion properties to flame retardant coatings.

- Enhancing the stability of coating properties under environmental influences such as weathering, aging, and UV radiation.

- Improving the adhesion and adhesion stability of different types of coatings to various underlying materials requiring protection.

- Advancing the development of nanocomposite materials, including improving the effectiveness of their dispersion.

A significant factor is the increasing number of important functions and properties of coatings, their parameters, and the growing diversity of combinations of coating components and base materials. This stimulates the development of methods for simulating coating compositions, manufacturing technologies, predicting their effectiveness, and others.

Influence of development problems of fire-protective coatings on investment policy

All the aforementioned factors have an impact on the investment climate in this field. When it comes to venture capital investment in technologies, several factors are taken into account:

- Emerging trends in the field.
- Latest competing advancements in the field.
- Development stage of the specific project seeking investment.
- Various risks associated with the project.

- Probability of achieving the minimum required commercial success.
- Potential for the development of the technology and understanding of the pathways to achieve it.
- Probability of achieving a breakthrough.
- Amount of investment required, and others.

Depending on the investor's goals and policies, different factors may carry different weights. Regardless of the investor's priorities and policies, all these factors hold significance and need to be considered.

The objective of this article is to provide initial guidelines for comparing the feasibility of investing in various developments in this field.

Main concepts of modern flame retardant coatings

Methods for imparting fire-protective properties to polymer materials focus on preventing ignition, blocking flame propagation, or inhibiting heat transfer within the material. These methods vary depending on the type of material [7].

At a higher level, flame-retardant coatings can be categorized into two types: intumescent and non-intumescent [8]. The thickness of the coating film and the type of substrate significantly influence the rate of flame spread [9].

Intumescent coatings exhibit swelling when exposed to heat, forming a porous char layer that acts as a heat insulator. This char layer slows down the heat transfer between the hot gases and flames and the underlying protected material [10]. The intumescent coating can expand to a thickness up to 50 times its initial size [11].

Due to their superior flame-protective properties, intumescent coatings are often considered more promising than non-intumescent coatings, particularly for steel, wood, or hard mortar applications.

However, it should be noted that the durability of intumescent coatings poses challenges, as they may lack resistance to leaching, weathering, and aging [12]. These factors affect their long-term performance and reliability.

In [7], a comprehensive table outlines the principles of flame retardant systems based on material chemistry. These principles highlight the general mechanisms that flame-retardant coatings employ at high temperatures or during a fire:

- Inert (non-combustible) gas dilution: These coatings generate non-combustible gases that reduce the concentration of oxygen, combustible gases, and volatiles.

- Physical dilution: The concentration of the flammable material is reduced by incorporating fillers into the base material.

- Thermal quenching: Additives undergo endothermic degradation, which reduces the surface temperature of the underlying polymer.

- Chemical interactions: Retardant additives undergo thermal dissociation, producing radicals that neutralize combustible species in the gas phase.

- Protective char layer formation: Thermal decomposition leads to the formation of a protective char layer, which can be either intumescent or non-intumescent [13,14]. Intumescent materials are currently considered a priority direction for the development of new flame retardant coatings. Modern intumescent coatings often incorporate the mechanisms mentioned above.

Historically, significant achievements in flame retardancy have been made using halogen-based compounds. These compounds, particularly halogen radicals formed at high temperatures, effectively inhibit gas phase free radicals that sustain the fire. One suggested mechanism is the inhibition of the chain reaction involving active oxidative radicals by halogen radicals. This inhibits the exothermic reactions that produce energy, slows down flame propagation, and ideally extinguishes the fire [15].

To enhance the effectiveness of halogen-based flame retardants, advanced methods involve the use of compounds based on antimony, phosphorus, phenol, as well as metal hydroxides, zinc borate, and other compositions [16].

However, despite their efficiency and cost-effectiveness, halogen-based flame retardants do not meet modern requirements for health and environmental safety. During high-temperature exposure and burning processes, they emit harmful volatile fumes and smoke. Moreover, they pose challenges in terms of recycling and contribute to environmental issues. Consequently, they are not aligned with advancements in modern ecological regulations.

Main directions of progress in the composition of flame retardant coatings

Under normal environmental conditions, coatings should provide regular properties such as protection against external influences (waterproofing, wear resistance, anti-scratch, anti-corrosion, heat insulation, flame protection, antimicrobial properties), adhesion to the substrate, electromagnetic and optical parameters, absence of substance emissions into the air, and more.

The three main functional elements of fire-protective coatings are flame retardant additives (often referred to as flame retardants), binders, and fillers [7].

Flame retardants play a direct role in fulfilling the primary functions of fire-protective compositions, which include delaying the spread of flames, reducing heat transfer to the protected substrate, preventing and delaying ignition and combustion, slowing down the dripping of melted plastics, and reducing smoke formation.

The main functions of binders include [7, 16]:

- Maintaining uniform dispersion of flame retardants, fillers, and other components within the binder matrix.
- Providing adhesion to the substrate material.
- Facilitating the formation of catalytically active structures in intumescent processes.

The binder properties directly influence the efficiency of flame retardant coatings.

Fillers play important roles in flame retardant systems [7], providing the following functions:

- Reducing thermal conductivity, which slows down the spreading of heat.
- Modifying material viscosity to reduce the melt dripping of polymers.
- Absorbing a portion of the heat through their thermal degradation, thereby reducing or slowing down further temperature degradation. In this aspect, fillers function similarly to flame retardant additives.

Moreover, fillers can have specific and highly effective functions in intumescent coatings:

- Reducing the average diameter of gas cells formed in intumescent flame retardant coatings, which leads to a char layer with reduced heat transfer and enhanced protective abilities.
- Increasing the expanding abilities of the coating, particularly applicable to expandable fillers like graphene.

- Intensifying the formation of carbonized char.

Some fillers possess additional functions of their own. For example, metal hydroxides that emit water under high temperatures function as flame retardants and are sometimes referred to as such. Conversely, non-reactive flame retardants that remain as particles in the composition are sometimes referred to as fillers.

The choice of components for flame retardant coatings is greatly influenced by the type of underlying material (substrate). Different flame retardants, fillers, and additives are required to protect wood, steel, fabric, thermoplastic, and thermoset polymers [17,18].

The substrate, along with the flame retardant coating, forms a flame retardant system that should demonstrate durability and robustness in various applications such as industrial, architectural, transport, cables, textiles, etc. It should also be able to withstand corresponding environmental conditions, including indoor or outdoor application, temperature and moisture ranges, exposure to microbiota, chemicals, UV, etc.

Each component in the flame retardant system affects the coating's ability to adhere to the substrate and the final properties of the coating. Each component plays a specific or multifunctional role in providing durability and robustness. The final properties for different applications also depend on the interactions between the components in the formulation. There are various components in each flame retardant system, and there are complex processes that occur when they come into contact with high temperatures or flames [19,20].

Therefore:
a) Current research is focused on gaining new knowledge about polymers and compounds with flame retardant properties.
b) The methods of simulation, proper testing, and data analysis are crucial in the development of modern flame retardant systems. The ability to use these methods should be considered when discussing investments.

Through these paths, more advanced materials are being created. The ongoing progress leads to an inevitable convergence with practical applications.

However, achieving significant breakthroughs or progressive pivotal points still requires some time.

When evaluating the feasibility of investing, it is crucial to carefully consider the risks versus the potential benefits. Investors should thoroughly assess the potential of the new technology or platform compared to existing, well-established solutions.

The following sections present ingredients of flame retardant systems that have demonstrated notable robustness to date, categorized based on their non-bio (conventional) or bio-based origin. Conventional origin refers to chemicals derived from mineral or petroleum/gas materials, while bio-based origin encompasses any biomass-derived sources.

One of the most significant trends in the field is the transition from conventional or "non-bio" materials to bio-based alternatives.

Progressive non-bio FRs

Some of the most effective conventional, non-bio additives that show great promise as a foundation for new developments include phosphorous-based compounds such as ammonium polyphosphate, melamine, and melamine-polyphosphate [7,12,21]. Additionally, pentaerythritol phosphate alcohol, polyphosphonate, siloxane, polysiloxane [7], and dihydro-phosphaphenanthrene oxide derived compounds [22] are also regarded as highly effective additives.

In addition to the mentioned additives, there are many other additives that remain under consideration, including long-standing ones like magnesium and aluminum hydroxides, which also function as fillers, boric acid and its salts, and others.

To illustrate the challenges in making the right investment choice in innovation, we can take the example of melamine. Alongside ammonium polyphosphate and pentaerythritol, melamine has become a commonly used industrial intumescent flame retardant. It serves as an excellent example of a modern, multifunctional component in flame retardant systems. Melamine exhibits favorable eco-properties, such as low toxicity and environmental safety [23], as well as low smoke density [24], and cost-effectiveness [25]. Moreover, it offers advantages in corrosion resistance [26]. It demonstrates high specific efficiency when used in fire-protective coatings, particularly in intumescent coatings. This is attributed to its multi-mode mechanisms that interfere with the flame process at all stages. Melamine presents numerous opportunities for various synergies in flame retardant applications.

Indeed, when considering melamine, it is also important to take into account the possibilities offered by its extensive family of derivatives and homologues. This includes its salts with organic or inorganic acids, such as phosphoric, boric, cyanuric, pyro/polyphosphoric acid, as well as its homologues like melam, melem, and melon [26]. The potential for new combinatory developments based on melamine is vast, offering numerous opportunities for further exploration and innovation.

At this, it should be noticed that the possibilities of its numerous family of derivatives and homologues is to be taken into account: its salts with organic or inorganic acids, such as phosphoric, boric, cyanuric, pyro/polyphosphoric acid, and its homologues (melam, melem, melon) [26].

Nevertheless, it is important to recognize that despite its benefits, multi-functionality, and practical workability, melamine has not provided yet a significant breakthrough. There are still a huge number of options and possibilities to be explored to determine whether melamine can eventually become a game-changer in this area. Thorough evaluation of its potential still requires extensive research, and there is no guarantee of a breakthrough.

Similar conclusions can be drawn about many other promising agents in the field, for example the recently synthesized DOPO (9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide) and its modifications [22].

Therefore, in general, when investing is analyzed, a comprehension of whether the innovators possess methods to choose right direction or not should be important. Another issue of priority is whether they possess methods for proper advanced and fast testing. This may become crucial, especially when the long-term stability, non-emitting VOCs, resistance to weathering and ageing are critical to the supposed applications.

Progressive non-bio binders

Some conventional binders that appear to be the most effective and promising as a foundation for new developments, particularly in combination with effective halogen-free additives, include ethylene vinyl acetate and its homopolymers and copolymers [27], dibutyl maleate, esters of branched carboxylic acids [16], various epoxy resins, polyamides [7,28,29,30], acrylic, and urethane [31].

Extensive research has been conducted over the past two decades on the best conventional non-bio binders, exploring their hybridization with other effective constituents.

For instance, a publication [32] as old as in 2006 demonstrated attempts to improve compositions based on one of the most promising binders, acrylic binder, by incorporating other effective constituents such as melamine, ammonium polyphosphates, and nanofillers. However, despite these efforts, many challenges in this area still remain unresolved.

On the other hand, there are examples that illustrate the significant impact of combining known techniques. Despite polyamide being a well-studied binder, recent discoveries have revealed numerous novelties in its usage. Various synergistic combinations of polyamide-6 or polyamide-6,6 with other polymers, flame retardants, and fillers have been disclosed in recent years [29,30,33]. In 2022, a significant synergistic effect was reported with the addition of polyphenylene oxide to polyamide-6,6 [34]. This highlights the potential for significant improvements in fire protection systems using the best binders. However, finding new ways to surpass previous achievements is not an easy task.

Even well-known basic binders can still be considered promising for the development of new coatings through hybridization with other effective constituents. Therefore, exploring novel hybridization approaches with established binders holds potential for advancing flame retardant technologies.

The examples provided suggest that there are three general approaches that can lead to progress in the field of flame retardant coatings:

- searching for new synergistic combinations of known ingredients

- discovering new promising ingredients

- utilizing progressive technologies for coating application processes.

The first approach can be exemplified by the synergistic effect observed in the combination of a DOPO-based flame retardant and melamine, reinforced with nano-silica as a filler [35]. This combination demonstrates improved flame retardant properties compared to individual components, highlighting the potential for synergistic interactions between additives and fillers in enhancing the fire resistance of coatings.

The second approach involves the exploration of new modifications of bio-based compounds. As the industry increasingly focuses on sustainable and environmentally friendly solutions, there is a growing interest in bio-based additives and binders for flame retardant coatings. Researchers are actively developing and testing modified versions of bio-based compounds to improve their flame retardancy and compatibility with other components.

In both cases, having effective tools for scientific prediction of the properties and performance of new hybrid compositions is crucial. Accurate prediction methods can aid researchers in assessing the potential efficacy of novel combinations and guide decision-making processes when investing in innovations in this field.

Progressive non-bio fillers

Non-bio fillers play a crucial role in flame retardant coatings, and their properties, such as nature, size, and surface modification are key factors in determining their functionality. Different fillers have specific functions and mechanisms for their effective operation in flame retardant systems.

One important function of fillers is to absorb heat through their temperature decomposition. By absorbing and dissipating heat, fillers help prevent the spread of flame and contribute to the overall fire resistance of the coating. Additionally, certain fillers can release distinguishing substances that aid in extinguishing the flame or inhibiting its spread.

Fillers also serve other important purposes. They can help prevent the leaching of other agents, thus prolonging the durability of the coating and reducing the effects of aging. They can suppress smoke formation, reducing the dense and toxicity of smoke generated during a fire. Fillers can also reduce the dripping of the melt polymer base, which is essential for preventing the spread of fire and protecting the underlying materials.

Furthermore, fillers can enhance the adhesiveness of the coating to the protected material, ensuring its effectiveness in providing fire protection. They can contribute to the formation of a char protective layer, including intumescent chars, which act as a barrier against heat and flame. Some fillers are even considered "flame retardants" due to their inherent ability to fight against flames efficiently. Metal hydroxides, for example, release a high volume of water when heated, while lignin-based particles are effective in forming char under high temperatures.

Another important aspect is the synergistic effect that many fillers can have when combined with other components in flame retardant coatings. In hybrid synergistic combinations, fillers enhance the overall performance of the coating.

The wide range of available fillers provides a variety of their functions and mechanisms in their interaction with other components. It is precisely their interaction with base polymers and flame retardants that determines the selection of specific fillers to maximize the fire protection characteristics of coatings.

In modern developments, there is a focus on achieving synergistic effects through interactions between components. Therefore, combinations of different fillers are often used.

A trend has emerged in the use of fillers with complex structures.

This is well illustrated, for example, by the utilization of a filler combination comprising a relatively new agent, two-dimensional nanofillers of graphene oxide, and Mg-Al layered double hydroxides in a polyurea composite coating with modified ammonium polyphosphate as the flame retardant (FR) [36]. The results obtained demonstrate remarkable flame-retardant and fire-protective performance, a strong mechanical strain rate effect, and enhanced bonding between the polyurea polymer and the underlying steel.

As the industry increasingly moves towards bio-based compositions, the challenges related to the implementation of fillers become more complex in order to meet the efficiency requirements of modern consumers.

Trend towards bio-based flame retardant coatings

The use of biomaterials to create eco-friendly and non-hazardous coatings is considered one of the main trends in the coatings industry. This trend is driven by the increasing regulatory demands for ecological and human health considerations. Bio-based coatings offer several advantages in this regard, including low toxicity, renewability, and ecological compatibility.

As a result, there is a growing importance placed on the development of novel and efficient bio-based polymers, flame retardants, and other agents.

The shift from conventional, non-bio flame retardant coatings to sustainable bio-based coatings aims to meet economic, health, and ecological demands. However, there are specific challenges in implementing this trend in fire-protective coatings. One challenge is the relatively high flammability of biopolymers. Another challenge is their high hydrophilicity, which can affect their performance as coatings [12].

Research is being conducted on bio-based coatings for all three main constituents: flame retardant additives, which are crucial for the fire retardancy of the coating system, binders, and fillers. Additionally, the nature of the underlying material being protected also significantly influences the efficiency of the coating.

Bio-based flame retardants

Some research studies highlight the utilization of modified lignin, cellulose, polysaccharides, proteins, lipids, and chitosan macromolecules [37,38,39,40] in coatings intended for various substrates such as wood, steel, concrete, and fabric.

Other researchers are specifically focusing their efforts on developing sustainable biobased flame retardants (FRs) for plastic applications. These include substances such as phytic acid, tannic acid, isosorbide, diphenolic acid, deoxyribonucleic acid (DNA), β-cyclodextrin, metallic phytates, coffee/phosphorous modified particles, and various others [21, 44].

Here, we will leave aside some mix in terminology, when the same agent is sometimes referred as FR, and in other cases as a filler. This happens, for example, with metal hydroxides. These well-known fillers are sometimes called as FRs because their intensive flame-retarding action on producing water at high temperatures. Similarly, lignin- or starch-based additives are sometimes called as “fillers”, but they are quite often called as “flame retardants” because of their high ability to form char layer and do other functions. For this reason, we would call them “flame retardants”.

Out of all the bio-based fiber polymers, lignin is very effective for use in FR additives/fillers for the coatings due to its highly aromatic structure which provides effective charring at high temperatures, e.g. lignin-diethylenetriamine/red phosphorus nanoparticles [41]. Lignin -based fire-protective agents are especially effective in combination with hemicellulose. The similar effects were obtained with starch [37].

When considering various types of additives, organophosphorus flame retardants continue to receive significant attention [37,42]. Their effectiveness is further enhanced when combined with nitrogen, sulfur, boron, or silicon components. Organophosphorus flame retardants derived from biomaterials hold great promise due to the inherent advantages of bio-based materials. Moreover, they are less likely to face unforeseen restrictions in the future due to their eco-friendly properties. Additionally, the combination of phosphate-based components with nitrogen and/or silicon-based components has demonstrated synergistic effects [22,43,44]. For instance, isosorbide derived from starch can serve as a highly effective platform for the development of various phosphorus flame retardants [39,40]. Another example is the utilization of a novel phosphorus-containing furan-based epoxy curing agent as a flame retardant [45]. Furthermore, DOPA-modified flame retardants [22] have shown a wide range of opportunities for further advancement. Numerous other modifications of organophosphorus compounds are also being explored.

One more important point into this pull is the ability of organophosphorus-based flame retardants to provide and enhance intumescent coatings [46].

Above that, the chemistry of phosphorus-based flame retardants holds significant potential that is yet to be fully explored, owing to its wide and extensive applicability to various materials. This potential is further amplified by the broad range of reactivity exhibited by compounds of this nature.

This aspect is often highlighted when discussing polymers as bulk materials, rather than coatings, where flame retardant compositions are introduced to provide flame retardant properties directly to the product or bulk layer. It is well-known that reactive additives are generally effective for thermosetting plastics, while non-reactive additives perform better in thermoplastic polymers. [44].

An effective lignin-based phosphate–melamine FR was presented in [21].

Lignin exhibits flame retardant properties in both the gas and condensed phases. It enhances the performance of other flame retardants and plays a leading role in the formation of char [47]. The synergistic combination of lignosulfonate with ammonium polyphosphate (APP) results in producing of a stable carbon layer. Additionally, non-combustible gases such as NH3 and H2O are generated at high temperatures, thereby reducing the oxygen concentration [48].

Another example is the utilization of carboxymethyl chitosan microencapsulated melamine polyphosphate as a flame retardant (FR) in thermoplastic polyurethane coatings [49]. In this case, chitosan serves as a multifunctional additive, working in conjunction with melamine polyphosphate to provide flame retardancy. Chitosan executes several functions, including:

- improved compatibility: the hydrophobic structure of chitosan enhances the compatibility between melamine and the polymer matrix, facilitating the uniform dispersion of the FR throughout the matrix.

- intumescent char formation: chitosan contributes to the formation of intumescent char layers during combustion. These char layers create a protective barrier that helps to reduce heat transfer and inhibit flame spread.

- water resistance: chitosan imparts high water resistance to the thermoplastic material, further enhancing its durability and fire protection properties.

Another promising bio-based FR is phytic acid. It can enhance the matrix's catalytic charring and inhibit the combustion process due to its own phosphate groups [50]. Many new FRs were synthesized based on phytic acid [50,51].

One more promising bio-based FR is tannic acid. It provides several flame retardant mechanisms, leading to carbonization to form a protective carbon layer [52] and to generation of radicals which neutralize the radicals supporting combustion process, and so create distinguishing effect [53,54]

Yet one more promising bio-based FR is β-cyclodextrin. Its polyhydroxy structure defines its flame retardant mechanism. Cyclodextrin is dehydrated and carbonized during combustion to produce a large amount of carbon residue.

For example, a new type of cyclodextrin microencapsulated ammonium polyphosphate provides a synergistic effect of high carbonization ability and generating high volume of NH_3 and H_2O resulting in effective flame retardance [55].

Other bio-based flame retardants, such as those derived from starch, sodium alginate, proteins, DNA, and others, are also subjects of ongoing research.

Bio-based binders

Some specific research has been dedicated to addressing the challenges of combining flame retardants (FRs) with coat adhesives, including the exploration of suitable bio-based adhesives. It is worth noting that all bio-based polymers are inherently flammable, necessitating the use of flame retardants to enhance their flame resustance.

Incorporating bio-based FRs into bio-based binders enables the development of fully bio-based coatings and even construction materials.

It is important to mention that bio-degradable composites are sometimes referred to as bio-composites, regardless of their actual origin.

There are two main strategies for utilizing bio-based binders and polymers to improve flame retardancy [49].

The first approach involves using specific biopolymers such as modified lignin, cellulose, chitosan, starch, starch-derived cyclodextrins, polylactides, polyhydroxyalkanoates, polyamide-11, among others. For instance, in a specific study [21], α-cellulose and β-cyclodextrin were investigated as binders for flame retardant systems.

The second approach focuses on polymers similar to petrochemicals but derived from natural raw materials such as bio-based polyurethanes, epoxy resins, acrylic resins, and others.

At present, both strategies has their own advantages and disadvantages, leading to ongoing and intensive research in the field.

The aim of these studies is to develop bio-based binders and polymers that effectively enhance flame retardancy, leading to safer and more sustainable coating materials.

Currently, polylactic acid (PLA) based composites are being widely used in industry. An interesting example is the flame retardant system of bio-composite polylactic acid-thermoplastic starch, enhanced through glycerol phosphate treatment of the starch, and reinforced by modified flax fibers [56]. It demonstrates high flame retardancy parameters, and also well-balanced strength and stiffness. This system acquires even more advanced characteristics after introducing ammonium polyphosphate.

More recently, another interesting approach to improvement of PLA-based bio-composites was published [57]. There was implemented the Layer-by-Layer (LbL) method for the simultaneous improvement of the flame retardancy and the mechanical properties of PLA-based coating bio-composites. The LbL technique was used to modify the surface of the protected material using a four-layer structure of chitosan, sepiolite, and ammonium polyphosphate. Flame retardancy was significantly improved.

Similar to PLA, polyhydroxyalkanoates (PHAs) are polyesters derived from bio-based resources. Differing from PLA derived from plants, PHAs are produced by bacteria. PHAs are used to develop biodegradable composites, particularly in combination with other polymers [58,59].

Polyamide-11 is another bio-based adhesive that is utilized in flame retardant systems. The inherent fire resistance of pristine polyamide-11 is limited, so its flame retardancy is achieved through the incorporation of flame retardants and nanofillers, often in conjunction with another binder such as polylactic acid [50,60].

Bio-based polyurethanes are also an area of continuous research. One intriguing example is the incorporation of flame retardants during the synthesis of polyurethane. Flame retardants are introduced into bio-based polyols derived from sources such as soybean oil, orange peel oil, and castor oil [50].

Epoxy resins are widely recognized thermoset polymers that are effectively used as binders in flame retardant coatings [7]. There are ongoing research endeavors focused on substituting petrochemical-derived epoxies with environmentally friendly epoxy resins derived from biomass sources [61,62].

The issue of aging

An additional challenge that complicates and prolongs the development process is the issue of aging, particularly for outdoor applications. The impact of aging on polymers and flame retardant systems, including their durability and flame resistance under various conditions such as temperature, thermo-oxidation, moisture, UV radiation, ionizing radiation, chemical solvents, and physical stress, has been investigated in numerous publications [7,63,64,65,66]. However, these studies were not as extensive and systematic as the studies on flame retardants themselves. Nevertheless, they have revealed two key findings:

A) The results varied significantly for different polymers, adhesives, and flame retardant compositions.

B) The prediction of these results through chemical simulation or mathematical modeling proved challenging.

Consequently, there is still a long way to go in obtaining reliable long-term results in the field of aging studies. However, some progress is being made in this direction.

When evaluating the feasibility and expediency of investing, it is important to consider the extent of research conducted on aging and its prognosis.

Conclusions

This article provides a comprehensive overview of research in the field of flame retardant coatings and polymers. It paints the landscape of wide range of research directions and explains the inherent reasons behind this diversity.

The purpose of the article is to provide initial insights and guidance for analyzing the feasibility of specific investments in this field, taking into account the multitude of factors that complicate such analysis.

Several specific issues and points to consider when evaluating the expediency of investing of a project in this area are emphasized in italics throughout the article above. At this, the list of such really important points is wider and can be expanded in a more specific article.

Main features of this landscape

1. High Demand and Competition: The field of flame retardant coatings and polymers is highly sought after in various industries, leading to intense competition among developer groups and supporting companies.
2. Broad Research Scope: The research in this field encompasses a wide range of materials as objects of study, methods of chemical synthesis for key components, developing hybrid (combined) compositions, and advanced coating creation and application technologies. These studies involve highly qualified research teams with extensive experience in developing these methods.
3. Complex Interactions and Diverse Components: The large number of coating components and their mechanisms of action and interaction result in a factorial number of possible combinations. The unique properties, diversity, and complexity of these component interactions make it challenging to significantly limit their selection in advance when developing new materials. Confidently predicting the outcomes of new research is extremely difficult. As a result, there is a wide range of research directions and sub-directions, with a significant number of experimental studies within each development.
4. Transition to bio-composites: In the current key strategic direction, which is the transition to bio-composites, decisive results have not yet been achieved. This indicates that further progress is needed to fully explore and optimize the use of bio-based materials in flame retardant coatings and polymers. These systems should:
   - Be easily recyclable or biodegradable.
   - Not emit toxic substances under normal environmental conditions during their long service life.
   - Not release harmful volatile compounds under high temperature or flame.
5. Therefore, in principle, there is a room for entering this field with new ideas. In this field, there are numerous developments that have: a) achievements, as well as shortcomings and unresolved issues, and b) potential for further development.
6. Key sub-directions include the improvement of flame retardants (FRs), binders, fillers, and other additives; the creation of synergistic combinations among them; the development of multifunctional and smart coatings; advancements in coating application technologies, and more.

7. Due to the aforementioned reasons, it is impossible to determine in advance which of these developments are the most promising. That is why research continues in a very broad range. Analyzing investment proposals in this field is also significantly challenging. Some initial insights to consider during such analysis are presented in the sections of this review.

Preferred organizational conditions for investment entry

1. The first crucial requirement is the presence of an experienced team as only highly qualified groups of scientists can successfully implement complex synthesis and hybridization processes of various components necessary for the realization of new ideas.
2. The second crucial requirement is modern technical equipment, both general and specialized. This includes laboratory and technical capabilities for chemical synthesis and monitoring of its results, testing methods, including accelerated aging studies.
3. Additionally, access to modern software programs for preliminary modeling of the properties of synthesized materials is necessary.
4. A more thorough execution of a feasibility study is recommended to substantiate venture investments. One of the additional approaches capable of enhancing its credibility is the utilization of non-traditional specialized methods for researching patent information.

Approaches to the specific analysis of the prospects of a sub-direction or technology proposed for investment

Recommendations in this regard vary depending on whether the technology has been developed for a long time or if a new approach is being proposed.

For a technology that has been long-established and is gradually developing:

The risks of scientific or technical failure for such developments are relatively low. However, there are many competing systems of this type, each with its own real achievements, advantages, and disadvantages. Therefore, the chance of occupying a significant market niche is not big even in a case of scientific success.

Obtaining reliable expert assessments of their competitive commercial prospects is challenging. Therefore, the risks of being in a weak competitive position are relatively high. There are also significant risks of requiring substantial over-expected additional investment, as evidenced by similar developments in the past.

To address these challenges, special methods can be recommended to increase the reliability of forecasting the commercial prospects of such developments.

One precise and specialized method includes a thorough analytical examination of the patent landscape using specific techniques [2]. Despite the availability of modern commercial patent search and analytical services by the companies Questel, Clarivate, Patbase, etc., such studies remain unfamiliar and overlooked by investors and investment committees. However, when properly executed, these studies yield sufficiently accurate and reliable results [3].

For a technology implementing a significantly new approach

The risks of scientific and technical failure for such developments are relatively high. However, in the event of success, the probability of successful competitive commercialization, capturing a substantial market niche, is also considerable.

Obtaining a highly reliable expert opinion with a sufficiently confident forecast of prospects before obtaining experimental results is equally challenging as in the first case.

In such situations, a more thorough specific combined investigation of development prospects is recommended, involving close collaboration between a professional in the field and an expert capable of conducting unconventional analytical research of the patent landscape. Modern commercial analytical patent services offer unique opportunities for unconventional research using specialized methods.

Such a non-standard comprehensive analysis of the patent landscape in conjunction with expert insights can provide valuable information not only about the novelty and patentability, not only understanding the intellectual property landscape. It also can:

- help in reinforcing the scientific solutions, and
- expand potential commercial applications of the technology
- aid in identifying potential risks
- reveal unknown competitors that are still at a starting position.

All this facilitates making better-informed decisions regarding the development and potential investment.

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