# Alternatives to Halogenated Flame Retardants in Fire Fighter Station Wear

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# Table of Contents

**Table of Contents** **2**
**I. Executive Summary** **4**
**II. About the Authors** **5**
**III. Introduction:** **6**
Challenge 6
Background 6
**IV. Approach:** **7**
Boundary Conditions 7
Technical and Performance Criteria 9
Health and Environmental Criteria 11
**V. Strategy 1: Nitrogen-Phosphorous (N-P) Synergistic Effect** **12**
Inspiration 12
Baseline Textile 13
Proposed Alternatives 14
Melamine Phosphate: 14
Casein: 15
Phytic Acid: 15
Chitosan: 16
Technical Performance Assessment 16
Health and Environmental Performance Assessment 18
**VI. Strategy 2: Selectively Bred Cotton** **19**
**VII. Strategy 3: Re-evaluating the necessity of NFPA 1975 Standards** **21**
**VIII. Hazard Assessments** **22**
Human Health Assessment 22
Phytic Acid 22
Chitosan 23
Melamine 23
Phosphoric Acid 24
Casein 24
Environmental Assessment Strategy 1 25
Melamine Phosphate 25
Casein 26
Phytic Acid 26
Chitosan 26
Environmental Assessment Strategy 2 & 3 26
Selectively Bred Cotton 26
Merino Wool 27

**IX. Honorable Mentions (Sonal)** **28**
Nano Biocomposites as Flame Retardants 28
**X. Recommendations and Future Directions** **29**
**References** **31**

# I. Executive Summary

The NFPA 1975 standard necessitates the use of chlorinated, brominated, and antimony base flame retardants to meet the certification requirements for fire fighter base-layers and station wear, and over the past several decades, these chemicals have been the primary flame retardants used in fire fighter gear. These chemicals and metals are known endocrine disruptors, and some are known carcinogens, which pose an unnecessary risk to the fire fighters who wear these garments for upwards of 24 hours at a time and while under unique working conditions. While turnout gear has the purpose of providing a flame retardant, protective outer layer meant for coming in direct contact with fire, station wear is worn both underneath the turnout gear as a base layer and for the duration of the fire fighters' time in the station.

We present several potential alternatives to these halogenated compounds, including but not limited: (1) a Nitrogen-Phosphorus synergistic approach and a textile-based approach, (2) the introduction of a novel selectively-bred flame retardant cotton, and (3) a policy review that aims to evaluate the performance requirements set in the NFPA 1975 standards standards and whether outlined tests serve as true analogs to real-world working conditions and exposures. These strategies aim to mitigate human and environmental hazards and be safer alternatives that meet necessary performance standards while remaining cost-competitive and compatible with current manufacturing methods.

# II. About the Authors

**Cindy Calderon** is in her final year of her Masters in Public Health in Environmental Health Science. Her summer practicum at an industrial hygiene consulting company confirmed her interest in protecting the health of workers through prevention efforts and research. During her practicum, Cindy collaborated with the other interns and created an internal presentation on OSHA'S Blood Borne Pathogen Standard.

**Sonal Maroo** is a third year PhD student in physical chemistry with research focusing on the exploration and systematic manipulation of the electronic structure of 2D materials for applications in electrocatalysis. In this project, she will leverage her extensive chemistry background and quantitative problem-solving skills to identify, evaluate, and present viable alternatives for the materials under consideration.

**Jillian Pape** is a second year MPH student in the school of Environmental Health Sciences, in the Global Health and Environment track. Her interests lie in infectious disease dynamics, toxicology, and environmental justice, and her academic background in these topics will help with the identification and analysis of the occupational and environmental hazards of the materials at hand.

**Kevin Ru** is a second year MPH student in Epidemiology/Biostatistics with a focus on occupational and environmental epidemiology. He has working experience in exposure assessment in ventilation settings with extensive coursework in epidemiological methods and modes of statistical analysis. In particular, he has strong interests in occupational exposures and toxicology and will leverage that in approaching this challenge.

**Saoirse Stock** is a second year MPH candidate in the Global Health and Environment program at UC Berkeley and is focusing on toxicological environmental justice and the health implications of climate change and exposure to pollutants. From experience working in environmental health and safety to assisting with biomonitoring research for endocrine disrupting flame retardant chemicals, she brings a deep understanding of the health effects of POPs.

# III. Introduction:

## Challenge

The International Association of Fire Fighters (IAFF) is dedicated to safeguarding the occupational health of fire fighters by seeking to minimize avoidable hazards. Over the past several decades, halogenated flame retardants, composed of primarily groups of chlorine and bromine containing chemicals, have played a pivotal role in the fabrication of fire fighter station wear, uniforms, and base layers certified under the National Fire Protection Association (NFPA) 1975 standard. These chemical additives protect fire fighters by increasing textile fire resistance, but several have been identified as known endocrine disruptors or known carcinogens. This poses an unnecessary risk to the fire fighters who wear station wear for extended periods of time. While turnout gear has the purpose of providing a flame retardant outer layer meant for coming in direct contact with fire, station wear is worn both underneath the turnout gear as a base layer and for the duration of a fire fighters' time in the station. Therefore, it is crucial that fire fighters are both comfortable and safe while wearing these textiles for up to 24 hours at a time. To reduce the occupational health effects of exposure to halogenated flame retardants, the IAFF is seeking safer ways to make fire-resistant station wear.

## Background

NFPA is a nonprofit with a mission in elimination of death, injury, property, and economic loss due to fire, electrical, and related hazards. The NFPA 1975 standard has gone through 7 iterations since the standard was first introduced in 1985. Certified station wear is not considered primary protective equipment because they do not provide sufficient protection from hazards encountered during structural or wildland firefighting[1]. Instead, the standard outlines the minimum performance requirement needed to achieve baseline certification and optional certification systems. While the standard is not enforced by legislation, many fire stations in the United States adhere to them.

Halogenated flame retardants are effective in disrupting the spread of fire through physical and chemical means. Chlorinated flame retardants reduce textile flammability by emitting chlorine gas when exposed to elevated temperatures. Similarly, brominated compounds, particularly polybrominated diphenyl ethers (PBDEs), have been harnessed for their remarkable flame-retardant characteristics. Upon exposure to elevated temperatures, these compounds release bromine ions, impeding the ignition and combustion of textiles. This rendered brominated flame retardants an appealing choice across much of the industry.

Together, halogenated flame retardants are often combined with a synergist to increase their overall effectiveness. Antimony trioxide is the most common synergist, helping to form less flammable chars to protect against heat. Their primary function entails enhancing the overall effectiveness of other flame retardants, thereby rendering them more proficient in preventing ignition and retarding flame propagation. Notably, traces of antimony with lead were collected from fire fighter station wear.

Extensive research highlights the health and environmental consequences of these compounds. Their propensity to infiltrate ecosystems and accumulate within organisms has raised environmental concerns regarding toxicity, bioaccumulation, and potential ecological harm. Furthermore, there are known chemical hazards to human health and potential adverse health effects. Notably, chemicals such as tris (2-chloroethyl) phosphate (TCEP) and pentabromodiphenyl ether (pentaBDE) have been recognized as carcinogenic in California, while the National Toxicology Program has classified antimony trioxide as reasonably anticipated to be a human carcinogen. Though several chemicals such as PentaBDE, have been banned from new production by the United States since 2005, many remain persistent and still are found in fire fighter station wear samples. For instance, PBDEs have been found in deep tissues of whales, often driven by industrial wastewater practices. Additional burdens are borne by workers in garment manufacturing and among fenceline communities living close to sites of manufacturing or waste disposal.

# IV. Approach:

We aim to support the IAFF's mission with a multifaceted approach that involves: (1) a Nitrogen-Phosphorus synergistic approach and a textile-based approach, (2) the introduction of a novel selectively-bred flame retardant cotton, and (3) a policy review that aims to evaluate the performance requirements set in the NFPA 1975 standards and how they can be actively modified to reflect the removal of any harmful additives and textiles in station wear.

## Boundary Conditions

The boundary conditions for our proposed alternative must meet the minimum performance requirements stated in the NFPA 1975. Table 1 (NFPA 1975 Performance Requirements) shown below, provides the minimum performance requirements needed to obtain baseline certification and flame resistance certification for station wear. The NFPA 1975 is modeled after IS0 11612:2015 and the tests employed in the standard come from the American Society for Testing and Materials (ASTM). The certification process is performed by an accredited third-party organization. In addition, the garment must be tested before and after the washing and drying cycles or dry cleaning cycles.

The technical performance requirements for our alternative will reference the base requirements outlined in the 1975 standard with a primary focus on thermal stability and flame resistance capabilities. Washing durability and seam breakage requirement can only be determined with direct testing of the textile and is not within the scope of this project. The implications of this limitation will be addressed in the recommendation section. Lastly, our proposed alternative will be halogen-free, have a Limiting Oxygen Index (LO1) greater than 21, and will not bioaccumulate or be persistent.

| **Table 1. NFPA 1975 Performance Requirements** | | | |
|---|---|---|---|
| Test Name | Specimen Tested | Passing Testing conditions | Pass |
| **Base Requirements** | | | |
| Heat and Thermal Shrinkage Resistance | Textile fabrics, findings, and visibility markings | ≤ 260°C (500°F) | No melting, dripping, ignition,separation, and shrinkage. |
| Thermal Stability | All textile fabrics | ≤ 265°C (510°F) | • Does not melt or ignite<br>• Does not stick to glass plate<br>• Resistance to blocking is 1 or 2 |
| Thread Heat Resistance | All thread types | ≤ 260°C (500°F) | Does not melt |
| Seam Strength | • Wove textiles' Major seems*<br>• Knits | • 305 mm/min (12 inch/min)*<br>• Tensile machine with 25 mm diameter ball | Seam breaks at 133 N (30lbs) or greater |
| Label Print Durability | All garment labels | Observed at a 12 inch distance | Legible |
| Optional Flame Resistance | | | |
| Flame Resistance Test | Textiles and visibility markings | Held 38 mm(1.5 in.) above a flame | • Passes baseline requirements<br>• Afterflames is < 2 seconds<br>• Char length is < 150 mm (6 in.) |

***Table 1: NFPA 1975 Performance Requirements***

# Technical and Performance Criteria

To evaluate the efficacy of the proposed alternative flame retardants, a range of technical performance criteria are employed, with a primary focus on two essential categories: flammability and mechanical properties.

Flammability Assessment

- *Thermogravimetric Analysis (TGA):* TGA is a fundamental tool for assessing the thermal characteristics of materials. Specifically it quantifies a material's decomposition and degradation temperature, which are critical factors in the evaluation of its fire-resistance capabilities. A lower decomposition temperature may indicate a less effective flame retardant. TGA is instrumental in pinpointing the temperatures at which materials commence degradation, and the subsequent rate of degradation.

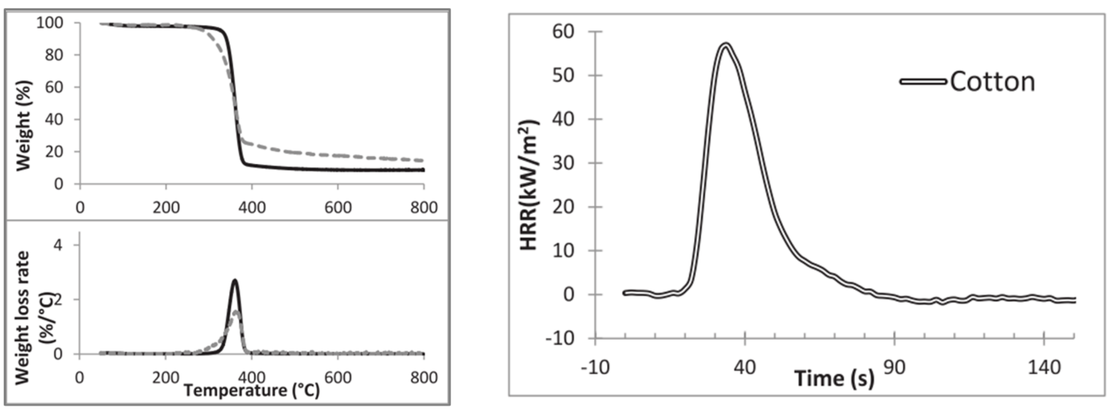



***Figure 1: Left- A typical TGA curve for cotton, Right- a typical cone calorimetry curve for cotton***

- *Cone Calorimetry: Peak/Total Heat Release Rate (PHRR/THR):* Cone calorimetry, conducted in compliance with ASTM E1354 and ISO 5660 standards, is a standardized method for quantifying the heat release rate of a material when exposed to a controlled heat source. PHRR denotes the highest heat release rate during combustion, while THR measures the cumulative heat release throughout the test. Reduced PHRR and THR values indicate improved flame retardant properties, indicating diminished heat generation and slower fire propagation.

- *UL 94 V Rating:* The UL 94 Vertical Burn Test is a widely accepted standard for appraising the flammability of plastics and diverse materials. This evaluation assesses the material's resistance to flame propagation and dripping, categorizing materials into various V ratings, with V-0 representing the highest level of flame resistance. A higher UL 94 V rating demonstrates a quicker self-extinguishing time of vertically oriented polymer specimens, indicating superior flame retardancy. The results are binary, signifying pass/fail, with the objective of securing a V-0 rating.

| Flammability rating UL 94 V | | | |
|---|---|---|---|
| Test Criteria | V-0 | V-1 | V-2 |
| Burning time of each individual test specimen (s) (after first and second flame applications) | ≤10 | ≤30 | ≤30 |
| Total burning time (s) (10 flame applications) | ≤50 | ≤250 | ≤250 |
| Burning and afterglow times after second flame application (s) | ≤30 | ≤60 | ≤60 |
| Dripping of burning specimens (ignition of cotton batting) | no | no | yes |
| Combustion up to holding clamp (specimens completely burned) | no | no | no |

***Figure 2: Flammability ratings UL 94 V specifications (Source: UL LLC)***

- *Limiting Oxygen Index (LOI)***:** LOI measures the minimum concentration of oxygen in the surrounding atmosphere required to sustain combustion. A higher LOI value indicates reduced susceptibility to ignition and combustion. Flame retardants that elevate a material's LOI contribute to enhanced fire safety. This parameter is governed by ASTM D2863 and BS EN ISO 4589 standards, with a target LOI value exceeding 27 for compliance with NFPA standards.

| Fibre | LOI (%) |
|---|---|
| Cotton | 18.4 |
| Viscose | 18.9 |
| Wool | 25 |
| Acrylic | 18.2 |
| Polypropylene | 18.6 |
| Nylon 6 | 20-21.5 |
| Polyester | 20-21.5 |
| Proban-treated cotton | 31-33 [36] |
| Pyrovatex-treated cotton | 29-30 [36] |
| Modacrylic | 29-30 |
| Nomex | 28.5-30 |
| Kevlar | 29 |
| Oxidised polyacrylonitrile | 55 |

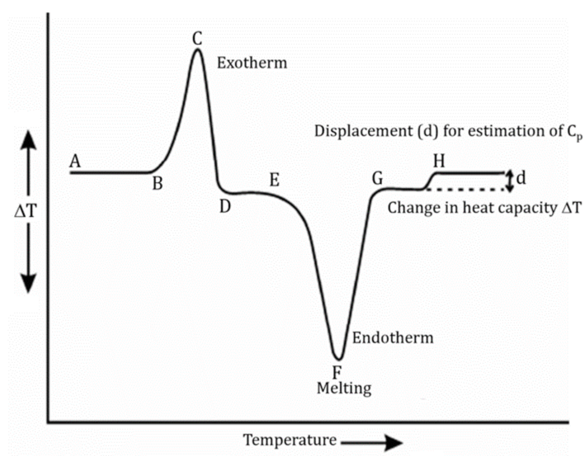



***Figure 3: Left - LOI values for some fibers, Right - Example of a DTA plot***

- *Differential Thermal Analysis (DTA):* DTA is a thermal analysis technique employed to investigate phase transitions and thermal reactions in materials. It proves particularly invaluable in scrutinizing the impact of flame retardants on the thermal behavior of a material. DTA furnishes insights into the changes in heat flow during combustion, facilitating the assessment of the efficacy of flame retardant additives.

Mechanical Property Evaluation

- *Loading Rate:* While our technical assessment prioritizes flammability, it is equally imperative to consider the influence of these additives and alternatives on the mechanical properties of the material. The loading rate, dictating the speed at which a load is applied to the material, assumes critical significance. Flame retardants must not compromise the mechanical strength or durability of the treated material. The examination of a material's behavior under diverse loading rates ensures its suitability for its intended application.

## Health and Environmental Criteria

Considering the scope of this project, human health criteria will be the main priority for our group, though we hope to address environmental health endpoints as extensively as possible within our given constraints. For both health and environmental performance criteria, we conducted a comparative hazard assessment following the general approach developed by the GreenScreen for Safer Chemicals[2]. Beginning with human health criteria, we reviewed authoritative listings, chemical evaluations conducted under the European Union's REACH regulation, and scientific literature. Where data gaps persisted, we employed predictive toxicological tools. To assess potential environmental impacts, we followed a similar approach, substituting knowledge gaps with scientific literature whenever possible.

**Example Hazard Assessment Criteria with Group 1 Human Endpoints:**

| | | Data Gap | Potential Concern | Very Low | Low | Moderate | High | Very High |
|---|---|---|---|---|---|---|---|---|
| Group 1 Human | Carcinogenicity | No literature found | Screening list | Very low | No reported effects | Suspected | Suspected | Known |
| | Genotoxicity/ Mutagenicity | No literature found | unverified hazard assigned | Literature review | Not classified | Suspected | Suspected | Known |
| | Reproductive Toxicity | No literature found | unverified hazard assigned | | Negative studies | Suspected | Suspected | Known |
| | Developmental Toxicity | No literature found | | | Sufficient data | Suspected | Suspected | Known |
| | Endocrine Activity | No literature found | | | Not classified | Evidence | Suspected | Known |

Table 2. GreenScreen Criteria

# V. Strategy 1: Nitrogen-Phosphorous (N-P) Synergistic Effect

## Inspiration

Our primary strategy for identifying safer flame retardants for station wear involves harnessing the synergistic effects of N-P compounds, a well-established technique utilized in various industries such as construction, polymers, and epoxy composites.

Phosphorus-based flame retardants, including phosphates and phosphonates, play a critical role in fortifying fire resistance by promoting the formation of a thermally stable char layer. When exposed to heat, these compounds undergo pyrolysis, generating phosphorus-containing radicals that interact with the material, facilitating the development of this protective char layer. This char layer acts as a robust barrier, insulating the material and impeding the diffusion of oxygen and flammable substances, effectively obstructing the combustion process. Furthermore, phosphorus compounds can catalyze the charring process and release water vapor, contributing to extinguishing the flames.

Simultaneously, nitrogen-based flame retardants, such as melamine and its derivatives, function by releasing inert gasses, such as ammonia, when exposed to heat. These gasses effectively dilute the flammable environment surrounding the material, reducing the concentration of oxygen and combustible gasses. Nitrogen-containing compounds make it challenging for fire to spread by absorbing heat and cooling the material. Additionally, they disrupt the combustion reaction by interfering with free radicals and combustion intermediates, breaking the chain reaction that sustains the fire.

P-N synergistic flame retardants effectively combine the strengths of phosphorus (P) and nitrogen (N) components, working together to enhance fire resistance in various materials when exposed to high temperatures. Together, it results in a more robust char layer that effectively shields the material from heat, oxygen, and flammable substances, thus slowing down the spread of flames. Concurrently, the release of inert gasses and the formation of a stable char layer contribute to a comprehensive fire suppression mechanism.

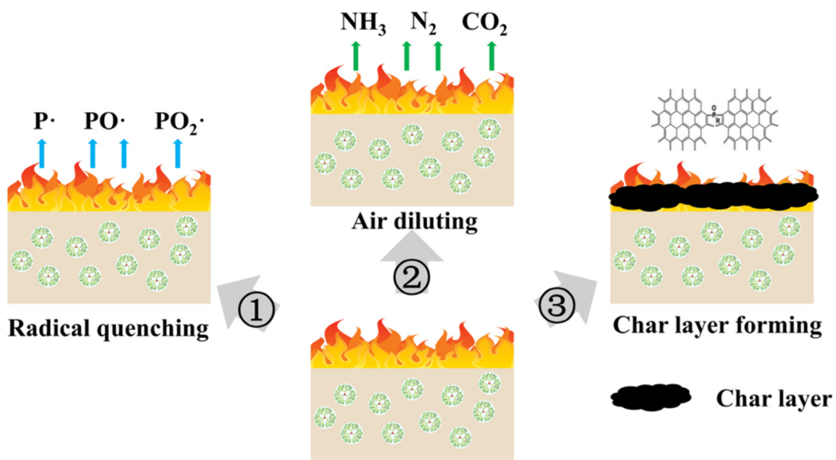



***Figure 4: Synergistic flame inhibition mechanism of Nitrogen and Phosphorous based flame retardants resulting in a stable char layer(Abdalrhem et al., 2023)***

## Baseline Textile

We have selected cotton as our foundational textile for the study of safe flame retardants, and this choice offers several compelling advantages over synthetic alternatives like Nomex, Kevlar, and PBI. Our rationale for this decision is rooted in significant concerns related to the manufacturing processes, environmental impact, health risks, and data reliability associated with these synthetic materials.

Synthetic flame-resistant materials, such as Nomex, Kevlar, and PBI, have garnered attention due to the concerns surrounding their production. These processes often demand a substantial amount of energy and involve the use of chemicals that can have detrimental effects on the environment. Furthermore, the potential hazards associated with the manufacturing and use of these materials, from both environmental and human health perspectives, have raised significant concerns. The absence of comprehensive data on health hazards and exposure risks further complicates the evaluation of these synthetic materials. Notably, much of the available information on these synthetics is provided by the manufacturers themselves, which may introduce potential biases and create doubts regarding the objectivity and completeness of the data.

In contrast, cotton is known for its breathability and comfort, making it an ideal choice for various textile applications, particularly in clothing where wearer comfort is of utmost importance. Cotton's non-toxic nature minimizes health risks, which is valuable in applications where the textile comes into direct contact with the skin.  Notably, cotton does not melt or drip when exposed to flames, reducing the risk of injury in fire incidents, setting it apart from certain synthetic materials. Furthermore, its biodegradable nature ensures it naturally decomposes over time, further advancing environmental goals. Additionally, as an individual component, untreated cotton, along with other natural fibers, exhibits relatively lower performance, leaving ample room for showcasing percentage improvements.

While cotton cultivation comes with its own set of challenges, including soil degradation, erosion, loss of forested areas and other habitats, and concerns such as child labor and unfair trade practices, we can explore the use of organic cotton as a more sustainable alternative. Organic cotton is cultivated without the use of synthetic pesticides and herbicides. Instead, it relies on natural solutions, like the application of proteins such as Bacillus thuringiensis (Bt), to protect crops from insect infestation and damage. Furthermore, we can require the use of Global Organic Textile Standard (GOTS) certified organic cotton to ensure that the material aligns with ecological and social health criteria. This includes measures such as wastewater treatment to prevent contamination, even from natural fertilizers, and the guarantee that farmers and farm workers receive fair, living wages.

Hence, the choice of cotton not only streamlines the assessment process but also reflects a safer and more environmentally responsible approach to understanding and enhancing flame resistance in textiles.

## Proposed Alternatives

Under our N-P strategy alternatives, we aimed to identify naturally occurring and biodegradable flame retardants. Our focus was on selecting options that prioritize fire safety while promoting a responsible and eco-friendly approach to combating flammability in different materials and products. We investigated Melamine Phosphate, Casein, Phytic Acid, and Chitosan, considering their distinctive properties and potential applications.

### *Melamine Phosphate:*

Melamine (poly)phosphate (MPP) is a white crystalline compound that has shown promising flame-retardant properties. It is commonly used in various materials, including plastics, textiles, and coatings.

- **Mechanism of action:** It operates through a combination of gas-phase and condensed-phase actions. In the gas phase, melamine phosphate releases ammonia when exposed to high temperatures, diluting the flammable atmosphere and reducing the concentration of oxygen and combustible gasses. In the condensed phase, it promotes char formation, creating a protective barrier that insulates the material and hinders the diffusion of oxygen and flammable volatiles.
- **Existing applications:**
    - Used in flame-retardant coatings for wood and fabric.
    - Incorporated into plastic products to reduce flammability.

    - Added to intumescent fireproof paints for structural applications.
- **Safety profile:** Melamine is derived from melamine resin, which can be sourced from renewable materials. It does not introduce harmful or persistent chemicals into the environment. Melamine phosphate can biodegrade over time, minimizing its environmental impact.

### *Casein:*

Casein is a protein derived from milk and has been explored as a natural flame retardant. It contains phosphorus and nitrogen, which are known to enhance flame resistance in various materials.

- **Mechanism of action:** It functions in both the gas and condensed phases. In the gas phase, casein releases ammonia when exposed to heat, reducing the flammability of the surrounding environment. In the condensed phase, it promotes the formation of a stable charr.
- **Existing applications:**
    - Used in flame-retardant coatings for textiles, such as curtains and upholstery.
    - Incorporated into foam materials for fire-safe mattresses and cushions.
- **Safety profile:** Casein's natural origin and biodegradability make it a sustainable choice for flame retardant applications.

### *Phytic Acid:*

Phytic acid, also known as inositol hexaphosphate, is a naturally occurring compound found in plants, particularly in seeds and grains. It has gained attention for its flame-retardant properties due to its ability to chelate with metal ions.

- **Mechanism of action:** It operates mainly through the release of phosphorus-containing radicals during pyrolysis. These radicals react with the material, promoting char formation. The char layer acts as a protective barrier, hindering the diffusion of oxygen and flammable volatiles, thus impeding the combustion process. When incorporated into materials, phytic acid can capture metal ions and prevent them from catalyzing the combustion process. This metal-chelating mechanism also contributes to the fire-retardant properties of phytic acid.
- **Existing applications:**
    - Used in fire-resistant coatings for wood and paper products.
    - Incorporated into textiles to enhance their flame resistance.
- **Safety profile:**Phytic acid is naturally found in plants and grains, making it a sustainable resource. It doesn't introduce harmful chemicals into the environment and is biodegradable.

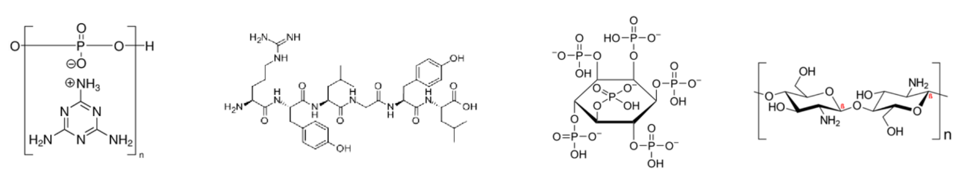
## *Chitosan:*

Chitosan is a biopolymer derived from chitin, which is found in the shells of crustaceans like shrimp and crabs.

- **Mechanism of action:** In the gas phase, it releases ammonia, carbon dioxide and water vapor, when exposed to heat, reducing the concentration of oxygen and combustible gases. In the condensed phase, chitosan promotes the formation of a char layer, which acts as a protective shield, insulating the material and slowing down the spread of flames.
- **Safety profile:** Biodegradable and non-toxic.

Below, Figure 5 summarizes the mechanism of action and chemical properties of the flame retardants, presenting various ways in which they operate. As depicted in the figure, different flame retardants function through distinct mechanisms. Consequently, combining them provides access to a diverse set of means to inhibit fire. When combined, these flame retardants work synergistically, leading to enhanced flame retardancy. Melamine (poly)phosphate is currently utilized under various commercial brands such as Melapur200 and BUDIT341. Therefore, it would be readily available if IAFF considers it as an alternative option. The figure illustrates the elemental composition of nitrogen (N) or phosphorus (P) in each of these chemicals, aiding our understanding of the sources of flame retardancy.

**Ideal** (green)
**Needs additives** (yellow)
**Thermodynamically not feasible** (red)
**Data N/A** (grey)



| **Flame retardancy mechanism** | **Melamine phosphate** | **Casein** | **Phytic acid** | **Chitosan** |
|---|---|---|---|---|
| Flame poisoning | Yes | Yes | | Yes |
| Cooling | Yes | No | Yes | |
| Char formation | Yes | Yes | Yes | Yes |
| Intumescence | Yes | Yes* | Yes | Yes |
| Oxygen dilution | Yes | Yes | No | Yes |
| Free radical trapping | Yes* | No | Yes | No |
| Combustion By-products | $N_2$, $NH_3$, other N species, and poly(phosphoric acid | CO, $CO_2$, $NH_3$, $NO_x$ | $H_2O$, $CO_2$, CO, inositol, phosphoric acid and derivatives | $H_2O$, $CO_2$, CO, $NH_3$, $CH_4$ |
| Element content (wt%) | P (12%), N (42%) | N (3.2%), P (0.9%) | P (28%) | N(6-8%) |
| Commercially available | Melapur 200, AFLAMMIT®PMN 200, BUDIT® 341 | - | - | - |

## Technical Performance Assessment

We evaluated the aforementioned chemicals either individually or in composite forms. These FRs include Melamine phosphate, Casein, Chitosan-Phytic acid (CS-PA10), and Ammonium phytate (APA) (20%). Each of these exhibits a form of N-P synergism, contributing to their efficacy as flame retardants.

The table presented below provides a comprehensive overview of the technical performance of our proposed alternatives in comparison to the currently employed FRs, which encompass penta-BDE and Nomex. The inclusion of penta-BDE was driven by our objective to explore halogen-free FRs and assess whether our safer alternatives could deliver comparable performance. It's worth noting that the performance standards for station wear, as distinct from turnout gear, are relatively less stringent. To provide a more practical reference point, we incorporated Nomex, which constituted the primary material in the station wear samples obtained from IAFF.

Most comparison values are expressed as a relative percentage change due to the slight variations in the baseline material, namely cotton, across different studies. Consequently, directly comparing the flame retardancy effects of different chemicals becomes challenging. Utilizing relative percentages ensures a more uniform comparison. The selection of cotton as our foundational textile has already addressed the issue of dripping. The incorporation of these flame retardants has resulted in the self-extinguishing property of the treated fabric, a crucial requirement according to NFPA standards. Additionally, there is a noticeable reduction in char length, a consequence of flame inhibition and self-extinguishing properties. Char length is again listed as a percentage decrease, and since different studies employ different lengths of fabric, using a relative percentage allows us to directly compare these chemicals.

Other parameters listed in the table include $T_{10\%}$, $T_{max1}$, and $T_{max2}$, obtained through Thermogravimetric Analysis, representing the temperatures at which 10% weight loss occurs, as well as the first and second inflection temperature points of weight loss, respectively. These temperatures signify crucial points at which chemical or physical transformations occur. A higher temperature ($T_{10\%/max1/max2}$) indicates greater resistance to flame. Although a slight decrease in $T_{max1}$ has been observed in the TGA analysis for all these flame retardants, this phenomenon is attributable to the chemical reactions that ultimately promote char formation, creating a protective barrier that insulates the material, consequently leading to an increase in $T_{max2}$.

The next set of parameters includes Limiting Oxygen Index (LOI) and ULV ratings. There is a substantial increase in the LOI for all proposed flame retardants. Notably, the minimum LOI requirement for certain materials used in curtains, draperies, and other window treatments is set at 27. In comparison, Nomex, currently prevalent in most station wear, has an LOI range of 28.5

- 30. All of our proposed alternatives surpass these values, underscoring their effective flame-retardant properties, as evidenced by a notable reduction in heat release rates (PHRR and THR) obtained from cone calorimetry.

In summary, our proposed alternatives exhibit promising flame retardancy properties. Nevertheless, the practical adoption of these alternatives requires a comprehensive assessment of additional factors, including mechanical performance, durability under wear and tear, responses to washing cycles, and resistance to leaching. Assessing these metrics, while beyond the scope of this project, remains of utmost importance. It is worth emphasizing that these metrics hold significant relevance in evaluating the overall effectiveness of flame retardants. Also, the values of existing FRs presented in the table are based on zero wash cycles to ensure a fair and equitable comparison.

Currently used FRs | Higher FR | Not significant impact | Lower FR | Data gaps | * Calculated per g

| Paratmeters (Δ%) vs untreated Cotton | Cotton | Melamine Polyphosphate | Casein | Chitosan-Phytic acid(CS-PA10) | Ammonium phytate (APA) (20%) | Penta BDE | Nomex |
|---|---|---|---|---|---|---|---|
| $T_{10\%}$ (°C) | 320 | -19.4% | -23.9% | -21.2% | -18.9% | | |
| $T_{max1}$ (°C) | 342 | -13.7% | -3.7% | -22.8% | -19.5% | | +29.1% |
| $T_{max2}$ (°C) | 485 | +8.7% | +0.8% | +18.0% | - | | +18.5 % |
| LOI (%) | 18.4 | 50.9 ± 0.6 | 32-44 | 30.8 | 43.2 | 32.4-34.2 | 28.5 - 30 |
| UL94 V | v1 | V0 | V0 | V0 | V0 | V0 | V0 |
| PHRR% ($kW/m^2$) | 175.11 | -70.1% | -19 % | - | -94.5% | | -65.7 %* |
| THR ($mJ/m^2$) | 7.75 | -64.2% | -(71.8-89.2) %* | - | -60.0% | | -29.4%* |
| Char length (mm) | Burns completely | -73.3% | -69% | -76% | -89.7% | | -85.9% |
| Self-extinction | No | Yes | Yes | Yes | Yes | Yes | Yes |
| Dripping | No | No | No | No | No | No | No |

$T_{max1/2}$: T at which max heats are released LOI: Limiting Oxygen Index PHHR: Peak Heat Release Rate THR: Total Heat Release

# Health and Environmental Performance Assessment

Environmental and Health Safety Aspects:

Our proposed alternative strategies for flame retardants offer some significant improvements over existing methods, particularly when compared to halogenated chemicals and antimony trioxide, which have long been known to have negative effects to both the environment and human health. Existing flame-retardant chemicals can release harmful byproducts when exposed to fire, which pose risks to both nature and our well-being. Halogenated flame retardants like PentaBDE and synergists like antimony trioxide have raised red flags about the health of those exposed, especially with long-term exposure like you'd see in fire fighters. Known health effects include thyroid and endocrine disruption, immunotoxicity, reproductive toxicity, many types of cancer, and adverse reproductive development, and atypical neurobehavioral function. In contrast, the alternatives proposed in this strategy are expected to reduce health risks. This is especially important when these flame-retardant-treated materials come into direct contact with our skin, as the alternatives are non-toxic and natural.

One of the most promising aspects of these strategy alternatives is the choice of eco-friendly alternatives like Melamine Phosphate, Casein, Phytic Acid, and Chitosan. These options come from natural sources; they break down harmlessly in the environment and don't introduce harmful or persistent chemicals into our surroundings. This shift towards more sustainable flame retardants is a big step in the right direction given the known issues associated with traditional flame retardants.

However, it's important to acknowledge that there are still some potential impacts and uncertainties that need to be addressed. We should closely study the environmental impact of widely using these alternatives including examining how they affect soil, water, and ecosystems, and understanding any long-term effects on the environment. Assessing the impact on aquatic life is crucial, particularly in terms of bioaccumulation. Any chemicals used in the flame retardants should be rigorously examined to understand their behavior in aquatic environments. The potential for these chemicals to accumulate in aquatic organisms and ecosystems, which can then lead to harm up the food chain, must be carefully evaluated. This includes considering the long-term effects on aquatic ecosystems and the health of aquatic species. As of now, the aquatic toxicity of casein is unknown, melamine phosphate and phytic acid are considered low, and chitosan is considered safe. The persistence of melamine phosphate and phytic acid are unknown, phytic acid is considered high, and chitosan is considered safe. We are not yet sure how fast these alternatives break down in different environmental conditions. So, it's crucial to find out how they degrade in real-world settings and check if any leftover substances or byproducts are a concern.

The health and safety of textile workers should always be a priority. Even if the flame-retardant materials used in the final product are considered safe, it's essential to assess whether the production process puts workers at risk. This includes the handling, application, and processing of the flame-retardant chemicals. Adequate protective measures, worker training, and monitoring should be in place to ensure the well-being of those involved in the production of flame-retardant-treated garments. There is low concern for worker health with phytic acid, an unknown risk for melamine phosphate, little to no known risk for chitosan, but there is high respiratory risk for workers involved in producing casein.

# VI. Strategy 2: Selectively Bred Cotton

The USDA Agricultural Research Service (ARS) has developed four self extinguishing cotton lines through breeding Multi-Parent Advanced Intercross (MAGIC) populations[3]. By using transgressive segregation, they were able to create combinations of genes that allowed for a phenotypic expression that is superior to the parent lines in self-extinguishing capabilities.

The researchers at the ARS discovered that flame retardancy did not come from a single gene in the cotton lines, instead they found that multiple genes created a phenotype that allowed for lower heat release capacities, which is quantified by the maximum rate of heat release divided by the heating rate. 257 recombinant inbred lines (RILs) were narrowed down to five that demonstrated the lowest heat release capacities as measured by microscale combustion calorimetry (MCC). Four out of five textiles fabricated from these parents exhibited self extinguishing properties through the 45 degree incline flammability test (Figure 6). The incorporation of this discovery into agricultural production will be encouraged by the desired agronomic and fiber quality traits in breeding and consumer usage.

Through the development of these lines, we postulate that the addition of potential chemical additives would be unnecessary should a garment be manufactured with just the selectively bred cotton textiles. Not only does the textile have self-extinguishing properties, it is also comfortable and safe to be worn for the duration of the fire fighter's time in the station.

Because this is a fairly new endeavor, the USDA has communicated that it will take some time for these textiles to come to market. However, the US military has already displayed interest, and they are starting to test the garment in their own facilities. Because of this demand, we hope that the time to market will be expedited.

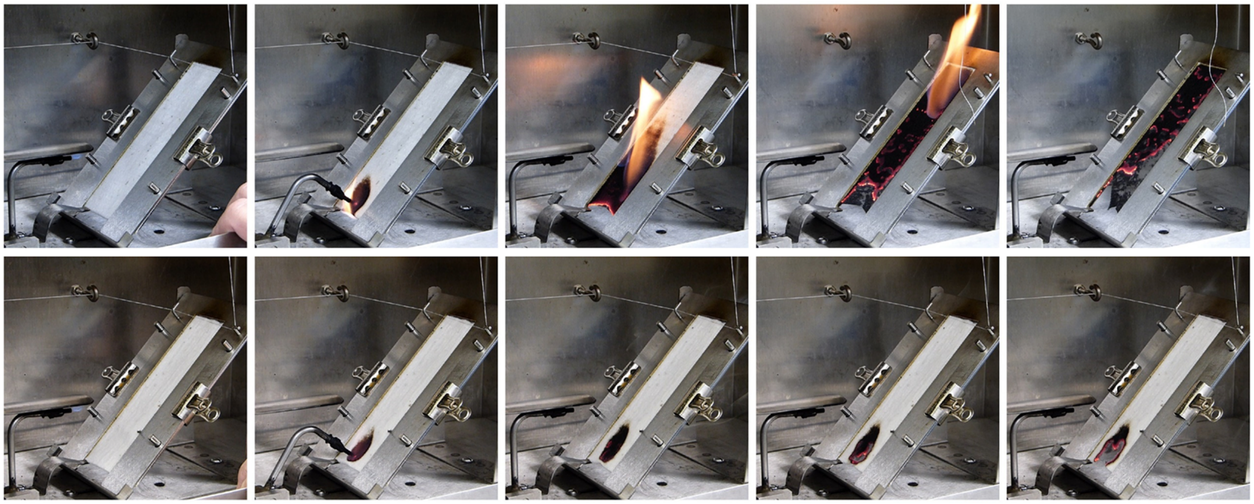


**Figure 6: 45 degree incline flammability test at the USDA ARS. Top - one sample of regular cotton, Bottom - one sample of selectively bred cotton**

# VII. Strategy 3: Re-evaluating the necessity of NFPA 1975 Standards

Our third strategy for eliminating flame retardants in firefighter station wear involves a critical re-evaluation of the NFPA 1975 standards. This standard, which is an optional guideline for US fire departments rather than enforceable legislation, may not universally apply to all firefighting scenarios and departments[1]. We recommend tailoring guidelines to the specific needs of each department, considering the varying risk factors associated with different firefighting environments.

In urban and structural firefighting responses, where burns make up a lower injury percentage compared to smoke inhalation, thermal stress, and physical injuries [4], the use of flame retardants in station wear is questioned. A study by Campbell & Hall found that fire or chemical burns accounted for only 6% of the 60,750 firefighter injuries in the US during 2021. While more research is needed to understand if this low incidence is due to effective flame retardancy in station wear, we currently find it doubtful. We need to carefully assess the cost-to-benefit ratio of utilizing flame retardant chemicals to prevent burns, considering the potential negative health effects associated with prolonged occupational exposures. Striking a balance between burn safety measures and the health implications of long-term exposure is essential for ensuring the overall well-being of firefighters.

As mentioned earlier, station wear is worn for extended periods, including downtime activities such as cooking, sleeping, and relaxing, and wearing flame-retardant clothing close to the skin during such activities seems unnecessary. Additionally, station wear is worn beneath a thick, flame-retardant layer of turnout gear in the field during fire responses which prompted us to include the suggestion that additive flame retardant chemicals in station wear may be classified as unnecessary and burdensome for most structural and urban fire fighters. Looking to countries like New Zealand, where firefighters rely on Merino wool and other natural fiber textiles for base layers and station wear due to their naturally flame-resistant properties[5], offers a safer alternative. This practice could serve as a model for rethinking flame retardant standards in firefighter apparel in the US, providing a low-hazard, cost-effective, and easily accessible fire-resistant base layer.

It's important to note that this strategy may not apply to all types of firefighters. For instance, wildland fire departments like Cal Fire often opt for a single layer of flame-retardant clothing without turnout gear due to the risk of overheating. In these cases, a nitrogen-phosphorus coating strategy might still be relevant, although this was beyond the scope of our current project and warrants consideration for future research.

# VIII. Hazard Assessments

## Human Health Assessment

### *Phytic Acid*

To fill the gaps in the hazard information for human endpoints I, we referenced existing literature, a hazard screening by the Environmental Working Group (EWG)[6], and a safety assessment review by the Cosmetic Ingredient Review (CIR)[7]. All sources were used to cross reference the low hazards assigned for human endpoints I. Phytic acid's natural origin and current applications in cosmetic and dietary supplements is an indication of its low hazard. Additionally, phytic acid has numerous health benefits including its anticancer, anti-inflammatory, anti-microbial, and neuroprotective properties [8]. The moderate hazard score for acute toxicity and systemic toxicity are based on the hazard score on Pharos and LD50 reported on the CIR safety assessment. We were unable to locate studies to confirm the hazards for skin and eye irritation. However, the hazard classification labels found on ECHA warrant it as a potential concern (H314,H318,H319). Phytic acid is considered an antinutrient due to its chelating properties [9]. However,a well balanced diet and proper food preparation should address these concerns [10]. Despite the existing gaps, we feel the low hazards assigned to phytic acid are appropriate in comparison to our baseline chemicals.

### *Chitosan*

The hazard assessment by the Australian government follows the Inventory Multi-tiered Assessment and Prioritisation (IMAP) framework and was conducted by National Industrial Chemicals Notification and Assessment Scheme (NICNAS). Chitosan underwent a Tier I Human Health assessment by the NICNAS, "chemicals on this list are not expected to pose unreasonable risk to the health of workers and public health". Chitosan's current applications and properties further support its low hazards for human endpoints I. Chitosan is known for its biocompatibility, biodegradability, antibacterial properties, antifungal properties, and tumor inhibition. No adverse effects have been reported with some of chitosans current application in wound healing,drug delivery, & bone regeneration [11,12]. No skin or eye irritation has been reported from animal studies on rabbits,guinea pigs, and pigs [13].

Chitosan is not a suspected carcinogen. There was no reported increase in tumor size after a dietary intake of 5% chitosan in rat studies [13]. No direct studies have been found for chitosan as an endocrine disruptor. However, chitosan has been reported to adsorb organic and inorganic chemicals like Bisphenol A (BPA) from aqueous solutions and as a supramolecule [14,15].

Chitosan's ability to adsorb organic and inorganic pollutants are potential indicators of its low hazard as an endocrine disruptor. Two separate studies confirm Chitosan's low hazard for acute oral toxicity [16,17]. No deaths were reported for the irradiated and nonirradiated forms of chitosan at median lethal doses of LD50 > 5000 mg/kg [16,17].

## *Melamine*

Melamine has been used since the 1930's and is considered toxicologically safe at low levels [18]. Potential concerns for Melamine include carcinogenicity (H351), repeated organ toxicity (H372), and endocrine disruption. The Australian government's assessments reveal melamine's low acute toxicity for dermal, oral, and inhalation exposure. Melamine's oral median lethal dose in male F344 rats is 3161 mg/kg bw and 3828 mg/kg bw in females. Additionally, no eye or skin irritation was observed in the animal studies reviewed by the Australian government [19]. Although melamine has a low acute toxicity, its hazard for carcinogenicity and systemic toxicity are of concern. Formation of stones in the urinary tract of male F344 rats is observed from repeated exposure of melamine at concentrations of 72 -1700 mg/kg bw/day. The dosage and presence of cyanuric acid determine the formation of stones in the urinary tract [20]. Overall, at low concentrations melamine demonstrates low acute toxicity and shows potential as a safer alternative.

## *Phosphoric Acid*

The assigned hazards for phosphoric acid are based on the CIR's final report for phosphoric acid and the human health tier II assessment by NICNAS [21,22]. Phosphoric acid's low hazards for carcinogenicity and reproductive toxicity are based on phosphoric acid's ability to be in equilibrium with its conjugate base. The acute toxicity studies reported in CIR's final report support the moderate to low hazard for acute toxicity. The reported median lethal doses depend on the concentration of phosphoric acid in the solution. Six out of the 7 studies report a median oral LD50 greater than > 2000 mg/kg. The reported repeated dose oral toxicity values also meet the low hazard green screen criteria of 100 mg/kg-bw/day. Negative studies have been reported for phosphoric acid's genotoxicity. Highly concentrated phosphoric acid is corrosive to the skin and eyes (H314,H318). We were unable to fill the existing data gaps for endocrine activity, neurotoxicity, skin sensitization, and respiratory sensitization and would recommend further testing for these endpoints.

## *Casein*

The low hazards for Casein are based on the Tier I Human Health assessment by NICNAS and its wide application in different industries. Casein is used in health supplements, tissue engineering, cosmetics, and drug delivery [23–25]. The only study found for casein's acute toxicity is for the consumption of antihypertensive peptides made from milk. No adverse effects were reported in the single (2000 mg/kg bw) and repeated (1000 mg/kg bw) exposure studies [26]. Casein's high hazard for respiratory sensitization is due to its appearance on the asthmagen list by the Association of Occupational and Environmental Clinics. Two case studies were found to further support casein's respiratory sensitization in the occupational setting. Both case studies showed adult onset of rhinitis and asthma after repeated inhalation of casein powder [27,28]. If casein is pushed forward, it is important to further investigate its respiratory sensitization and reduce workers' exposure through engineering controls. Overall, casein's biocompatibility, biodegradability, and low toxicity indicates its potential as a safer alternative.

| | PentaBDE | Phytic Acid | Chitosan | Casein | Melamine | Phosphoric Acid |
|---|---|---|---|---|---|---|
| Carcinogenicity | **M** | **L** | **L** | **vL** | **M** | **L** |
| Genotoxicity/ Mutagenicity | **DG** | **L** | **L** | **vL** | **L** | **L** |
| Reproductive Toxicity | **M** | **L** | **L** | **vL** | **pC** | **L** |
| Developmental Toxicity | **M** | **L** | **L** | **vL** | **pC** | **M-L** |
| Endocrine Activity | **H** | **L** | **L** | **vL** | **H** | **DG** |
| Acute Toxicity | **DG** | **M** | **L** | **L** | **L** | **M-L** |
| Systemic Toxicity *repeated | **M** | **M** | **L** | **L** | **M** | **L*** |
| Neurotoxicity | **M** | **DG** | **L** | **L** | **L** | **DG** |
| Skin Sensitization *repeated | **DG** | **L** | **L** | **L** | **L** | **DG** |
| Respiratory Sensitization *repeated | **DG** | **DG** | **L** | **H** | **L** | **DG** |
| Skin Irritation | **DG** | **pC** | **L** | **L** | **L** | **vH** |
| Eye Irritation | **H** | **pC** | **L** | **L** | **L** | **vH** |

Table 3. Comparative health hazard assessment for strategy 1

| **vH** | **H** | **M** | **L** | **vL** | **DG** | **pC** |
|---|---|---|---|---|---|---|
| Very High | High | Moderate | Low | Very Low | Data Gap | Potential concern |

## Environmental Assessment Strategy 1

The environmental hazards associated with our strategies were evaluated by the following factors: persistence, bioaccumulation, acute aquatic toxicity, chronic aquatic toxicity, and reactivity. We looked at these hazards in comparison to our baseline example of PentaBDE and found numerous restrictions and evidence from around the world listing PentaBDE as extremely persistent in the environment, bioaccumulative, and had both acute and chronic aquatic toxicity[29].

### *Melamine Phosphate*

Melamine phosphate, according to the German FEA, is a potential concern for human and/or aquatic toxicity and/or persistence and/or bioaccumulation. The New Zealand HSNO Chemical Classifications (GHS) also found it to be both acute and chronic aquatically toxic. We were not able to find any reliable information on the reactivity so we left this as a data gap to be filled in with further research findings.

### *Casein*

There have been few studies looking at these factors for casein being used in textiles, however, given that it is a protein derived from milk which is generally considered safe in the environment and frequently consumed by humans safely, we feel confident naming this as a very low environmental hazard substance across the board.

### *Phytic Acid*

Phytic acid, commonly found in plant seeds and legumes, demonstrates biodegradability and low acute and chronic aquatic toxicity. However, its persistence in the environment may vary [30]. Additionally, ChemSec and the EU - Manufacturer REACH hazard submissions, highlight its classification as persistent, bioaccumulative, and reactive with metals. More research is needed to determine how it would present when added to a textile.

### *Chitosan*

Chitosan, derived from chitin in shellfish shells and some mushroom species, is assumed to be biodegradable with low toxicity levels due to its harmless presence in ocean life. Studies have found chitosan to be non-persistent and non-bioaccumulative [31], and we further this assumption by asserting that its natural occurrence somewhat suggests minimal environmental concern. We must also consider the potential for contact allergic reactions as shellfish is a common allergen.

## Environmental Assessment Strategy 2 & 3

### *Selectively Bred Cotton*

Cotton, a naturally existing fiber, is widely considered biodegradable and non-toxic. The self-extinguishing cotton line from the USDA, which is selectively bred and not genetically modified [3], is expected to have a similarly low environmental impact to regular cotton. However, the overall environmental impact of any cotton textile is influenced by cultivation practices, including pesticide use and synthetic dyes or textile processing[32].

### *Merino Wool*

We are suggesting merino wool as a natural and readily biodegradable fiber suitable as a base layer in strategy three, with a very low expected environmental hazard.

| | PentaBDE | Melamine Phosphate | Casein | Phytic Acid | Chitosan | Cotton | Merino Wool |
|---|---|---|---|---|---|---|---|
| **Ecotox** | | | | | | | |
| Acute Aquatic Toxicity | vH | H | vL | vL | vL | vL | vL |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Chronic Aquatic Toxicity | vH | H | vL | vL | vL | vL | vL |
| **Fate** | | | | | | | |
| Persistence | vH | pC | vL | H | L | vL | vL |
| Bioaccumulation | vH | pC | vL | H | L | vL | vL |
| **Physical** | | | | | | | |
| Reactivity | DG | DG | vL | M | vL | vL | vL |
| Flammability | DG | vL | vL | vL | vL | vL | vL |

Table 4. Environmental Hazard Table

| vH | H | M | L | vL | DG | pC |
|---|---|---|---|---|---|---|
| Very High | High | Moderate | Low | Very Low | Data Gap | Potential concern |

Based on these compiled findings it's evident that our alternative strategies perform better on almost all environmental hazard factors, with casein, chitosan, cotton, and merino wool performing the best.

# IX. Honorable Mentions

## Nano Biocomposites as Flame Retardants

Nanobiocomposites, a novel class of composite materials, have emerged as a promising solution for advanced, high-performance, lightweight, and environmentally friendly nanocomposites. They are being investigated as substitutes for conventional non-biodegradable plastic materials, especially in industries like automotive and construction. Our primary focus lies in their role as flame retardants, addressing the burning deficiency of natural fiber composites. The integration of flame retardant (FR) nano-fillers, encompassing clay-based nano-fillers, layered double hydroxides, carbon-based materials, and metal oxides, have been found to enhance the flame retardant properties of biocomposites. These nanosized FR agents boast low or non-toxic environmental impact, aligning with sustainability goals[33].

The geometry and shape of nano-fillers, such as nanodispersion of nanoclay, can influence the flame retardancy of nanobiocomposites. The combination of clay-based nano-fillers with other nanosized or microsized FR agents can significantly improve thermal stability and flame retardant properties, opening avenues for a new class of nanocomposite materials. The potential impact spans various industries, especially in automotive and construction, where these materials can offer sustainable and eco-friendly alternatives to conventional non-biodegradable plastics. Overall, nanobiocomposites as flame retardants represent a noteworthy advancement in creating environmentally friendly and sustainable materials with applications across industries. Ongoing research in this field is anticipated to further shape the future of flame retardant materials.

***Figure 7: Incorporating nanofillers within biocomposite materials for enhanced flame retardancy while maintaining biodegradability (Kovačević et al', 2021)***

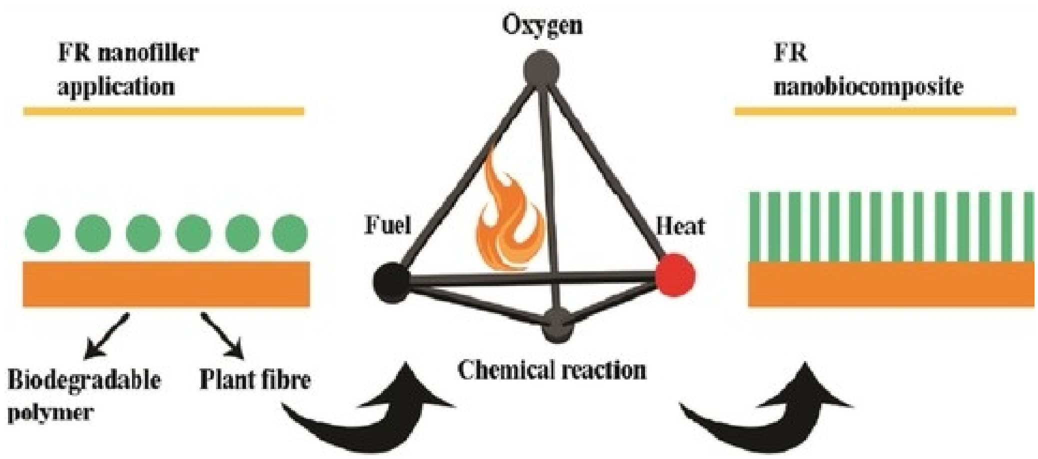



***Table 3: Different nanofillers based on their dimensionality***

| Plate Like (1D) | Nanofibres/Nanowhiskers (2D) | Nanoparticles (3D) |
|---|---|---|
| • Layered Silicates (Montmorilonite-MMT, Hectorite, Saponite) | • Carbon Nanotubes (Single-walled and Multi-walled) | • Silica Particles ($SiO_2$) |
| • Layered Double HydroxIdes—LDHs | • Cellulose Nanofibrils | • Metal Oxides ($TiO_2$, $Al_2O_3$, MgO, ZnO, $Fe_2O_3$, $Fe_3O_4$) |
| • Graphene Nano Sheets/ExPanded Graphite | • Cellulose Nanocrystals | • Metal Hydroxides (Nanomagnesium Hydroxide) |
| • Layered MoS2 Nano Sheets | • Bacterial Cellulose | • Metal Nanoparticles (Ag, Au, Cu, Fe) |
| • Layerd Nano α-Zirconium Phosphate | • Sepiolite Nano Rods | • Polyhedral Oligomeric Silsesquioxane (POSS) |
| • Pseudo-Boehmit (AlOOH) | • Halloysite Nanotubes | • Fullerene |
| • Black Phosphorus | • Gold or Silver Nanotubes | • Carbon Black |
| • MXenes Nano Sheets (Matal Carbides and/or Carbonitrides) | • Wormlike Rubber | • Spherical Nano Rubber |
| • Hexagonal Boron Nitride | • Boron Nitride Nanotubes | • Quantum Dots |

Source: Progress in Biodegradable Flame Retardant Nano-Biocomposites by Zorana Kovačević, Sandra Flinčec Grgac and Sandra Bischof, Polymers 2021, 13(5), 741

# X. Recommendations and Future Directions

The exploration of alternatives to halogenated flame retardants in firefighter station wear opens up several intriguing research avenues, particularly in the realm of selectively bred cotton. Future directions should focus on assessing the market feasibility of this cotton variant, including its scalability and cost-effectiveness. An important aspect of this research would be establishing a realistic timeline for production, taking into account the time needed for selective breeding, testing, and mass production. Durability is another critical factor, as the material must withstand the rigors of a firefighter's duties. This involves evaluating how well selectively bred cotton can endure repeated use and exposure to high temperatures without compromising its flame-retardant properties. A key test would be its performance in seam breakage tests, as the integrity of the garment is crucial for safety. Additionally, the longevity of the non-halogenated (N-P), particularly in terms of how many wash cycles the flame-retardant properties can withstand without significant degradation, should be a primary focus. This research will not only contribute to the safety of firefighters but also promote environmental sustainability by reducing the reliance on harmful chemicals.

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