Alternatives to Halogenated Flame Retardants Used in Firefighter Station Wear

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Problem Statement: Halogenated flame retardants added to firefighter station wear are harmful to humans as known carcinogens and endocrine disruptors. Recommended replacements should maintain flame retardancy without exposing humans and the environment to dangerous chemicals.

01 Identify

Safer alternative to the current flame retardants employed in NFPA 1975 certified firefighter station wear

02 Assess

These alternatives through chemical and environmental hazard and technical performance evaluations

03 Investigate

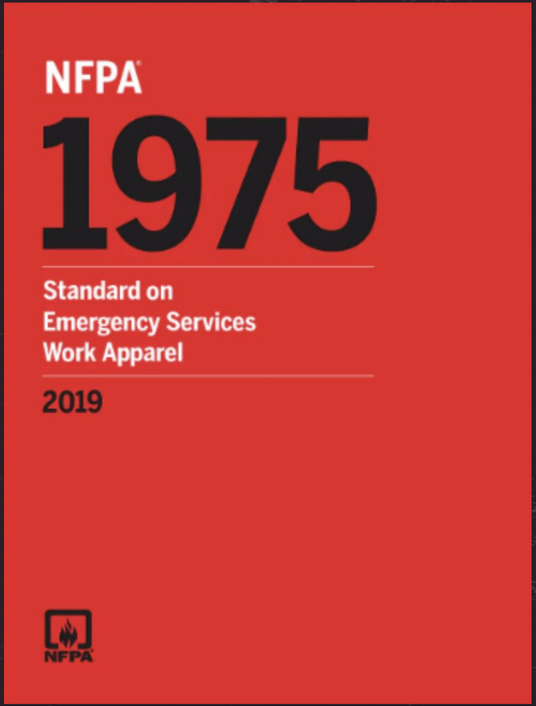
NFPA 1975 to see if it overly stringent requirements, with the goal of simplifying them while maintaining safety standards

Station Wear vs Turnout Gear

- Station wear is worn under the turnout gear and while in the station
- Turnout gear is worn as a protective outer layer during fire response
- Station wear can be for 24 hours at a time
- Necessitates comfort, as well as safety

NFPA 1975 Standard

- **Safeguards emergency services personnel**
- **Establishes requirements for flame-resistant station uniform clothing that won't cause or exacerbate burn injuries**
- **Industry standard, NOT regulatory and as such is not enforced by legislation**
  - Some states may enforce legislation that may contain either **more stringent** or **less restrictive** regulations on certain requirements



NFPA 1975 Station Wear Performance Requirements			
Test Name	Item Tested	Required Testing Conditions	Pass
Base Requirements Certification			
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 Does not stick to glass plate Resistance to blocking is 1 or 2
Thread Heat Resistance	All thread types	≤ 260°C (500°F)	Does not melt
Seam Strength	Woven textiles' Major seems* Knits	305 mm/min (12 inch/min)* 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 Certification			
Flame Resistance Test	Textiles and visibility markings	Held 38 mm(1.5 in.) above a flame	Passes baseline requirements Afterflames is < 2 seconds Char length is < 150 mm (6 in.)

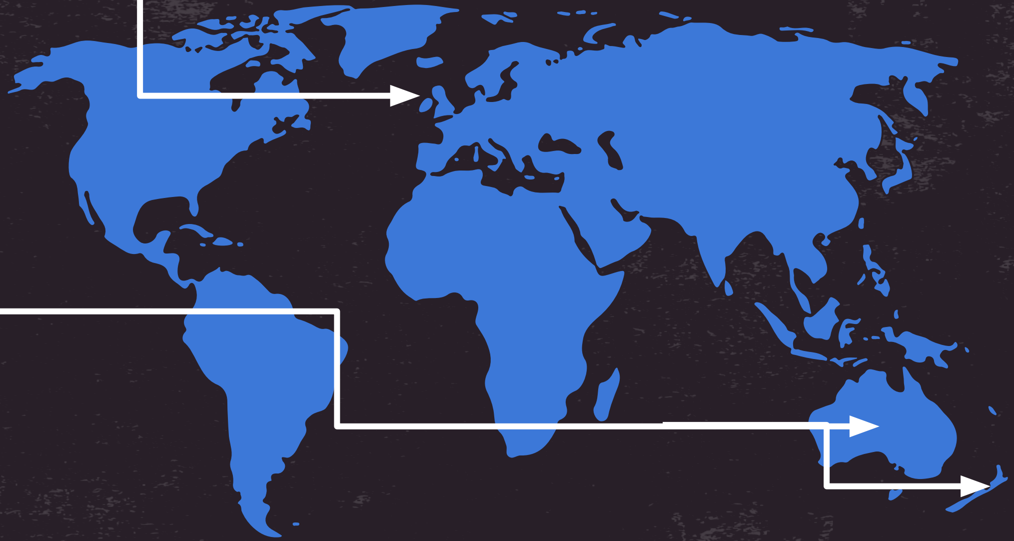
NFPA 1975 Comparison

European Union (EN 469)

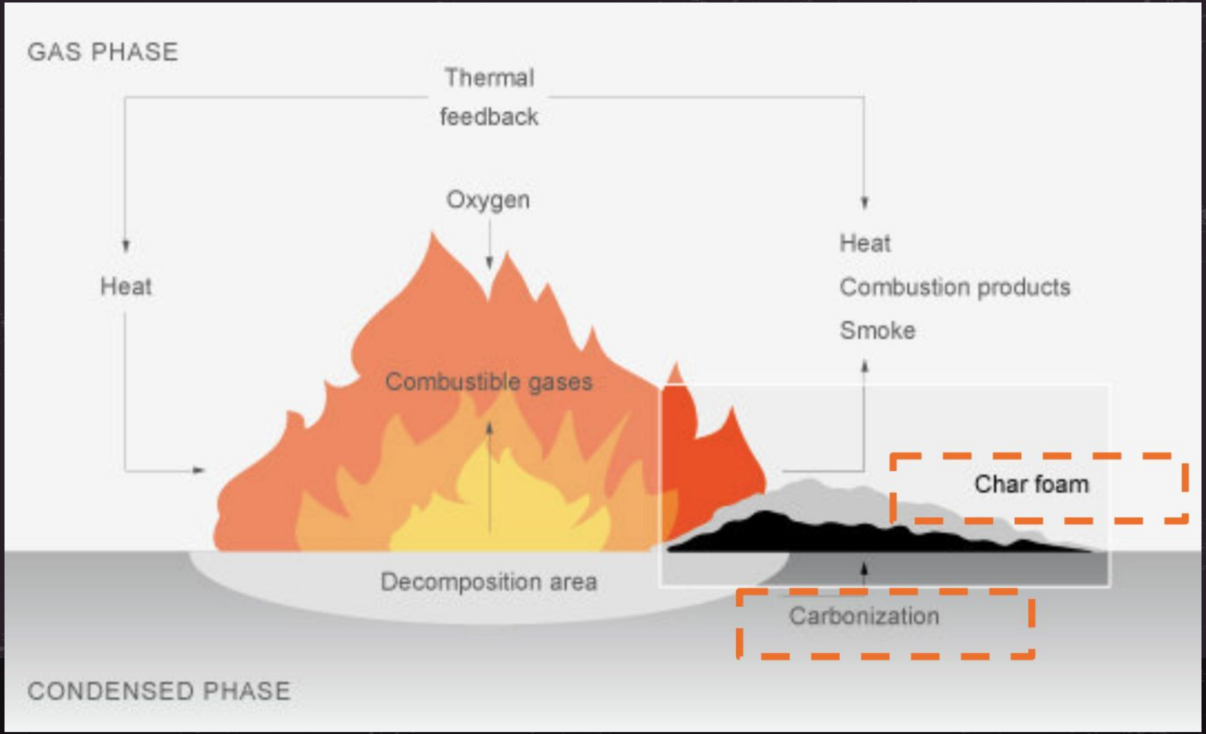
Foused on protective clothing for fire fighters engaged in firefighting and associated activities, **not specific to just station wear as NFPA 1975.**

Australia & New Zealand (AS/NZS 4967)

Similar to EN 469, this standard focuses on protective clothing for structural firefighting.

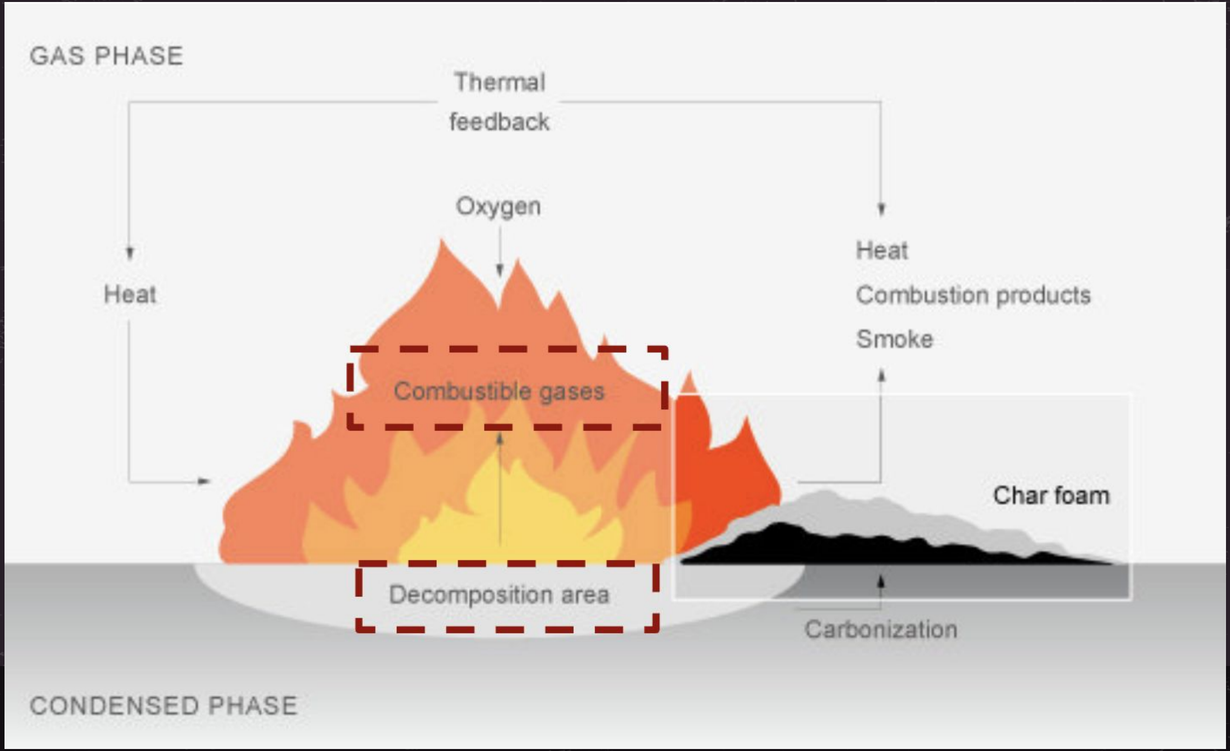


Flame retardants slow down or interrupt the combustion process by physical or chemical action



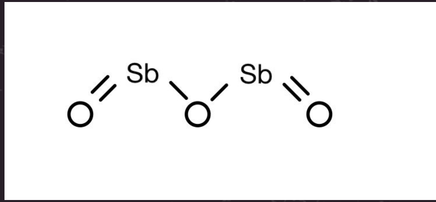
Source: Clariant

Flame retardants slow down or interrupt the combustion process by physical or chemical action



Source: Clariant

Chemicals Found in Station Wear*

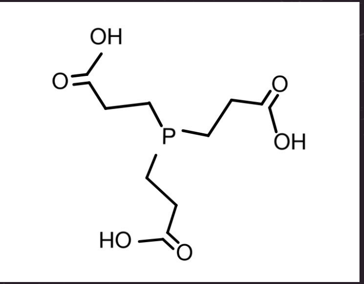


Antimony trioxide (Sb_2O_3)

Not a halogenated flame retardant

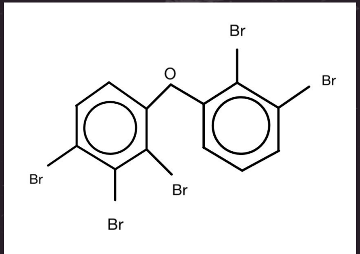
Used as synergist

Traces have been found in station wear



TCEP (tris(2-carboxyethyl)phosphine)

Emits fumes of POx and chlorides



Pentabromodiphenyl ether (Penta BDE)

Banned new manufacturing without evaluation in the United States in 2005

Emits Brominated Dioxins and Furans, Hydrogen Bromide (HBr), Carbon Monoxide (CO)

***This is not a comprehensive list of all chemicals found in station wear depending on different materials/manufacturers used across firefighting stations.**

Health Hazard	PentaBDE	TCEP	Antimony Trioxide
Carcinogenicity	*M*	H	H
Genotoxicity/ Mutagenicity	DG	M	M
Reproductive Toxicity	*M*	M	*M*
Developmental Toxicity	*M*	M	*L*
Endocrine Activity	*H*	*M*	DG
Acute Toxicity	DG	*M*	L
Systemic Toxicity	*M*	DG	H
Neurotoxicity	*M*	vH	L
Skin Sensitization	DG	L	L
Respiratory Sensitization	DG	DG	DG
Skin Irritation	DG	M	M
Eye Irritation	H	M	M

	PentaBDE	TCEP	Antimony Trioxide
Ecotox			
Acute Aquatic Toxicity	H	H	H
Chronic Aquatic Toxicity	H	M	M
Fate			
Persistence	H	M	vH
Bioaccumulation	H	vL	vL
Physical			
Reactivity	DG	L	*L*
Flammability	DG	L	L

vH	H	M	L	vL	DG
Very High	High	Moderate	Low	Very Low	Data Gap

How existing flame retardants are applied to textiles

Inherently Flame resistant	Flame resistant fibers	Flame treated fabric
Chemical Structure	Flame retardant chemicals	Chemical dipping
Synthetic or natural	Fiber formation process	Finishing coat
Wool or Nomex	Rayon	Fabric blends

Technical Performance Criteria Breakdown (NFPA 1975)

Flammability Criteria
Thermogravimetric analysis (TGA)

TGA
• Degradation temperature • Rate of degradation • Final residue percentage

Technical Performance Criteria Breakdown (NFPA 1975)

Flammability Criteria

Thermogravimetric analysis (TGA)

Peak/Total Heat Release(PHHR/THR)

PHHR/THR

- Time to ignition
- Sample mass variation
- Smoke density
- CO concentration
- CO2 concentration

Technical Performance Criteria Breakdown (NFPA 1975)

Flammability Criteria
Thermogravimetric analysis (TGA)
Peak/Total Heat Release(PHHR/THR)
UL 94 V Rating

UL 94 V Rating

- Self-extinguishing time
- A pass/fail test

Technical Performance Criteria Breakdown (NFPA 1975)

Flammability Criteria
Thermogravimetric analysis (TGA)
Peak/Total Heat Release(PHHR/THR)
UL 94 V Rating
Limiting oxygen index(LOI)

LOI

- LOI measures the minimum concentration of oxygen in the surrounding atmosphere required to sustain combustion.

Technical Performance Criteria Breakdown (NFPA 1975)

Flammability Criteria
Thermogravimetric analysis (TGA)
Peak/Total Heat Release(PHHR/THR)
UL 94 V Rating
Limiting oxygen index(LOI)
Differential thermal analysis (DTA)

DTA

- Provides insight into the phase transition and thermal reaction
- Proxy for thermal behavior of material

Mechanical Properties

- Loading rate

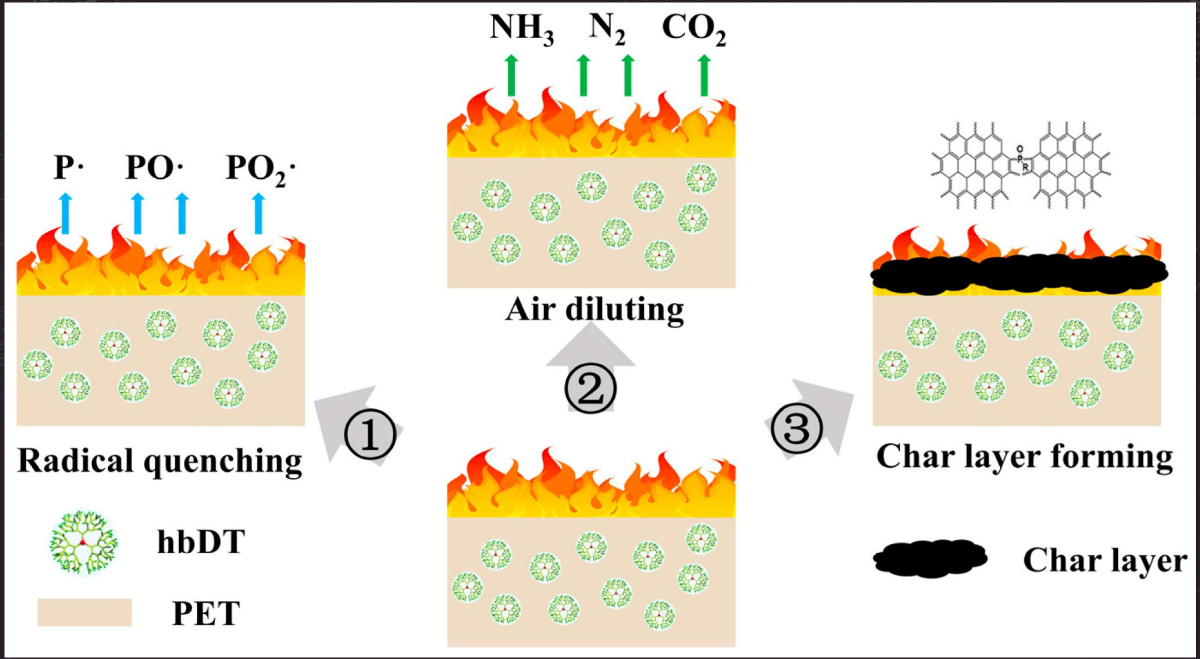
01

Strategy One

Nitrogen-Phosphorous (N-P) Synergistic approach

Strategies

Nitrogen-Phosphorous (N-P) Synergistic approach



(Abdalrhem et al., 2023)

Strategy 1 Candidates

Casein

Chitosan

Phytic Acid

Melamine Phosphate

(Images sourced from Wikimedia)

Flame retardancy mechanism	Melamine phosphate	Casein	Phytic acid	Chitosan
Flame poisoning	✓	✓		✓
Cooling	✓	✗	✓	
Char Formation	✓	✓	✓	✓
Intumescence	✓	(!)	✓	✓
Oxygen Dilution	✓	✓	✗	✓
Free radical trapping	(!)	✗	✓	✗

(!) Yes with synergist

✓ Yes

✗ No

	Baseline FRs	-	Data gaps		Alternative		Higher FR		Not significant impact		Lower FR

Parameters (Δ%) vs untreated Cotton	Penta BDE	Nomex	Cotton	Melamine Polyphosphate	Casein	Chitosan-Phytic acid(CS-PA10)	Ammonium phytate (APA) (20%)
$T_{10\%}$ (°C)	-	-	320	-19.4%	-23.9%	-21.2%	-18.9%
T_{max1} (°C)	-	+29.1%	342	-13.7%	-3.7%	-22.8%	-19.5%
T_{max2} (°C)	-	+18.5 %	485	+8.7%	+0.8%	+18.0%	-
LOI (%)	32.4-34.2	28.5 - 30	18.4	50.9 ± 0.6	32-44	30.8	43.2
UL94 V	V0	V0	v1	V0	V0	V0	V0
PHRR% (kW/m²)	-	-65.7 %*	175.11	-70.1%	-19 %	-	-94.5%
THR (mJ/m²)	-	-29.4%*	7.75	-64.2%	-(71.8-89.2) %*	-	-60.0%
Char length (mm)	-	-85.9%	Burns completely	-73.3%	-69%	-76%	-89.7%
Self-extinction	Yes	Yes	No	Yes	Yes	Yes	Yes
Dripping	No	No	No	No	No	No	No

Strategies

02

Strategy Two

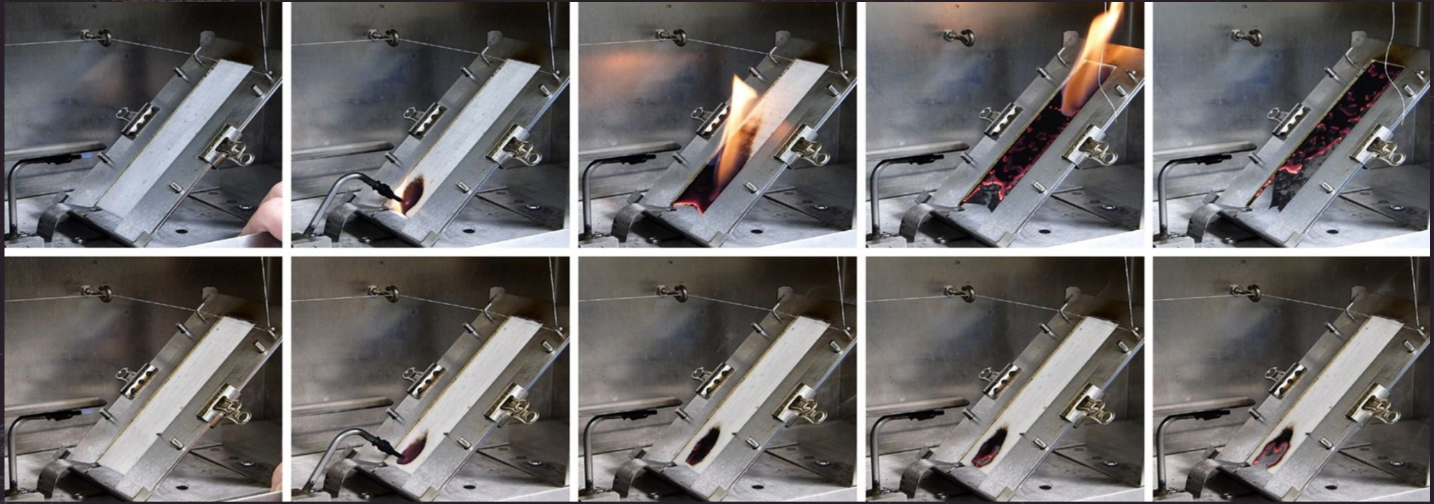
Selectively Bred Cotton

Selectively bred cotton from the USDA

- Researchers at the U.S. Department of Agriculture's (USDA) Agricultural Research Service (ARS) bred four cotton lines that can be used to make self-extinguishing textiles
- Reduces the need for flame-retardant chemical additives
- US military already interested

    A flame retardant uniform that has an increase in the amount of cotton in the blend, due to popular demand

How Selectively Bred Cotton Self Extinguishes



- When tested in the standard 45 degree incline flammability test, regular cotton (top) burned instantly when exposed to an open flame while selectively bred cotton (bottom) self-extinguished under the same conditions.
- Flame retardancy did not come from a single gene - multiple genes created a phenotype for fibers with significantly lower heat release capacities.

⅘ lines exhibited inherent flame resistance

1. A screen of 257 recombinant inbred lines for naturally enhanced flame retardance (FR) was conducted.
   a. All 11 parents produced a flammable fabric

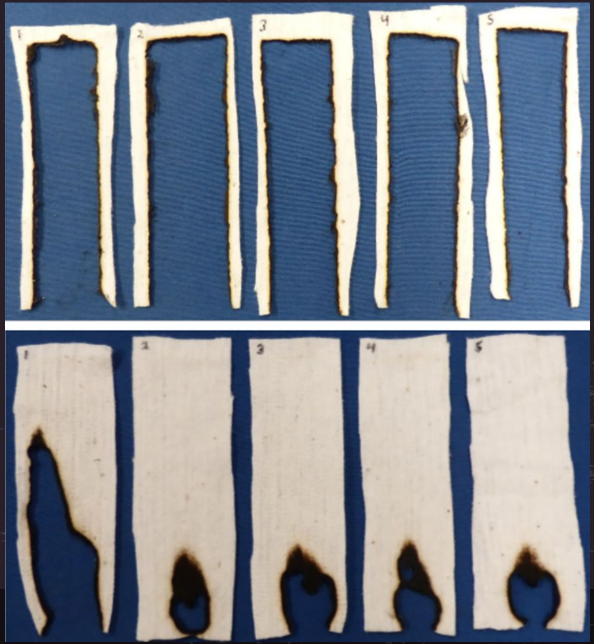
2. MAGIC recombinant inbred lines that produced fibers with significantly lower heat release capacities (HRC) as measured by microscale combustion calorimetry (MCC) were identified

3. 5 superior lines were identified

4. Four exhibited the novel characteristic of inherent flame resistance.

5. Four fabrics self-extinguished.

Flame resistant cotton lines (Thyssen et al., 2023)



Fire resistant cotton vs. regular cotton

Performance metrics for selectively bred cotton

What we know

- Cotton engineering garnered a phenotype for fibers with significantly lower heat release capacities.
- The new cotton lines also possess the desired agronomic and fiber quality traits, making the lines sought after for breeding and consumer usage.

To be determined

- Lacking performance metrics due to the novel stage of the cotton production
- In conversation with researchers at the USDA-ARS lab in New Orleans

03

Strategy Three

Re-evaluating the necessity of NFPA 1975 regulations

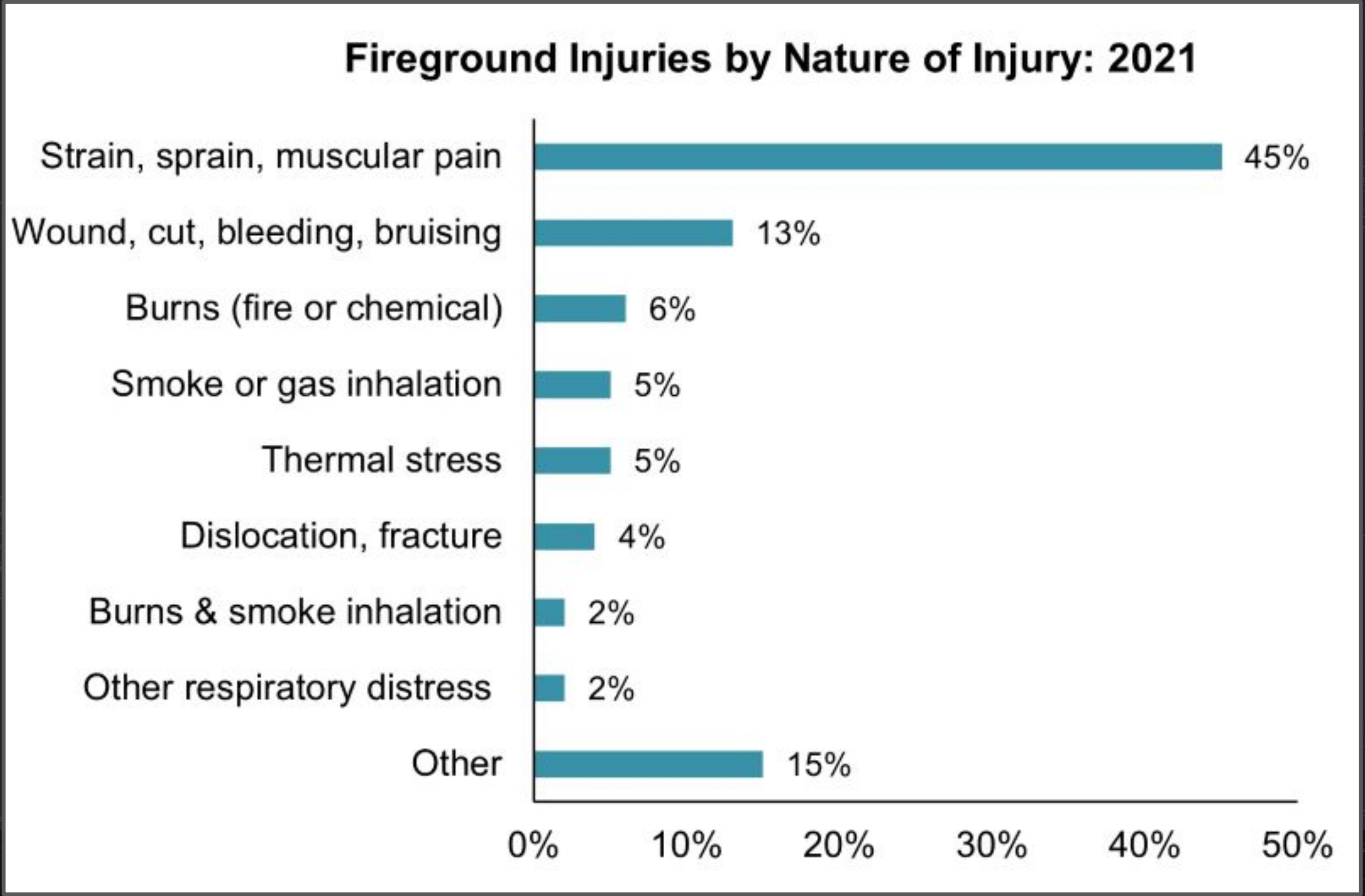
Are the NFPA 1975 standard guidelines necessary for all fire fighters?

Recommendations should be tailored to the specific needs of each department.

In many urban fireground responses, burns are a comparatively lower injury compared to smoke inhalation, thermal stress, wounds, and muscle strains.

For wildland fire departments like Cal Fire, where firefighters tend not to wear turnout gear due to the risk of overheating, the use of a nitrogen-phosphorus coating strategy may still be needed for a flame retardant alternative.

This flame retardant base layer isn't necessary for all departments.



(Campbell & Hall, 2022)

New Zealand's Approach

The NFPA 1975 standard is a guideline and is not enforced or required by legislation.

Firefighters in New Zealand don't consider the same NFPA 1975 guidelines as many of the departments in North America.

Many firefighters in New Zealand wear Merino wool textiles as base layers and station wear underneath their turnout gear given its naturally flame resistant properties.

Merino wool and other natural fiber textiles like cotton present little to no hazard to the wearer and would be a safer alternative if worn under a thick flame retardant outer layer.

Hazard Assessment of our Alternative Strategies

Hazard Assessment

		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

Hazard databases → Literature review → Computational tools

Low confidence	**High confidence**
Predictive tools	**Authoritative list**
Authoritative B list	**High quality data**
Computational tools	
Screening list	

Strategy ONE

Health Hazards of N-P

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

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

Assessment

Strategy ONE

Environmental Hazards of N-P

	Melamine Phosphate	Casein	Phytic Acid	Chitosan
Ecotox	Score			
Acute Aquatic Toxicity	M	vL	vL	vL
Chronic Aquatic Toxicity	L	vL	vL	vL
Fate	Score			
Persistence	H	vL	M	vL
Bioaccumulation	H	vL	vL	vL
Physical	Score			
Reactivity	DG	vL	L	vL
Flammability	DG	vL	L	vL

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

Assessment

Environmental Hazard	Score
Ecotox	
Acute Aquatic Toxicity	L
Chronic Aquatic Toxicity	L
Fate	
Persistence	vL
Bioaccumulation	vL
Physical	
Reactivity	vL
Flammability	vL

Health Hazard	Score
Carcinogenicity	vL
Genotoxicity/ Mutagenicity	vL
Reproductive Toxicity	vL
Developmental Toxicity	vL
Endocrine Activity	vL
Acute Toxicity	vL
Systemic Toxicity	vL
Neurotoxicity	vL
Skin Sensitization	vL
Respiratory Sensitization	vL
Skin Irritation	vL
Eye Irritation	vL

Strategy TWO

Selectively Bred Cotton

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

Assessment

Recommendations & Remaining Questions

Recommendation One

Fiber

- Organic, non-synthetic dyed cotton or merino wool

+

Flame Retardant Coating

- One of our Nitrogen + Phosphorus based compounds

Recommendation Two

Flame Resistant Fiber

- Selectively Bred Cotton that self-extinguishes

Recommendation Three

Redesign industry standards

- Reserve strategies 1 & 2 for necessary situations
- Use Merino wool for structural / city fires

Remaining Questions

- Feasibility of selectively bred cotton in the market
- Timeline for production
- Durability
    - Will it pass the seam breakage test?

References

1. AICIS. (2022a). 1,3,5-Triazine-2,4,6-triamine (melamine)—Evaluation statement—30 May 2022.
2. AICIS. (2022b). Chemicals unlikely to require further regulation to manage risks to environment—Evaluation statement—14 January 2022.
3. Bier, M. C., Kohn, S., Stierand, A., Grimmelsmann, N., Homburg, S. V., Rattenholl, A., & Ehrmann, A. (2017). Investigation of eco-friendly casein fibre production methods. IOP Conference Series: Materials Science and Engineering, 254(19). https://doi.org/10.1088/1757-899X/254/19/192004
4. Carosio, F., Di Blasio, A., Cuttica, F., Alongi, J., & Malucelli, G. (2014). Flame Retardancy of Polyester and Polyester–Cotton Blends Treated with Caseins. Industrial & Engineering Chemistry Research, 53(10), 3917–3923. https://doi.org/10.1021/ie404089t
5. Chang, S., Condon, B., Smith, J., & Nam, S. (2020). Flame Resistant Cotton Fabric Containing Casein and Inorganic Materials Using an Environmentally-Friendly Microwave Assisted Technique. Fibers and Polymers, 21(10), 2246–2252. https://doi.org/10.1007/s12221-020-9965-x
6. Ding, D., Liu, Y., Lu, Y., Liao, Y., Chen, Y., Zhang, G., & Zhang, F. (2022). Highly effective and durable P-N synergistic flame retardant containing ammonium phosphate and phosphonate for cotton fabrics. Polymer Degradation and Stability, 200, 109964. https://doi.org/10.1016/j.polymdegradstab.2022.109964
7. Emsley, A. M., & Stevens, G. C. (2008). 14—The risks and benefits of flame retardants in consumer products. In A. R. Horrocks & D. Price (Eds.), Advances in Fire Retardant Materials (pp. 363–397). Woodhead Publishing. https://doi.org/10.1533/9781845694701.3.363
8. Environmental Working Group. (n.d.). EWG Skin Deep® | What is PHYTIC ACID. EWG. Retrieved November 8, 2023, from http://www.ewg.org/skindeep/ingredients/704845-PHYTIC_ACID/
9. Fang, Y., Sun, W., Li, L., & Wang, Q. (2022). Bio-based Phytic Acid/chitosan and Polycarboxylic Acid for Eco-friendly Flame Retardant and Anti-crease of Cotton Fabric. Journal of Natural Fibers. https://www.tandfonline.com/doi/full/10.1080/15440478.2021.1964123
10. Feng, Y., Zhou, Y., Li, D., He, S., Zhang, F., & Zhang, G. (2017). A plant-based reactive ammonium phytate for use as a flame-retardant for cotton fabric. Carbohydrate Polymers, 175, 636–644. https://doi.org/10.1016/j.carbpol.2017.06.129
11. Flame Retardants. (n.d.). National Institute of Environmental Health Sciences. Retrieved November 9, 2023, from https://www.niehs.nih.gov/health/topics/agents/flame_retardants/index.cfm
12. Głąb, T. K., & Boratyński, J. (2017). Potential of Casein as a Carrier for Biologically Active Agents. Topics in Current Chemistry (Cham), 375(4), 71. https://doi.org/10.1007/s41061-017-0158-z
13. Levchik, S. (2014). Phosphorus-Based FRs. In Non-Halogenated Flame Retardant Handbook (pp. 17–74). John Wiley & Sons, Ltd. https://doi.org/10.1002/9781118939239.ch2
14. National Toxicology Program (NTP). (2017). NTP Technical Report on the Toxicity Study of Chitosan (CASRN 9012-76-4) Administered in Feed to Sprague Dawley [Crl:CD(SD)] Rats (93; p. 93). https://doi.org/10.22427/NTP-TOX-93
15. NFPA. (2019). NFPA 1975: Standard on Emergency Services Work Apparel. https://link.nfpa.org/free-access/publications/1975/2019
16. Oatway, L., Vasanthan, T., & Helm, J. H. (2001). Phytic Acid. Food Reviews International, 17(4), 419–431. https://doi.org/10.1081/FRI-100108531
17. Pharos. (n.d.). Pharos. Retrieved November 9, 2023, from https://pharosproject.net/
18. Polymers | Free Full-Text | Synthesis of DOPO-Based Phosphorus-Nitrogen Containing Hyperbranched Flame Retardant and Its Effective Application for Poly(ethylene terephthalate) via Synergistic Effect. (n.d.). Retrieved November 9, 2023, from https://www.mdpi.com/2073-4360/15/3/662#B12-polymers-15-00662
19. Solis, M. T. (n.d.). Flammability of Combustible Solids in Spacecraft Environments.
20. Sonnier, R., Taguet, A., Ferry, L., & Lopez-Cuesta, J.-M. (2018). Towards Bio-based Flame Retardant Polymers. Springer International Publishing. https://doi.org/10.1007/978-3-319-67083-6
21. Thyssen, G. N., Condon, B. D., Hinchliffe, D. J., Zeng, L., Naoumkina, M., Jenkins, J. N., McCarty, J. C., Sui, R., Madison, C., Li, P., & Fang, D. D. (2023). Flame resistant cotton lines generated by synergistic epistasis in a MAGIC population. PLOS ONE, 18(1), e0278696. https://doi.org/10.1371/journal.pone.0278696
22. Vahabi, H., Saeb, M. R., & Malucelli, G. (2022). Analysis of Flame Retardancy In Polymer Science. Elsevier.
23. Wang, S., Du, X., Jiang, Y., Xu, J., Zhou, M., Wang, H., Cheng, X., & Du, Z. (2019). Synergetic enhancement of mechanical and fire-resistance performance of waterborne polyurethane by introducing two kinds of phosphorus–nitrogen flame retardant. Journal of Colloid and Interface Science, 537, 197–205. https://doi.org/10.1016/j.jcis.2018.11.003
24. What's the Fuss About Organic Cotton? (2023, April 11). Sustainably Chic. https://www.sustainably-chic.com/blog/what-is-organic-cotton

Thank You!

Questions?