MONDAY, JUNE 6, 2022

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POSTER ABSTRACTS

Fire and Polymers

June5-8, 2022

Embassy Suites By Hilton Napa Valley

Napa, CA

1.

SENSITIVITY ANALYSIS OF THE PYROLYSIS MODEL OF NON-CHARRING AND CHARRING MATERIALS USING MORRIS SCREENING METHOD

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Sensitivity Analysis allows to determine the most influential input parameters of a numerical model. It was applied for the analysis of pyrolysis models but those methods were 'local methods', i.e., they do not consider the influence of a parameter in the whole domain of possibilities. Also, these methods do not highlight the possible interactions between the parameters. In this study, we propose to fill the gap by using a powerful screening method: the Morris method. We applied Morris method using the pyrolysis code, ThermaKin and we examined two materials in the conditions of cone calorimetry: the PMMA a non-charring material, and the PVC a charring one. The most influential parameters are the activation energy and emissivity. The second most influencing parameters are conductivity, heat of capacity and density. Then, the other parameters without any influence on the output parameters, like the gas properties (***Figure 1*** for illustration on the influence of the input parameters on time to ignition).

The method of Morris and its advantages will be presented in detail. The results of the study will be discussed, and the focus will be on the ability of the method to methodically perform sensitivity studies and to highlight the possible interactions between input parameters.

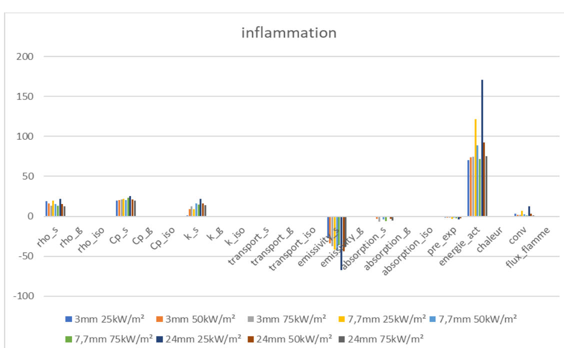

Figure 3: Influence of the input parameters on the inflammation (PMMA, different thicknesses and incident heat fluxes). The result Morris method allows to distinguish the input parameters from the most influential to the lesser ones. It allows also to determine in which sense and to point out potential interactions.

2.

Development of Computational Fluid Dynamics Models for Flame Retardant Thermoplastics in Electric Vehicle Applications

Lei Chen, Byeongjin Baek, Scott Corneillie, Cheryl Patchett, Amol Prabhakar Avhad, Swamy SM, Han Goossens, Sreekanth Pannala

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The rapid development of electric vehicle (EV) technology with anticipated growing electric or hybrid automotive market share [1] poses both opportunities and challenges on high-strength, lightweight, and flame retardant (FR) thermoplastic composite materials. Comprehensive computational fluid dynamics modeling approaches were developed with ANSYS Fluent and Fire Dynamics Simulator (FDS) to investigate external flame, polymer pyrolysis, intumescence and char formation, as well as the thermal and chemical interactions between fire and polymer. The polymer pyrolysis kinetic schemes were developed from thermogravimetric and calorimetric analysis of FR polypropylene samples. User defined scalars and functions were developed to model the polymer and char volume fractions, as well as the thermal property changes. The model was validated against experimental data in plaque-scale flame tests to provide insights into the behavior of FR thermoplastics with flame exposure, and can be used to predict the FR performance in thermal abuse events for EV battery packing applications.

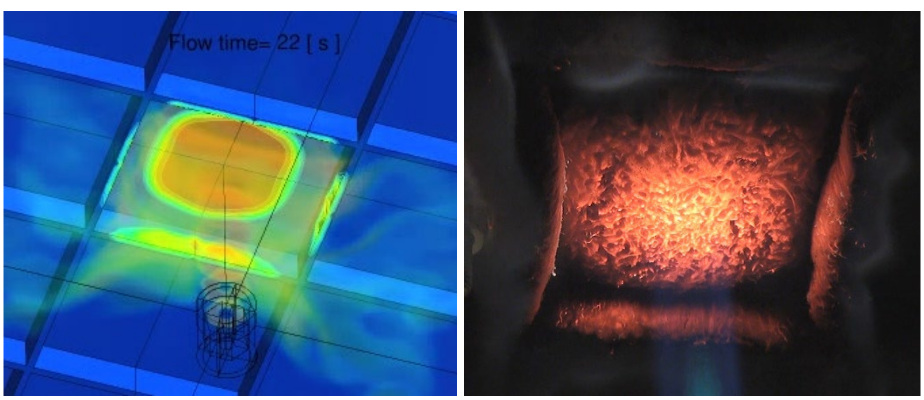

Figure: Comparison of the three-dimensional transient CFD modeling results of char volume fraction on the surface of the Flame Retardant Polypropylene (left), and the flame test experiments image (right).

[1] Fortune Business Insights, Market Research Report ID: FBI101678, Published Feb 2021

3.

Tannic acid-based super-intumescent coatings for prolonged fire protection of cardboard and wood

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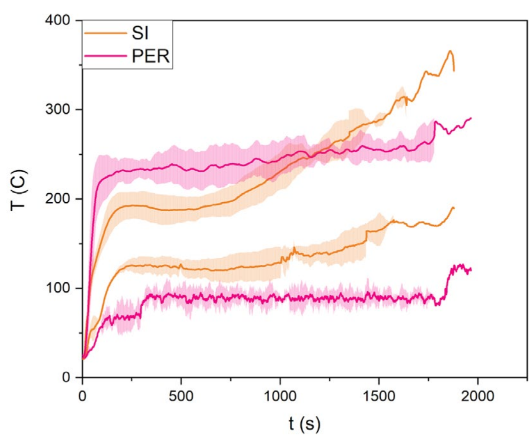
Tannic acid (TA) has recently gained recognition for its application in formulating environmentally friendly fire retardants. TA-based intumescent composites (SI) were developed and evaluated against control composites containing pentaerythritol (PER), a common intumescent char-forming agent. Components of the formulation were analyzed individually to provide a necessary baseline for comparison. The components were then compounded in epoxy resin to create intumescent coatings. The SI system produces highly expansive coatings which significantly outperforms the PER system in both heat dissipation and time-to-failure. Quantitative analysis followed using cone calorimetry. TA composites displayed lower peak heat release values (211 vs. 108 kW/m^2s^{-1}), lower total heat release values (37.2 vs. 24.4 MJ/m^2), and lower fire growth rates (2.43 vs. 1.27 kW/m^2) relative to PER composites. To complement cone calorimetry data, a number of structural analyses were performed on the resultant char to provide a structure/property understanding. These techniques include compressive testing, XPS, BET, and Raman spectroscopy. Support from Underwriters Laboratories is gratefully acknowledged.



Analysis of Thermal Exposure and Ignition of Western Red Cedar Subject to Glowing Firebrand Piles

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The prevalence and severity of wildland-urban interface fires leading to destruction of communities across the world has been continuously increasing. Post-fire studies indicate that firebrand exposure is responsible for a large percentage of structure losses during these wildfire events. In this work, a bench-scale wind tunnel setup was employed to analyze the mechanisms contributing to the ignition of a typical exterior structural fuel, Western Red Cedar (WRC) when exposed to glowing firebrands. Two types of ignition events were identified: direct ignition of the firebrand pile and surface ignition of the WRC board, with the WRC surface ignition event more likely to lead to further fire growth. Most of the WRC surface ignition events originated upwind from the air-flow-facing edge of the firebrand pile. Back surface temperature measurements, obtained with an infrared camera, were used to quantify the firebrand pile thermal exposure to an inert substrate using a thin ceramic fiber insulation board (Kaowool PM). Increasing the firebrand pile size increased the thermal exposure and the WRC surface ignition probability. Increasing air flow, up to 2.4 m s-1, increased the thermal exposure and the WRC surface ignition probability. Further, increases in the air flow speed decreased both quantities. This decrease was attributed to competition between an increased supply of oxygen promoting solid-phase firebrand combustion and increased convective cooling. Time-resolved CO2 and CO concentration measurements were used to compute heat release rate profiles and identify the nature of the combustion process. Smoldering was found to be the dominant mode of combustion for the WRC-firebrand pile systems.

5.

Development of silica microfibres and application as flame retardant additives in poly(lactic acid)

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Silane-based reactive surface modification of natural fibres is generally performed to improve the fibre-matrix interaction in polymeric composites. Surface treatment of reinforcing natural fibres was also found to effectively promote the charring and improve the fire resistance of intumescent flame retardant (IFR) systems. Nevertheless, various forms of silica-based additives have proven synergistic efficacy in phosphorus-based flame retardant systems.

In this study, neat silica microfibers and silane-treated polysaccharide microfibers were prepared using a solvent-based high-speed electrospinning technique and then applied as potential synergists in the IFR system besides melamine polyphosphate to obtain flame retarded poly(lactic acid) composites. The effect of the silica microfibres, differing in dimensions and chemical composition, was comprehensively investigated based on morphological, spectroscopic and thermal analyses, flammability (cone calorimetry, LOI, UL-94) and mechanical testing of the composites.

6.

Experimental measurements of full-scale fire growth for fire model validation

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A series of full-scale flame spread experiments was conducted to assess the impact of material composition on flammability response. In each test, two parallel panels, each with dimensions 2.45 m tall and 0.3 m wide, were spaced 0.3 m apart to support one of 17 unique materials with a wide range of chemical compositions and burning behaviors (charring, sooting, deformation, and ignitability). Samples were ignited at their base (60kW burner) allowing for upward flame spread. Measurement data collected in these experiments include: flame-to-surface heat flux, heat release rate, species yields, total mass loss, and visual recordings. Final datasets will be archived in a comprehensive, searchable, and freely-available database, which can be used for validation of CFD flame spread simulations. This poster provides a summary of the methodology by which these full-scale experiments were performed, how the measurement data was collected, and how this data was analyzed and processed for end-users.

7.

Flame retardancy investigations on composites for lightweight electric vehicle battery housings

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The automotive sector increasingly demands safety technologies such as flame-retarded materials used for electric vehicles. Suitable materials are needed for the fire protection of a rechargeable energy storage system (REESS) - including battery, housing and control electronics - against an external source of damage such as a fuel fire outside the car, and also against internal technical failure of the REESS such as an internal fire and (in the worst case) thermal-runaway of the entire REESS. To meet the requirements, the flame retardancy of the REESS housing materials is of great importance.

Here, we report the flame retardancy behavior of thermoplastic and thermoset composites in the event of an external fire, studied by a bench-scale fuel fire test which simulates the fire treatment of the UNECE-R100-8E on component level.

8.

Scale-up and Testing of New Self-Extinguishing Polymer

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We will present the scale-up and testing a new flame-resistant polymer. The issues of scale-up from laboratory scale to pre-production scale will be discussed. With the production of the polymer on the 1-kilogram scale, testing is the next priority. We will present the tests and testing involved as the polymer is scaled.

9.

Combustion Kinetics of Hydrothermally Carbonized Lignocellulosic Biomass by Cone Calorimeter

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This study focused on converting corn stover into carbon-rich biopolymer through Hydrothermal Carbonization (HTC) and evaluating the combustion kinetics in cone calorimeter at three heat fluxes (30-50 kW/m2). The biomass goes through HTC at 200, 230, and 260 °C for 30 mins. Resulting solid, also known as hydrochar, possess higher lignin but lower cellulose/hemicellulose biopolymers than biomass. The O/C and H/C ratios are significantly reduced augmenting heating value. The hydrochars are combustible at lower critical heat flux and ignition temperature. However, hydrochars also show higher ignition time and thermal response because of high lignin content. The combustion of hydrochar is mostly driven by the loss of volatile matter than the fixed carbon. Activation energy for oxidation of fixed carbon and volatile matter are significantly reduced through HTC, suggesting smoother combustion of biopolymers. The combustion of hydrochar follows first order kinetics. Hydrochars, overall, shows an increased combustibility than raw biomass.

Keywords: Hydrothermal Carbonization; Hydrochar; Biopolymers; Reaction Kinetics; Combustion; Cone calorimeter;

10.

Simple Surface Functionalization Method for Multifunctional Textiles with Flame and Vector Protection

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Nylon-cotton (Nyco) blends are currently used in a wide range of civilian and military textile applications because of their excellent strength and abrasion resistance provided by nylon, and comfort provided by cotton. However, there is a need to address the inherent flammability of Nyco and also impart insect repellent characteristics to the fabric . Nyco has a potential fire risk because cotton fibers catch fire at relatively low temperatures (ignition point ~ 350 °C) while Nylon 66 fibers tend to melt and burn continuously, adhering to the char formed by the cotton. Currently, there are very few cost-effective and durable flame retardants (FR) and insect repellent (IR) solutions available for Nyco fabrics. A novel method to impart safer & durable flame retardant (FR) characteristics and insect repellency to Nylon-cotton blends through covalent functionalization is explored. This involves the use of a biobased phosphorus-containing compound, phytic acid which is covalently attached to hydroxyl groups in Nyco. The FR functionalized fabric is then treated with insect repellent permethrin using plasma assisted crosslinking. The surface of the functionalized fabric was characterized using Fourier transform infrared spectroscopy, the thermal analysis and FR performance of the functionalized fabric was performed using thermogravimetric analysis, microscale combustion calorimetry, and vertical flame test. The insect repellency effects of the treated fabric were also studied using a modified World Health Organization Susceptibility Test. Detailed characterization of FR performance and insect repellant characteristics of this multifunctional fabric will be discussed.

11.

Polymeric Coacervate Coating for Flame Retardant Paper

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Cellulosic paper (from wood fibers) is a highly flammable material that is used in corrugated carboard, packaging, printing, and construction. While there is significant work focused on depositing a flame retardant coating onto the individual wood pulp fibers, there are very few studies that apply flame retardant coatings to already-cast paper. In an effort to improve the flame retardant properties of paper, a polymer-dense coacervate composed of polyethylenimine (PEI) and poly(sodium phosphate) (PSP) was deposited in a single step and subsequently crosslinked with glutaraldehyde. In a vertical flame test, the crosslinked PEI/PSP coacervate-coated paper achieves self-extinguishing behavior, and an average char length of 3.4 in, with only a 35% weight gain. Additionally, the crosslinked coating retains its flame retardant properties after water immersion and conditioning tests. This coacervate system is the first polymeric coating to be successfully deposited onto commercially available cellulosic paper for the purpose of flame retardancy.

12.

Phytic Acid-rich Flame Retardant UV-Curable Coatings for Metal Substrates

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We propose a formulation principle to include phytic acid in organic coating resins usable on steel substrates. Phytic acid (PA), a bio-based phosphorous containing functional molecule, is highly hydrophilic in nature, and incorporation of this molecule into organic fire-retardant organic coatings is a challenging task. We developed a UV curable polymeric material, which is prepared by reacting isophorone diisocyanate with PA first, to form a poly-isocyanate that was further reacted with hydroxymethyl acrylate to form methacrylated urethane resin. These phytic acid rich urethane-acrylate coatings were chemically characterized by 1H NMR, FTIR and XPS. We fabricated coatings on steel panels using these phyto-urethane-acrylate (PUA) resins via UV-curing using a photo initiator, Omnirad 1173. Coatings prepared using the PUA resin showed superior coating properties and higher glass transition temperature (T_g) compared to that of a commercially available resins. Our preliminary studies demonstrated that PUA based coatings showed 30% lower peak heat release rate (PHRR), and augmented fire-retardant properties as compared to control coatings.

13.

Renewable Nanocoating for Flame-Retardant Cottonid Paper

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Cottonid based-materials, made of 100% cellulose, have gained great interest in the bio-architecture field due to their comparable mechanical properties to wood and some technical plastics. These materials are manufactured by a parchmentizing process, in which several sheets of raw cotton-based paper (or cottonid paper) are joint together through a chemical reaction. Unfortunately, much like wood and other cellulose-based materials, cottonid is highly flammable. In an effort to reduce flammability, thin films of fully renewable and environmentally benign polyelectrolytes [chitosan (CH) and phytic acid (PA)] were deposited on cottonid paper via layer-by-layer (LbL) assembly. Only 4-bilayers of the CH/PA coating are required to achieve self-extinguishing behavior. Microcombustion calorimetry confirmed that coated cottonid paper reduces peak heat release rate and total heat release by at least 43% and 75%, respectively, relative to the uncoated control. These results demonstrate that this renewable intumescent LbL assembly provides an effective flame retardant treatment for these environmentally-friendly, climate-adaptive construction materials.

14.

Bioinspired Routes Towards Flame Protection of Wood-Plastic-Composites

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To overcome problems such as environmental pollution and the release of hazardous byproducts during combustion known from typically used flame retardant additives, organisms and biological structures which have evolutionarily adapted to fire-prone habitats are considered promising candidates for the development of biogenic and bioinspired alternatives.[1],[2],[3]

Thus, synthetical polymer-based materials mimicking the composite used by wasps for nest construction were prepared by extrusion and injection molding. Various natural proteins as well as different wood species were incorporated into polymeric matrices at several loadings to investigate their influence on the polymer's combustion behavior through modified versions of common flammability tests, e.g. UL94 or B2. Furthermore, the thermal behavior of the composite materials and each individual component was determined by TG-FTIR focusing on possible synergistic effects regarding thermal decomposition. Ultimately, the morphology of the material before and after combustion as well as the structural influence on the flammability was investigated by scanning electron microscopy.

[1] F. Laoutid, L. Bonnaud, M. Alexandre, J.-M. Lopez-Cuesta, P. Dubois, *Mater. Sci. Eng. R Rep.* **2009**, *63*, 100.
[2] A. Salamova, M. H. Hermanson, R. A. Hites, *Environ. Sci. Technol.* **2014**, *48*, 6133.
[3] X. Zhang, R. Sühring, D. Serodio, M. Bonnell, N. Sundin, M. L. Diamond, *Chemosphere* **2016**, *144*, 2401.

15.

Synthetic papers mimicking structure, composition and flame-retardancy mechanisms of wasp papers

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In order to find toxicologically less harmful and more environmentally friendly flame retardants, we investigate the natural flame protection mechanisms incorporated in wasp papers from different parts of the wasp nests. Throughout our investigations we separated structural and compositional influences to find and better understand biological mechanisms that are able to reduce the flammability of paper like materials.

For this, we produced biomimetic papers from wood particles of different tree species and used various commercial proteins that mimic the main component of the wasp saliva. The diversely processed papers were flame tested and investigated by TG-FTIR to classify their combustion behavior. The papers as well as their burnt residues were structurally characterized and compared with common papers and wasp papers. Thereby we confirm the influence of quantity and distribution of proteins on the flame retardancy properties of the biological blueprint.

16.

Bio-sourced Multilayer Nanocoating for Self-Extinguishing Nylon-Cotton Blend Fabric

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In 2020, 7,169 clothing related burn injuries were reported in the United States with the average total treatment cost being $73,532 per patient. Nylon-cotton blended fabric (NYCO), commonly used in military uniforms for its comfort and resilience, presents an inherent fire risk with its high flammability and high heat release. There are few effective flame retardant treatments for NYCO that are environmentally-benign and maintain the hand of the fabric. A layer-by-layer (LbL) assembled 15 quadlayer (QL) coating consisting of chitosan (CH), phytic acid (PA), and tannic acid (TA) was applied to NYCO. While individually TA and PA paired with CH are not self-extinguishing, they work synergistically in the QL system to create an effective intumescent coating. This completely bio-sourced coating self-extinguishes in a vertical burn test (ASTM D6413) with only 16.6% weight added, yielding 91.4% post-burn residue and a significant decrease in peak heat release rate. This novel coating highlights the potential of green materials to replace less environmentally-benign flame retardant treatments.

Polymeric Materials in Under-ventilated and Vitiated Environments - An investigation into control variable sensitivity for the controlled atmosphere cone calorimeter

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The controlled atmosphere cone calorimeter (CACC) is a bench scale apparatus addressing some of the limitations of the traditional cone calorimeter (CC) design, namely its inability to replicate later stage enclosure fires of equivalence ratio ≥1 where fire behaviour becomes ventilation controlled. Cone calorimetry provides an important link between polymer analysis and fire science. The addition of a controlled chamber offers an opportunity to examine worst case fire conditions, considering the toxic and irritant yields, for many materials. However, academic exploration on the sensitivity of control variables to collected results has been limited (both in terms of number of papers and materials explored). Therefore, this work builds upon the work of a previously published paper to examine the influence of inflow rate of air/nitrogen mixture into the CACC chamber. The current work expands on the method of oxygen reduction (flow rates causing both vitiation and under-ventilation), irradiance and fuel type. Experiments were conducted using a CACC at 30, 50 and 65 kW/m^2 irradiance levels. Flow rates of 5, 10 and 20 L/min were used to investigate under-ventilated conditions whilst flow rates of 100, 150 and 180 L/min were used for vitiated tests. Vitiated tests were conducted in atmospheres with 17.5 and 20.95 vol% O_2. This study has broadened the investigation to include 6 mm HDPE, PMMA, plywood, as well as electric cables (EQQ [S05Z1Z1-U] B2ca in accordance with EN13501-6) and liquid fuel (isopropanol IPA-1000). The fuels represent a wide range of potential subjects for CACC experimental research.

18.

Acid-Doped Biopolymer Nanocoatings for Flame Retardant Polyurethane Foam

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Soft furnishing fires contribute to 29% of fire causalities and $8.7 billion in direct property damage annually in the United States. Polyurethane foam (PUF), a common component in soft furnishings known for its comfort and flexibility, can emit toxic gases and propagate fires due to melt dripping when ignited. Various acid salts were added to a layer-by-layer assembled nanocoating, consisting of chitosan and carboxymethyl cellulose, to improve PUF flame retardancy and to understand the influence of salt-doping on flammability. The 20-bilayer phosphoric acid-doped coating exhibits self-extinguishing behavior, with a 67% reduction in peak heat release rate, while maintaining the structural integrity of the foam. By depositing this completely environmentally-sourced coating on polyurethane foam, the inherent danger of soft furnishing fires can be significantly reduced in a non-toxic manner.

19.

Halogen-Free Flame-Retardant Finishings for Textiles

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Among all technical textiles, fabrics with a low flammability are often desirable. Nature-based compounds, involving phytic acid or keratin, can be used for flame-retardant coatings of different textile carrier materials such as cotton, polyester/cotton blends or polyester. Both substances may be obtained from renewable or industrial waste products and were used for water-based textile coatings. Artificial and water-soluble flame retardants, synthesized from cyclophosphazene, also enable waterborne textile finishings. Since nylon-cotton blends are known to be challenging substrates regarding their flame-retardant functionalization and its durability, Nyco was finished with two different cyclophosphazene derivatives. An extensive investigation of the flame-retardant performance and mechanism of the different textile finishings and coatings was conducted.

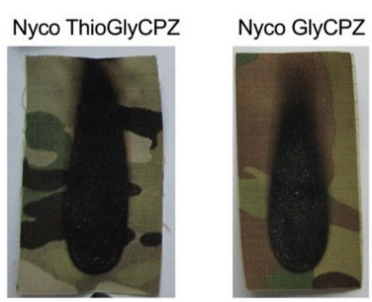

Figure 1. Flame tests of washed samples (10 times at 80 °C), according to ISO 15025.

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