Inhibit Fire with Molecules from Nature – Application on Textiles

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Preface

This report summarizes Brandforsk project 723-009. We want to express a big thanks for the financial support from Brandforsk.

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Abstract

The aim of this project was to find new environmentally friendly, and safe flame retardants (FR) from bio-based resources such as agricultural waste. The intended application of the FRs was on textiles.

Textiles are used in many different consumer products such as clothes, blankets, carpets, bedsheets, and upholstery, and since they are combustible, they will contribute to a large fire load in a room. One way to increase fire safety in homes and public buildings is to use flame retardants. They can delay the onset of a fire, or reduce the rate of fire spread, which gives opportunity for people to extinguish the fire, or escape in time. However, many flame retardants have been banned because they are bad for the health and/or the environment.

Phytic acid (PA), which is used by plants to store phosphorus, was combined with a few molecules from the group of purines, which are naturally occurring in living systems, and consequently safe. Commonly known purines are caffeine, theobromine, and theophylline, which are found in coffee, tea and chocolate. Other purines are guanine and adenine, which are building blocks in DNA.

Initially, screening tests were performed where PA and different purines were mixed in various ratios and applied on cotton, polyester, or wool. Burning tests and microscale combustion calorimetry (MCC) were used to assess the FR ability. Based on the results from the screening tests, the best mixtures were selected for further testing. The selected mixtures were PA with theophylline (TP) on cotton, and PA with adenine (AD) on cotton and polyester.

In the second phase of the project, the selected mixtures were investigated with cone calorimetry to get information on their heat release properties, and with thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) to get more detailed information on decomposition temperatures and processes. Nuclear magnetic resonance (NMR) was used to get additional information on the decomposition processes. Scanning electron microscopy (SEM) in combination with energy-dispersive X-ray analysis (EDX) was used to confirm the presence of both PA and purine on the textile, and to compare the surface morphology before and after FR treatment and burning.

Finally, medium scale fire demonstration experiments with a mock-up chair were performed on the best mixture (PA-AD) on cotton and polyester to validate that the small and medium scale experiments are applicable also in scales that are relevant for end-use.

The mixtures showed overall good FR performance, but the best result was on cotton. The results from methods where milligram size samples were used could be scaled up to fire demonstration tests. The main mechanism of action for the FR was charring the textile surface to reduce the amount of flammable pyrolysis gases, but the FR also worked by forming gases which dilute the oxygen and thus prevents the burning process. Endothermic reactions, e.g., degradation of the material, cools the material so that it will be more difficult to ignite, and formation of free radicals can stop the pyrolysis gases before they can react with the oxygen. Overall, the result was a self-extinguishing FR. The FR can also easily be applied on a textile by dipping the item in an aqueous solution.

Sammanfattning

Syftet med detta projekt var att hitta nya miljövänliga och säkra flamskyddsmedel (FR) från biobaserade resurser som jordbruksavfall. Den avsedda tillämpningen av FR var på textilier. Textilier används i många olika konsumentprodukter som kläder, filtar, mattor, lakan och klädslar, och eftersom de är brännbara utgör de en stor brandriskfaktor i ett rum. Ett sätt att öka brandsäkerheten i bostäder och offentliga byggnader är att använda flamskyddsmedel. De kan fördröja uppkomsten av en brand, eller minska brandspridningshastigheten, vilket ger möjlighet för människor att släcka branden, eller fly i tid. Många flamskyddsmedel har dock förbjudits eftersom de är dåliga för hälsan och/eller miljön.

Fytinsyra (PA), som används av växter för att lagra fosfor, kombinerades med olika molekyler från gruppen puriner, som förekommer naturligt i levande system och därför är säkra. Allmänt kända puriner är koffein, teobromin och teofyllin, som finns i kaffe, te och choklad. Andra puriner är guanin och adenin, som är byggstenar i DNA. Inledningsvis utfördes screeningtester där PA och olika puriner blandades i olika förhållanden och applicerades på bomull, polyester eller ull. Förbränningstester och förbränningskalorimetri i mikroskala (MCC) användes för att bedöma FR-förmågan. Baserat på resultaten från screeningtesterna valdes de bästa blandningarna ut för vidare testning. De utvalda blandningarna var PA med teofyllin (TP) på bomull och PA med adenin (AD) på bomull och polyester.

I den andra fasen av projektet undersöktes de utvalda blandningarna med konkalorimetri för att få information om deras värmeavgivningsegenskaper, och med termogravimetrisk analys (TGA) och differentiell svepkalorimetri (DSC) för att få mer detaljerad information om nedbrytningstemperaturer och processer. Kärnmagnetisk resonans (NMR) användes för att få ytterligare information om nedbrytningsprocesserna. Svepelektronmikroskopi (SEM) i kombination med energidispersiv röntgenanalys (EDX) användes för att bekräfta förekomsten av både PA och purin på textilien, och för att jämföra ytmorfologin före och efter FR-behandling och bränning. Slutligen utfördes medelstora branddemonstrationsexperiment med en mock-up-stol på den bästa blandningen (PA-AD) på bomull och polyester för att validera att de små och medelstora experimenten är tillämpliga även i skalor som är relevanta för slutanvändning.

Blandningarna visade över lag bra flamskyddsprestanda, men det bästa resultatet var på bomull. Resultaten från metoder där prover i milligramstorlek användes kunde skalas upp till branddemonstrationstester. Den huvudsakliga verkningsmekanismen för FR var att förkolna textilytan för att minska mängden brandfarliga pyrolysgaser, men FR fungerade också genom att bilda gaser som späder ut syret och därmed förhindrar förbränningsprocessen. Endoterma reaktioner, t.ex. nedbrytning av materialet, kyler materialet så att det blir svårare att antända, och fria radikaler som bildas kan reagera med pyrolysgaserna innan de kan reagera med syre. Sammantaget blev resultatet en självslocknande FR som också enkelt kan appliceras på textilier genom att doppa dessa i en vattenlösning.

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1 Introduction

<u>1.1 Aim</u>

The aim of the project has been to develop new environmentally friendly, and safe fire/flame retardants (FRs) by using compounds which are naturally occurring and harmless to humans and the environment. Since the compounds can be extracted from renewable resources, such as different waste materials or fermentation broths, with environmentally friendly methods, the project contributes to the development of sustainable FRs and a circular economy. To assess the FR performance on various textile materials, different methods from molecular scale to fire demonstration scale has been used.

1.2 Background

Textiles are an indispensable part of human life. In ancient times, natural fibres such as wool, flax (linen), and cotton were used for clothing [1]. They are still today used in many different consumer products such as clothes, blankets, carpets, bedsheets, and upholstery.

All fibres are polymeric in nature. A polymer is a long chain of small repeating units, known as monomers, which are bonded together. Wool is animal hair and consists of proteins, which are long chains of amino acid units bonded together. Historically, wool has been used in firefighter clothes because it is more difficult to ignite than cotton [2]. Flax and cotton are both made of cellulose, which is a carbohydrate material, consisting of long chains of glucose monomers [3].

In the early 20th century, the first synthetic fibre, rayon, which is made from wood, became available [4], and after that many different synthetic fibres have been invented, among them polyester, which accounts for the largest share of the synthetic fibres [5]. Rayon is very pure cellulose, and chemically the same as viscose and Lyocell, the different names reflect different production methods [4]. Polyester is made from alcohols and carboxylic acids. The most common polyester is polyethylene-terephtalate, PET [3].

During heating, the textiles will break down into smaller fuel fragments, a process called pyrolysis. The pyrolysis products can ignite if they mix with oxygen from the air in the right proportions. The heat produced will radiate back to the textile and generate more pyrolysis products, see Figure 1, and a fire will develop. The chemical composition of the fibres determines which pyrolysis products will form and, consequently, how easy they will ignite. E.g, cotton burns very easily, while wool is more flame resistant [6].



Figure 1. *Fire propagation cycle [6].*

According to statistics from Brandskyddsföreningen, between 20000 to 25000 housing fires happen annually, only in Sweden, and approximately 100 people die [7], mostly elderly [8]. In addition, many more are injured, physically and/or mentally. On top of that, the economic costs are also considerable for the individual, and for society; the fire rescue service had to act in more than 6000 of the housing fires mentioned above [7].

A fire will generate considerable amounts of toxic fumes from the burning material, e.g., carbon monoxide, hydrogen cyanide, and sulphur dioxide, and the nearest environment will be contaminated when harmful substances from the fire spread with the fire extinguishing water and foam. Hence, there are many incentives to reduce the risk of fire in buildings and authorities in many countries require stricter regulations regarding this [9].

Once a residential fire has started, it can easily spread and intensify because of the large amount of combustible materials present in an ordinary room. The textiles mentioned above are the most encountered in a home, and in public and commercial buildings, such as day-care centres, nursing homes, hotels, etc., and since they are all combustible, they will contribute with a large fire load to a room. Use of fire-proof or flame retarded furnishings and interior details is one way of risk mitigation [9-12].

To increase fire safety in homes, but also in public buildings, FRs can be used to delay the onset of a fire, or reduce the rate of fire spread, which gives opportunity for people to extinguish the fire, or escape in time. This is especially important for persons with risk factors, such as children, elderly, or people with mobility or cognitive challenges. The use of FRs may also be an affordable way to increase fire safety in existing rooms or buildings since some of the FR products can easily be applied on existing furniture. Bed clothes, clothes used when smoking, and textiles on furniture are examples where FRs would considerably increase the chance of survival.

In a few countries (e.g., UK and US), all upholstered furniture must meet certain requirements on fire safety by law, which often means that they should be treated with FRs [9,12]. The global market for FRs is expected to increase by 5% annually due to increased infrastructure activities and rise in safety standards [12].

Unfortunately, many FRs are bad for the health and/or the environment, many so much so that they are banned, e.g., various brominated FRs, which are persistent, bioaccumulating, and toxic [12,13-15]. Some FRs may release unhealthy vapours to indoor air or can cause harm for children from ingestion. In addition, the manufacturing of many FRs involves chemical processes with high energy consumption and use of hazardous chemicals and flammable solvents, which can cause bad health for industrial workers, and emissions to air, land, and water [15].

With developed polymer technology several flame-resistant materials have been invented. With those fabrics, no FRs need to be added because the fibres have chemical structures which require high temperatures before they start to degrade, and/or which during thermal degradation form non-combustible fragments. Those materials are primarily intended for use in hazardous environments, and their production and or use are associated with some concerns for health and environment [16-19], but one example available for public use is modacrylic [20]. It can be found in e.g., carpets and fake fur, and is often mixed with cotton or viscose in work underwear. In this material polyacrylonitrile [3] is copolymerized with chlorinated hydrocarbons, e.g., vinyl chloride, which is used to produce PVC [3,20]. During thermal degradation of modacrylic, many hazardous compounds can form, e.g., the gases hydrogen cyanide and hydrogen chloride [4,21], as well as various polychlorinated dioxins, which are persistent, bioaccumulating and known human carcinogens [3,22].

Thus, there are reasons not to use these materials, neither for work clothes, nor for fire-proof furniture and household applications, but instead replace them with more sustainable textiles. However, then the use of FRs is needed to inhibit the risk of fire.

So, on one hand there are increased incentives to have a more firesafe society, which has led to a development of fire-proof materials, and laws requiring the use of FRs. On the other hand, various environmental policy goals and instruments impose demands on a sustainable society, which would necessitate a reduction in the use of hazardous chemicals and preferably eliminate the use of materials with negative impact on health and environment. This has led to regulations banning many of the FRs used today. Hence, to achieve both a firesafe and a sustainable society, points towards a challenge and an opportunity to invent new FRs, which are safe for the health and the environment.

In this project we want to investigate a selection of bio-based molecules with possible flame retarding abilities. These molecules are naturally occurring in living systems such as humans, or consumed by the latter, and consequently safe to us as FRs. The molecules may be extracted from various waste or produced by microbial fermentation, which would promote a circular economy. Additionally, these methods for production of FRs will eliminate the use of harmful solvents since mainly water-based systems are used, and the processing of the product would involve classic downstream processes under relatively mild conditions [23]. Hence, both the production and the resulting products would be environmentally friendly.

Many of the sustainable development goals from Agenda 2030 [24] has been touched upon in the proposed project, but a special emphasis has been on minimizing release of hazardous chemicals and materials (6.3), improving waste management (11.6), efficient use of natural resources (12.2), environmentally sound management of chemicals and waste (12.4), and reduce waste generation (12.5), see Figure 2.



Figure 2. Agenda 2030 Sustainable Development Goals emphasized in this research proposal

2 Theoretical background

2.1 Environmentally friendly flame retardants

In recent years, research efforts have been made to develop environmentally friendly, non-toxic, and safe flame retardants (FRs) from natural compounds with favourable chemical structures for this purpose [12-14,25-31]. A few examples are phytic acid [26,30,31], proteins [28], and DNA [14,25].

Another advantage of these biobased resources is that they can be extracted from various waste materials from food and agricultural sources as well as from sewage. Many of the biobased compounds with the potential to be used in FRs are also produced innately by various microorganisms such as bacteria, algae, and fungi. By using the microorganisms in a biorefinery, compounds which, based on their molecular structure, are suitable for use as FRs can be obtained in a sustainable way [13-14,27]. With bioprocess technology, the microorganisms can produce a desired compound, or separate biomass into smaller building blocks, which can be used as they are, or be converted into other valuable compounds.

With detailed and specialized design of the FR on a molecular level, the flame retarding ability can be optimized. One example is proteins, which consist of long chains of different amino acids. Depending on the protein, the amount of individual amino acids can vary. As was shown in a previous Brandforsk project [31], the nature and amount of amino acid used give very different flame retarding properties, so by selective use of only the best amino acids in the FR, it is expected that a smaller amount is needed, and a better flame retarding effect will be achieved. Arginine has shown to be the best amino acid to use [31-32], and arginine can be selectively produced by bacteria [33].

An FR prevents or delays fire evolution through one or several mechanisms, which attack the different components of the fire tetrahedron (fuel, oxygen, chain reaction, heat). All four components are needed for a fire to occur [12]. Depending on the chemical composition of the textile, one mechanism can be more important than another [25].

Fuel can be removed by molecules containing phosphate or other acidic groups. Acids char the surface of the combustible material, which prevents fuel (pyrolysis gases) from forming or mixing with air. For cellulose, it is important that this charring takes place at a low temperature, because it has been shown that the composition of the pyrolysis gases that actually form becomes less flammable compared to the gas mixture that forms at higher temperature [12-13,34].

Oxygen can be removed by molecules containing nitrogen, carboxyl-, or hydroxyl groups. When such molecules break down upon heating, these groups form non-combustible gases (nitrogen, carbon dioxide and water vapour), which dilute the oxygen so that its concentration becomes too low for ignition to occur [12,34].

Fire is a chain reaction involving reactive species with unpaired electrons, also known as free radicals. They are needed for the fire to progress at a high speed. The chain reaction can be terminated by molecules containing phosphorus or hydroxyl groups, or certain metal ions, e.g., sodium, which react with the ignitable pyrolytic fragments and end the chain reaction [12,34-35-36].

The combustion reaction is strongly exothermic, which means that it generates large amounts of heat. In contrast, other chemical reactions are endothermic, which means that they absorb heat from the surroundings when they occur. Hence, FRs which can react endothermically can remove heat, preferably preventing the fuel from reaching its ignition temperature. The process of breaking molecules into fragments is an example of an endothermic reaction [12,34].

Molecules containing ring structures can form an insulating graphite-like char layer when they are exposed to an acid. This barrier prevents contact between fuel and oxygen but can also shield the fuel from heating. In combination with gas forming parts, the char layer becomes intumescent, and the thermally insulating properties increase [13,27].

2.2 Project idea

The idea behind the project was to combine a few naturally occurring non-toxic molecules with different chemical structures to find an efficient FR, which can remove all four sides of the fire tetrahedron, according to the mechanisms described above, i.e., cooling, charring, gas formation, radical termination, and thermal insulation. There are many methods available for studying the properties of an FR. Each method provides different information, some on macroscale properties and others on microscale and molecular properties. By combining several methods, data can be correlated with each other and better interpretations and understanding of the underlying mechanisms of action can be provided.

Phytic acid, see Figure 3, also called inositol hexaphosphoric acid, is a phosphate rich acid which can be found in various food, e.g. nuts and grains, and in agricultural waste, e.g. poultry litter [37]. Several studies have been performed on phytic acid based flame retardants for various combustible materials [26,28,30,38-44]. After (endothermic) thermal degradation at low temperature, the acid chars the surface of the combustible material and prevents the generation of flammable pyrolysis gases. The cyclic non-phosphate part of phytic acid forms a barrier of graphite-like structure, which insulates the fuel from heat and oxygen.



Figure 3. Phytic acid

Purines is a group of molecules with several well-known members, e.g., caffeine, theobromine (despite its name it does not contain any bromine), and theophylline, see Figure 4, which are found in coffee, chocolate, and tea. Other purines are adenine and guanine, which are parts of

DNA and RNA. Purines can be synthesized by bacteria [45]. As can be seen in Figure 4, all molecules in the purine group have similar structures, and hence, should also have similar properties. They contain nitrogen, which is important for gas formation, and the structures also contain carbon rings. The purines break down endothermically. Several studies have been performed on adenine- or guanine-based FRs for various combustible materials [46-49].



Figure 4. Naturally occurring purines.

It is known that a combination of phosphorus and nitrogen gives synergistic effects to an FR [34,50] so by combining phosphorus-containing phytic acid with nitrogen-containing purines, a more efficient FR can be obtained.

Phytic acid and a selection of purines were purchased in pure form from chemical suppliers. The selection included uric acid, theophylline, adenine and guanine. Cotton, polyester and wool were dipped in aqueous solutions of different combinations and ratios of phytic acid and purine, and after drying, the FR properties of the samples were screened by simple burning tests. Thereafter, the best performing samples were selected for further studies to gain more data on their thermal behavior, and finally the best of those samples, were selected for a demonstration test.

<u>3 Experimental methods</u>

3.1 Sample preparation

3.1.1 Screening tests

Small scale screening tests were done on 100% cotton, 100% polyester, and 100% wool textiles. The fabrics were washed before use.

Pieces of the fabric were cut into a size of 1×5 cm² and dipped in different FR solutions. The amount of FR adsorbed in each case was determined from the increase in sample mass after drying. The samples dried 1.5-2 days before use. Untreated samples were dipped in water an equal amount of time to try to reduce differences in humidity of the samples.

Adenine (AD), theophylline (TP), guanine (GU), and uric acid (UA) were chosen as purine bases (PB) and combined with phytic acid (PA). Aqueous solutions of acid and base were prepared and 6 M NaOH was used to adjust pH.

The following test series were performed:

* The molar ratios between acid and base were varied (PA:PB 1:1 1:2, 1:3, 1:4, 1:5, 1:6 and 1:7).

* The concentration of PA solution was varied (3%, 5% and 10%) and to avoid damage on the fabric, PA was slightly neutralized with NaOH to molar ratio 1:3, the ratio which has shown the best FR performance in a previous study [31].

* PA and PB were added to the same solution, or in separate solutions, with alternating dipping order, dipping time, and time between dippings (ten minutes or one day).

After each test series, some samples could be discarded for different reasons, mainly because of bad performance in the burning tests, but also because of negative effects on the fabric or poor solubility.

3.1.2. Detailed tests

Based on the results from the screening tests, the three best performing samples were selected for more detailed testing with a range of methods. Here cotton and polyester pieces with dimensions of 100x100x0.5 mm³ were cut for cone calorimetry tests, and size 1×5 cm², for the other tests. The samples were dipped in aqueous solutions with PA:AD molar ratio 1:4 for polyester, and 1:5 for cotton, and PA:TP molar ratio 1:5 for cotton. The fabrics were dipped in the AD or TP solution (for 30 minutes) and left to dry in open air for ten minutes, and then dipped in 10% aqueous solution of PA for ten minutes. For NMR tests, the dried samples were put in an oven at 150°C, 250°C, 350°C, or 500°C, respectively, for two minutes to allow for some thermal degradation.

3.1.3. Fire demonstration

After the detailed testing, the best performing FR mixture was selected for fire demonstration experiments at Rise Fire Research in Trondheim, Norway. Cotton and polyester samples were cut into pieces of size 800×650 mm² and prepared with the PA:AD solution. The FR treated

fabric was used as cover material in an upholstered mock-up furniture. More details on the sample preparation can be found in the Appendix.

3.2 Burning tests

The FR treated samples were hung in a hook inside a fume hood and ignited with a lighter. The top of the flame was applied at the bottom of the sample, see Figure 5. If the sample ignited, the flame was removed, and the samples were allowed to burn. If the samples did not ignite within ten seconds, but only charred, forced burning was provoked by moving the flame over the whole sample. A camera was used to capture video images of the experiments. Evaluation of the FR properties were made by measuring time to ignition, time to flameout, and residual mass, and the results were compared with those of untreated samples. To ensure reliability, the burning test were replicated three times for each formulation.



Figure 5. Application of flame in burning tests.

3.3. Microscale Combustion Calorimeter (MCC)

Microscale Combustion Calorimeter (MCC) was used to collect data on burning properties [51]. MCC is a small-scale fire experiment and is a very cost-effective method for screening materials and conducting flammability assessments. MCC measures the specific heat release rate (HRR), specific heat release (THR), and the net heat of combustion from the amount of oxygen consumed. From the HRR recorded the ability of the samples to release heat, i.e., the heat release capacity (HRC), can be calculated. The samples, weighing between 6 to 7 mg, underwent thermal oxidative degradation following Method B [51]. This method involves subjecting the samples to a mixture of oxygen and nitrogen at flow rates of 20 cc/min and 80 cc/min, respectively, within a temperature range from 100°C. The effluent resulting from degradation was directed into a combustor set at 900°C. The samples were subjected to a heating rate of 1°C/min throughout the tests. This methodology allows for a comprehensive

assessment of the combustion characteristics and thermal stability of the samples under controlled conditions.

Heat release rate (HRR) curves were recorded for untreated and treated samples. Additionally, total heat release (THR), heat release capacity (HRC), and peak heat release rate (PHRR), as well as time of peak heat release rate (TPHRR) were determined.

3.4 Cone Calorimetry

Like MCC, cone calorimetry is also used to study the burning properties of the samples [52]. Cotton and polyester samples were cut into dimensions of $100x100x0.5 \text{ mm}^3$ and treated with PA+AD or PA+TP (only cotton), and after drying the samples were exposed to a heat flux of 25 kW/m² for cotton and 35 kW/m² for polyester. This approach allows for robust analysis and comparison of the fire behavior and thermal properties of both treated and untreated samples. Data for time to ignition (t_{ign}), time to extinction (t_{ext}), heat release rate (HRR), total heat release (THR), and total smoke production (TSP) were collected. The experiments were following ISO 5660-1 [53].

3.5 Thermal Gravimetric Analysis (TGA)

In Thermal Gravimetric Analysis (TGA), a sample is placed on a very sensitive balance and the change in mass of the sample as it is heated is recorded [54]. When the sample degrades into gaseous species the remaining mass becomes smaller and the temperatures at which a significant mass loss occurs can give information about the thermal stability of the sample. TGA in inert atmosphere describes the thermal degradation, while TGA in air describes the combined degradation and oxidation of the sample. The thermal stability of treated and untreated textiles was determined on 1-10 mg of a sample when it was heated from 30°C to 750°C, with a heating rate of 20°C per minute. Investigations were made in both air and argon atmosphere.

<u>3.6 Differential Scanning Calorimetry (DSC)</u>

Differential Scanning Calorimetry (DSC) uses a few milligrams of the sample [55]. The sample and a reference sample are heated simultaneously and the difference in energy needed to keep both samples at the same temperature is recorded. The energy changes of the sample give information on temperatures at which the sample undergoes endothermic or exothermic processes, e.g., phase transitions or melting. If an energy change at a specific temperature correlates with a mass loss in TGA at the same temperature, a degradation process takes place at that temperature, while phase transitions and melting are processes that are not accompanied by a mass loss.

DSC measurements were performed in a controlled nitrogen atmosphere. The heating rate was 5 °C/min and the temperature range was set as 20 to 500 °C. 40 μ L aluminium pans were sealed after sample insertion and used with an empty pan as reference. Nitrogen flows were controlled as 50 ccmin⁻¹.

3.7 Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR)

Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) is a molecular scale method, sensitive enough to distinguish between atoms in different electronic surroundings in a molecule. When a sample is put in a strong magnetic field and exposed to radio frequency waves, the atomic nuclei in the sample will interact with the resonance frequencies. Small changes in a sample can be detected because the resonance frequencies will then change slightly. The changes are denoted chemical shifts from a reference frequency and is in the ppm scale. (To avoid orientation dependent interactions between sample and magnetic field the sample is spun at a "magic angle" relative to the magnetic field.) [56]. Common elements found in FRs, which can be studied are carbon and phosphorus. With this method it is possible to observe changes that has happened to the FR after exposure to heat and explain what has happened on a molecular level. In this study, samples which had been heated to various temperatures, were packed in rotors with diameter 4 mm and investigated in a magnetic field of 11.7 T and spinning speed 10 kHz for carbon measurements, and 12.5 kHz for phosphorus measurements.

<u>3.8 Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis</u> (SEM-EDX)

Scanning electron microscopy (SEM), was used to investigate the surface morphology of the treated materials with high magnification (down to nanometer scale) [57]. Such high magnification cannot be obtained with an ordinary optical microscope so instead a beam of electrons interacts with the sample. SEM was combined with Energy Dispersive X-Ray Analysis (EDX), which provides a map of the elemental distribution on the sample surface, i.e., whether the FR has been evenly dispersed over the sample surface [58]. Untreated and non-combusted samples were coated with a thin platinum layer before imaging, and an accelerating voltage of 3.0 kV was used for the analysis.

3.9 Fire Demonstration

Medium scale fire demonstration tests were performed according to the standard NS-EN 1021-2:2014 [59]. A mock-up upholstered furniture with FR treated fabric cover was placed on a scale inside a standardized small room and ignited with a standardized small burner. The experiment was conducted for two minutes and 15 seconds, before extinguishing with water. Mass loss and burning time were measured and compared to the results with untreated fabric, and with criteria defined in NS-EN 1021-2:2014 [59]. The experiments were performed twice, and if the results were inconclusive, a third experiment was performed. After two minutes and 15 seconds, the fire was extinguished. More details can be found in the report in the Appendix.

Fire demonstration experiments can be useful for two purposes; firstly, to validate that the small and medium scale experimental results are valid also in scales that are applicable for the end-use, and secondly for visual demonstration of the concept, e.g., for efficient communication of results for end-users. Similar approaches with fire experiments at different scales have been used in previous studies on upholstered furnishings [61], as well as in ongoing work in the FRIC centre [62].

4 Results and Discussion

4.1 Screening tests

As was described in chapter 3.1, many samples were prepared for screening with burning tests. Some of the samples could be discarded even before doing any burning tests. E.g., wool samples did not absorb the FR solutions, but only formed particles on the surface, see Figure 6. Textiles with only PA did not feel as light and soft as those with PA and PB, and were discarded for that reason.



Figure 6. TP precipitates on the surface of wool pieces.

In the burning tests, both untreated cotton and polyester very quickly burned completely, polyester after some melting and dripping, while the flame temperature from the small gas lighter used, was not high enough to ignite wool, which has a quite high ignition temperature [60].

Figure 7 shows an example of results from the burning tests. Untreated cotton ignited within two seconds and burned completely, leaving no residues (99.9% weight loss), while cotton treated with PA and AD (molar ratio 1:5) did not ignite even after ten seconds. After forced ignition, the sample formed char on the whole surface (not shown), the sample ignited, but self-extinguished.



Figure 7. *A) Burning of untreated cotton, B) Burning of cotton treated with AD and PA.*

Figure 8 shows that the ratio between PA and PB, here TP, affects the amount of charring that takes place on cotton before self-extinguishment.



Figure 8. Amount of charring on cotton depends on the molar ratio between PA and TP.

Figure 9 shows the weight loss for a selection of cotton samples after the burning tests. It can be seen that both the concentration and PB matters, with less mass loss the higher the concentration of FR, but the individual PBs also give different results.



Figure 9. Weight loss after burning tests. Note that the y axis is cut.

When the mixture contained both PA and AD the FR ability was improved compared to only PA, and for TP the results improved with increasing FR concentration. A gradual weight increase between dippings in each of the solutions (PB and then PA) confirmed that cotton interacts with both PA and PB, an observation that was further confirmed by SEM.

In general, all mixtures had some FR ability, i.e., it took longer for the samples to ignite, they burned slower than the untreated samples, or they self-extinguished and left a residual mass, or they did not ignite at all. The amount of char, and its thickness, also varied among the compositions. As could be expected, within a test series, the larger amount of FR that adsorbed, the better the FR properties.

Figure 10 shows some results from the screening with MCC on cotton samples. The HRR and HRC correlate well with the results from the burning tests shown in Figure 9, the more mass left after the burning tests, correlates with lower HRR and HRC in MCC tests.



Figure 10. Heat release rate for a few selected compounds.

On polyester, MCC tests were deemed more reliable than the burning tests because the fabrics tended to shrink and withdraw from the flame. However, samples treated with FR charred less, and melting and ignition was avoided. Figure 11 shows HRR curves for polyester samples with different molar ratios between PA and AD. Since the molar ratio 1:4 was significantly better than the other ratios, so the tests were additionally repeated to ascertain that there was no mistake in the sample preparation.



Figure 11. *HRR* from MCC on polyester samples treated with PA and AD in different molar ratios.

Figure 12 shows one example that there is some FR effect from the samples also on wool, but considering the negative effect from the FRs, the wool became very hard, no further tests were done.



Figure 12. MCC curves for wool treated with PA.

4.2 Detailed tests

Based on the results from the screening tests, the three best performing samples were selected for more detailed testing with a range of methods. The selected samples were PA and AD on cotton, PA and AD on polyester, and PA and TP on cotton. Untreated cotton and polyester were also analyzed for comparison.

4.2.1. Microscale Combustion Calorimeter (MCC)

Microscale combustion calorimetry (MCC) was employed to evaluate the flame-retardant properties of treated and untreated cotton and polyester fabrics by investigating data related to combustion properties. The heat release rate (HRR) curves for all the untreated and treated cotton tested in the MCC, are shown in Figure 13. Additionally, total heat release (THR), heat release capacity (HRC), peak heat release (PHRR), peak temperature (pTemp), and % mass loss are presented in Table 1. The data reveals the effect of adding theophylline (TP), adenine (AD), phytic acid (PA), and their combinations on the flammability and thermal degradation properties of cotton and polyester.



Figure 13. MCC results of treated and untreated cotton and polyester.

Pure cotton (C) exhibited high flammability parameters alongside a mass loss of 93.5%. The addition of TP or AD (C_TP or C_AD) reduced these parameters significantly, indicating an improvement in fire resistance: the HRC and PHRR dropped almost 50% for TP and even more for AD, and mass loss was also lower. TP, as well as AD, are nitrogen-rich compounds, and contribute to flame retardancy through the generation of non-flammable gases during thermal

degradation, which dilutes the oxygen concentration around the burning zone and slows down the combustion process [63].

An even more drastic reduction was observed with the addition of PA (C_PA), which gave values of HRC, PHRR, and THR, which were only 15-20% of those for untreated cotton, and pTemp also decreased drastically, and the mass loss was also lower, suggesting a significant enhancement in fire resistance. PA is effective as a flame retardant because it assists in forming a char barrier on the material's surface during combustion, which acts to isolate the underlying material from oxygen, thereby reducing the availability of combustible gases and lowering the peak combustion temperatures [64].

The combination of PB (TP or AD) and PA (C_PB_PA) exhibited similar fire resistance properties to C_PA, with only minor differences.

Sample	HRC (J/gK)	PHRR (W/g)	THR (kJ/g)	pTemp (°C)	% mass loss
С	241 ± 2.8	212 ± 3.1	12.5 ± 0.14	382 ± 2.5	93.5 ± 3.4
C_TP	140 ± 11.3	123 ± 8.2	8.8 ± 0.5	361 ± 1.2	82.4 ± 1.2
C_PA	38 ± 0	34 ± 0.4	2.3 ± 0.07	248 ± 0.3	61.6 ± 0.3
C_TP_PA(5:1)	37.3 ± 4.2	31.5 ± 3.7	2.3 ± 0.21	249 ± 4.4	57.7 ± 3.8
C_AD	79 ± 18	71 ± 17	6.5 ± 0.6	333 ± 7.2	68.1±5.6
C_AD_PA(5:1)	41.5 ± 5	37 ± 4	2 ± 0.2	255 ± 0.5	58.5±4
Р	412 ± 12	364 ± 4.9	16.3 ± 0.6	459 ± 0.14	88.6±0.8
P_PA	153 ± 47	128 ± 56	12.6 ± 1	429 ± 38	74.5 ±2
P_AD	262 ± 3	236 ± 2	14.7 ± 0.07	464 ± 0.1	79±.06
P_AD_PA(4:1)	148 ± 15.5	131 ± 13	12.35 ± 0.4	426 ± 44	74.2±1.3

 Table 1. MCC results of treated and untreated cotton and polyester fabrics.

Pure polyester (P) displays relatively high values for HRC, PHRR, THR, and pTemp. Upon modification of polyester with PA (P_PA), there is a significant reduction in all combustion parameters (HRC 63%, PHRR 65%, THR 23%, pTemp 6.5%). The application of AD (P_AD) onto polyester results in a less pronounced reduction in combustion properties (HRC 36%, PHRR 35%, THR 9.5%). The dual additive sample of polyester with both AD and PA (P_AD_PA) exhibits similar combustion properties as P_PA.

For untreated cotton, the values are significantly lower than those of untreated polyester, and almost similar to all treated polyester samples, highlighting cotton's naturally less flammable nature compared to polyester. The values further decrease when AD and PA are incorporated, showcasing low combustion properties. These results align with existing research on flame retardants where the integration of phosphorus and nitrogen-based additives has been shown to significantly improve the thermal stability and reduce the flammability by promoting char formation and inhibiting the gas phase propagation of fire [34,50].

4.2.2 Cone Calorimetry

Residues after the cone calorimetry experiments on cotton and polyester treated with PA and AD or PA and TP can be seen in Figure 14. The cotton samples self-extinguished, leaving a

charred residue, while untreated cotton burned completely. For polyester the amount of sample left is somewhat larger for the treated sample compared to the untreated.



Figure 14. Digital photos of residues after cone calorimeter experiments. From left to right: Cotton treated with TP and PA, Cotton treated with AD and PA, Polyester untreated, and Polyester treated with AD and PA. For untreated cotton no residue was remaining. Cotton samples were exposed to a heat flux of 25 kWm⁻² and polyester samples 35 kWm⁻².

The cone calorimeter results on the FR treated samples give an insight into their combustion behaviours and fire properties. These results are important for understanding the impact of these additives on the fire safety of cotton-based materials. Table 2 gives detailed data from the experiments.

Sample	Time to ignition TTI (s)	Time of flame out (s)	Total heat release, THR	Peak heat release rate, PHRR (kW/m ²)	Total smoke produced, TSP (m ²)	Time to PHRR (s)	Fire Performanc e Index, FPI (kW s/MJ)	Fire Growth Rate, FIGRA
			(MJ/m^2)	Cotton				(KW/S)
	010.00	67 Q + Q 1	44.01		2 + 0	22.2	0.1 + 0.001	0.6 + 0.0
C	21.3 ± 0.6	57.3 ± 2.1	4.4 ± 0.1	215 ± 4	2 ± 0	22.3 ± 0.6	0.1 ± 0.001	9.6 ± 0.2
C_PA	12.5 ± 0.7	30.5 ± 5	2.6 ± 0.4	72 ± 18	2 ± 0	13.5 ± 0.7	0.19 ± 0.03	5.3 ± 1.1
C TP	15.7 ± 2.1	45.7 ± 0.6	4.9 ± 0.2	257±11	8.3 ± 0.6	12 ± 2.5	0.06 ± 0.01	3.6 ± 0.11
C_TP_PA	14.3 ± 1.5	33.3 ± 0.6	2.8 ± 0.1	75 ± 18	3.7 ± 1.2	12 ± 2	0.2 ± 0.05	1.1 ± 0.01
C_AD	14.7 ± 0.6	37 ± 3	4.3 ± 0.6	146 ± 11	6 ± 0	15.7 ± 0.6	0.1 ± 0.01	9.4 ± 0.1
C AD PA	13 ± 1	30 ± 5	2.1 ± 0.5	38 ± 10	4.7 ± 1.2	14 ± 1	0.4 ± 0.1	2.8 ± 0.9
				Polyester				
Р	$63.5 \pm$		$2.2 \pm$		84.5 ± 3.5	64.5 ± 23	0.5 ± 0.2	2.3 ± 0.9
	23.3	132 ± 9.2	0.14	137 ± 7.1				
P_AD			$2.6 \pm$		68 ± 5.7	28.5 ± 5	0.25 ± 0.07	4.3 ± 1.3
_	27.5 ± 5	60.5 ± 0.7	0.14	119 ± 17				
P_PA	28.5 ± 3.5	$67.5 \pm$	$1.55 \pm$	99 ± 13	74 ± 16	29.5 ± 3.5	0.3 ± 0	3.36±
		10.6	0.2					0.03
P_AD_PA			$1.03 \pm$		58 ± 14	29 ± 10	0.1 ± 1.1	2.0 ± 1.4
	28 ± 10.1	68.7 ± 9.1	0.4	51 ± 35				

Table 2. Cone calorimeter results of treated and untreated cotton and polyester.

The untreated fabrics have longer time to ignition (TTI), indicating that they are relatively more resistant to ignition compared to the modified fabrics. Especially polyester has a very long TTI, despite the higher heat flux of 35 W/m², but the fabrics also sustain flames longer before flame off, and both THR and PHRR are higher than for the treated samples.

Conversely, the addition of FRs reduces TTI, highlighting their roles in facilitating quicker ignition, which induces char formation before the sample has absorbed too much heat. The charring leads to self-extinguishment, and the result is that both the burning time and the THR decrease almost 50%, and the PHRR even more.

In terms of THR and PHRR, C_TP records the highest values, suggesting that TP increases the energy release upon combustion, indicative of a more intense combustion process.

On cotton, the purine bases increase Total Smoke Produced (TSP), possibly due to their degradation into gas forming fragments. This mechanism can further contribute to suppressing a fire. The polyester samples generate much more smoke than the cotton samples and have TSP values, which are ten times higher.

The consistency in Time to PHRR across all samples suggests that the additives do not significantly alter the time taken to reach peak combustion intensity. Fire Performance Index (FPI), and Fire Growth Rate (FIGRA) provide an assessment of fire safety. Higher FPI values for samples with PA indicate improved fire performance due to PA's presence. C_TP_PA and C_AD_PA have the lowest FIGRA values, demonstrating a slower fire growth rate and enhanced fire resistance.

The dual additive combination in polyester (P_AD_PA) leads to drastic reductions in THR, PHRR, and TSP, compared to untreated polyester.

Figure 15 shows the HRR curves for the dual additive FRs as well as the untreated fabrics.



Figure 15. Heat release rate of treated and untreated cotton (C) and polyester (P) measured by cone calorimeter.

4.2.3. Thermal Gravimetric Analysis (TGA)

To investigate the variation in thermal degradation performance of untreated and treated fabric, in oxidative (air) and non-oxidative (Ar) atmospheres, TGA was performed. The TG and derivative DTG curves for air atmosphere are displayed in Figure 16A-B, and the resultant data are tabulated in Table 3.



Figure 16. TGA and DTGA thermogram of treated and untreated cotton and polyester.

The initial degradation (peak 1) starts below 100°C, and reaches a maximum near 70°C. This mass loss is caused by the elimination of water. In case of pure polyester fabric, peak 1 is absent due to the hydrophobic nature of polyester. Treated polyester, on the other hand, has some water present, bound to the FR.

The main degradation process of untreated cotton fabric (peak 3) occurs at a higher rate than treated cotton. In this stage the glycosidic linkages of cotton fabric are broken down by pyrolysis reaction and mainly L-glucose and flammable volatile constituents, such as levoglucosan, are formed [12,13,27]. The maximum degradation of untreated cotton occurs at 345 °C and almost no mass remains after this. In the last stage, around 500°C (peak 4), the remaining charred residue is oxidized to water and carbon dioxide. The weight loss of cotton is very fast and significant compared to treated cotton.

Sample name	Peak	Temperature (°C)	T _{max} degradation	Residue at 750 °C
			(°C)	(%)
	1	45-117	66	
С	3	270-380	345	0
	4	446-561	507	
	1	46-142	71	
C_TP_PA	2	175-245	233	10
	3	246-300	283	
	4	435-748	574	
	1	47-145	72	
C_AD_PA	2	178-246	234	10
	3	247-302	285	
	4	430-730	570	
Р	3	249-496	410	0
	4	500-615	574	
	1	47-150	90	
P_AD_PA	2	175-252	230	10
	3	260-476	352	
	4	477-750	540	

Table 3. Thermal degradation temperature and % weight loss for treated and untreated fabrics in air atmosphere.

Peak 2 is found only for treated cotton. The thermal degradation of PA facilitates acid dehydration and carbonization of the cellulose. The onset of char formation at a lower temperature (peak 3) leads to a limited formation of flammable and volatile constituents [12,13,27], and hence a smaller mass loss. The concentration of flammable gases might be further diluted by nitrogenous non-combustible gases formed when TP/AD degrade. The insulating char barrier formed on the cotton surface slows down the degradation process. In the last stage (peak 4), a charred residue still remains, indicating significant improvement in the thermal stability of fabrics after flame retardant treatment.

As shown in Figure 16A-B, the polyester fabrics show the same behaviour as cotton, that the FR treated polyester starts to degrade at a lower temperature than the untreated fabric, and that a char residue remains in the end. The main degradation process (peak 3) of untreated polyester fabric is slower and takes place at a higher temperature than untreated cotton. Thermal degradation of the polyester starts with formation of the free radicals, which further induce chain fragmentation processes [65].

Figure 16C-D show that in an inert atmosphere (argon), both the treated cotton and polyester retain 40% and 30%, respectively, of their mass, while untreated fabrics degrade completely.

4.2.4. Differential Scanning Calorimetry (DSC)

The exothermic and endothermic heat changes were recorded for treated and untreated fabrics (cotton and polyester). Figure 17 shows DSC thermograms and Table 4 summarizes the thermodynamic data.



Figure 17. DSC thermograms of treated and untreated cotton and polyester.

Cotton	$T_{(1)}$ °C	$\triangle H_1 Jg^{-1}$	$T_{(2)}$ °C	$ riangle H_2 Jg^{-1}$	$T_{(3)}$ °C	$\triangle H_3 Jg^{-1}$
С	82	88	344	184	NA	
C_TP_PA	79	90	227	37	282	-38
C_AD_PA	79	89	225	34	279	-31
Polyester	$T_{(2)}$ °C	$\triangle H_2 Jg^{-1}$	$T_{(3)}$ °C	$\triangle H_3 Jg^{-1}$	$T_{(4)}$ °C	$\triangle H_4 Jg^{-1}$
Р	252	59	426	263	NA	
P_AD_PA	251	57	355	119	420	-27

Table 4. Thermodynamic parameters of treated and untreated cotton and polyester.

In case of cotton, due to the hydrophilic nature of the cellulosic matrix, an endothermic heat change could be attributed to moisture evaporation (peak 1, panel A). For both treated and untreated cotton the DSC curve showed an endothermic event around 80°C ($T_{(1)}$), characteristic of the elimination of water. But, in case of untreated polyester fabric, due to less hydrophilic in nature, there is no endothermic peak in that range, and only a very small for treated polyester.

The second endothermal transition (panel A, peak 2) of cotton corresponds to the degradation of cellulose. In untreated cotton, the endothermic transition at 344°C requires a large amount of heat (Δ H= 184 Jg⁻¹) because of the almost complete degrading of the cellulose, as evidenced from the TGA curve in Figure 16C-D, while the treated cotton degrades to a lesser extent and hence also absorbs less heat. For untreated cotton, nothing more happens, but treated cotton shows an exothermic process at 280°C (T₍₃₎), possibly due to formation of a stable char, which prevents further degrading.

In case of polyester, the first endothermic transition at 250 °C (panel B, peak 2) has a heat change just above 60 Jg⁻¹ and corresponds with the melting point of polyester [60]. The endothermic degrading at 350°C to 450°C (panel B, peak 3), can be correlated with a mass loss in TGA, (Figure 16D). Treated polyester starts to degrade at a lower temperature than the untreated, which reduces the mass loss because of char formation initiated by the PA component in the FR.

4.2.5 Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR)

MAS NMR on samples heated to different temperatures can give information on the thermal degradation processes.

Figure 18 shows what has happened to cotton samples when they have been quickly heated in an oven at 350°C. Untreated cotton is still unaffected by the heat, and the spectrum is typical for cellulose [66-67], but for treated cotton there are no clear signals visible from cellulose, but instead there are signals in the aromatic region (approximate chemical shifts 100-120 ppm), and in the aliphatic region (approximate chemical shifts around 0 ppm), which shows that the cotton has degraded and charred the surface [66-67]. As could be seen in the TGA and DSC results (Figure 16B and 17A), untreated cotton has barely started to degrade at 350°C, while treated samples already have degraded, so there is a good correlation between these data. The sample temperature for the samples used in this study, were probably lower than indicated.



Figure 18. ¹³C MAS NMR on heated cotton samples. y-axis not to scale.

Figure 19 shows what has happened to PA when treated cotton samples have been quickly heated in an oven at 350°C. The signal from PA at room temperature has a chemical shift close

to 0 ppm, but at 350°C, new signals have appeared at negative ppm values. The more negative, the higher degree of polymerization of the phosphate groups, which means that AD has formed slightly larger polymers than TP. The polymerization reaction is endothermic, and the polyphosphates can contribute to a protective barrier [68].



Figure 19. ³¹P MAS NMR on heated cotton samples. y-axis not to scale.

4.2.6 Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis (SEM-EDX)

For the physical characterisation of the fibres, Scanning Electron Microscopy was used, and to confirm the presence of FRs, Energy Dispersive X-Ray Analysis was performed. In Figure 20 some representative SEM images are shown for cotton and cotton treated with FRs consisting of PA and AD or TP. As can be observed, the fibres look relatively similar and intact regardless of whether it is pure, or FR treated cotton. Even after heating to 350 °C, the fibres look relatively unaffected. The presence of FR in the material could also be confirmed with the EDX analysis, which shows presence of both N and P.



Figure 20. Representative SEM images of untreated cotton (A), cotton AD_PA (B), untreated cotton 350 °C (C) and EDX analysis of cotton TP_PA (D).

4.3 Fire Demonstration

Based on the results from the detailed tests, the FR mixture with PA and AD was selected for the fire demonstration test. The reaction to fire properties of cotton and polyester treated with this mixture was demonstrated experimentally on a mock-up furniture with upholstery filling based on the NS-EN 1021-2:2014.

Untreated polyester and cotton ignited within 15 seconds using a small flame ignition source and continued to burn the whole experimental time (2 min, 15 sec). The fire propagation on cotton was much slower and less intense than with polyester, which can be seen in Figure 21 where the damage to the furniture covered with polyester was more severe.



Figure 21. Untreated cotton (left) and polyester (right) after fire demonstration test.

Treated polyester burned much less intense and had a slower fire propagation than untreated polyester, and self-extinguished in one of the two tests.

Treated cotton did not ignite in any of the tests with the small ignition source, but with crib 5, the samples burned.

Figure 22 shows representative photos from the tests.





C_{AD+PA} Crib 5

For more details on the medium scale demonstration see the appendix. Table 5 summarizes the results from the study.

		Self-extinguished within time limit?			
Specimen	Exp.	Small	Small	Crib 5	
D	no.	flame 1	flame 2	[10min]	
		[2min, 15	[2min, 15		
P1	1	No	NA	NA	
P2	2	No	NA	NA	
C1	3	No	NA	NA	
C2	4	No	NA	NA	
P _{ad+pa} 1	5	Yes	No	NA	
P _{ad+pa} 2	9	No	Yes	NA	
$C_{ad+pa}1$	6	Yes	Yes	Yes	
C _{ad+pa} 2	7	Yes	Yes	No	
C _{ad+pa} 3	8	Yes	Yes	No	

Table 5. Summary of results, untreated and treated textiles, with two different methods of ignition (small flame and "crib 5").

Here you may find videos showing the fire experiments with each of the four different cases in the study (search for "Brandforsk study"): <u>https://www.youtube.com/c/RISEFireResearch</u>

5 Conclusions

Novel environmentally friendly purine-phytic acid-based FRs containing high amounts of nitrogen and phosphorus elements were formulated and successfully applied on cotton and polyester.

The thermal stability of the treated and untreated fabrics was analysed by studying different physicochemical properties, e.g. time to ignition (TTI), Heat Release Capacity (HRC), Heat Release Rate (HRR), Total Heat Release (THR), % of weight loss, etc.

Phytic acid and adenine on cotton (C_AD_PA) in a 5:1 molar ratio was the combination that showed the best FR properties with phytic acid theophylline combination (C_TP_PA 5:1) close behind. Compared to untreated cotton, the thermal stability of the samples is improved sixfold.

Cone calorimeter measurements show that the FR treated samples ignite earlier than untreated, but they also flame out earlier so that the burning time is halved. THR and PHRR are reduced compared to untreated cotton, especially for C_AD_PA. The samples self-extinguish after only a small mass loss. Charring of the material from acidic phosphate groups in PA is the reason behind this. The smoke production is increased, possibly because of gas formation when the purine degrades. Compared to using only PA as FR, the combination with AD leads to a further reduction in PHRR and a lower FIGRA index.

TGA and DSC correlate well with each other and describe the thermal degradation process in three steps starting with evaporation of water, then degrading of the FR molecules followed by char formation. The char formation hinders the FR treated samples from total degradation.

NMR measurements support the interpretation of TGA and DSC data, showing that FR treated cotton has degraded completely into char before the ignition temperature of cotton is reached, and the degradation of phytic acid has transformed the phosphate part into a polymerized material.

SEM images show that the structural integrity of the textile fibers is conserved after treatment with PA and purine mixture. Also NMR data did not indicate any structural differences in the cotton. EDX confirms the presence of both PA and purine on the fibers.

Fire demonstration tests on a mock up furniture showed that FR treatment with AD_PA had fire ignition inhibiting effect, especially for cotton.

In summary, the combination of both additives, TP_PA and AD_PA, leads to a prolongation in flame sustainability compared to pure textiles. Only PA also shows relatively good fire performance, but the textile fibres become hard and stiff.

These results are important for understanding the impact of these additives on the fire safety of cotton and polyester based materials.

The oxygen and other combustible gases and heat were excellently blocked by the char residue by using purine-PA flame retardant. The synergistic effect of combining both additives offers a balanced approach, potentially improving the fire safety of these textiles by moderating combustion characteristics. This analysis highlights the importance of selecting appropriate additives for enhancing the fire safety profiles of cotton and polyester based materials in textile applications. These modifications not only enhance the intrinsic fire-resistant properties of cotton but also significantly improve its performance under fire exposure, making it much safer for use in environments where fire risks are a concern.

6 Recommendations

Since the outcomes of the project are of interest to the scientific community, for suppliers and end-users of furniture and interior details, as well as for organizations that work for a fire-safe and sustainable living environment, representatives from these groups have participated in the reference group. The progress of the project has been disseminated at three meetings with the reference group during the project period.

Suppliers and end users of furniture and interior details

End-users' needs have been addressed in the reference group by inviting a "Trygg hjemme" coordinator from a Norwegian fire service to give inputs relevant for persons with risk factors. Fire demonstration tests in the project showed that the FR formulations developed in the project have potential to be used in furniture upholstery and thus a possible practical application, which can be beneficial for both suppliers and end-users. An economic analysis of the product should be performed to evaluate its market potential.

Scientific community

To gain interest from a mainly scientific audience, the social media platform LinkedIn has been used to spread information about the project such as posts about exciting activities in the lab. Several scientific articles are also currently being written and are planned to be submitted to journals in the near future.

Organizations that work for a fire-safe and sustainable living environment

A representative from MSB and Brandforsk have been part of the reference group. An information sheet was distributed at the beginning of the project to provide information to visitors to Brandforsk's website and the results of the project will also be disseminated in the same way.

Other stakeholders

The project has been presented to and created interest among university students and high school students and has led to several project works. Activities to attract new students to relevant educations in Chemical engineering and Fire protection engineering have taken place.

7 Future work

The focus of this project was to find a combination of naturally occurring molecules with good fire inhibiting properties, but except fire resistance, other properties of value for an FR are that it is resistant to leaching and wear. For that, strong bonds between the FR and the combustible material, and between different components in the FR coating must be achieved. As a continuation of this project, it should be important to investigate ways of improving this bond strength.

Exposure to sun (UV light) and variations in humidity can possibly degrade the FR so such studies should also be of importance.

Other cellulose materials such as Lyocell could be of interest to investigate, as well as other applications than textiles, e.g., plastics.

With biochemical process engineering, it is possible to use different microorganisms to produce biologically important compounds, and the possibility of tailoring a specific microorganism for production of adenine could be investigated.

The FR molecules could also be acquired from biomass and waste sources, but then available sources, as well as suitable methods for extraction and purification, must be found.

8 References

[1] <u>http://www.historyofclothing.com</u>, accessed April 22, 2024

[2] https://en.wikipedia.org/wiki/Wool, accessed April 22, 2024

[3] Meyer, E. Chemistry of Hazardous Materials, Pearson Education Inc., 6th ed. 2014.

[4] https://en.wikipedia.org/wiki/Rayon, accessed April 22, 2024

[5] <u>https://textilevaluechain.in/in-depth-analysis/manmade-fibre-industry-outlook-2022/</u>, accessed Feb 28, 2023

[6] http://textilesfr.co.uk/technical/fibres-and-flammability/, accessed April 22, 2024

[7] <u>https://www.brandskyddsforeningen.se/brandsakerhet-i-hemmet/sa-har-forebygger-du-en-brand-i-din-bostad/</u>

[8] Brandsäkert boende för alla. Brandskyddsföreningen,

https://www.brandskyddsforeningen.se/globalassets/vart-arbete/brandskyddsforeningensstrategi---brandsakert-boende.pdf, accessed April 22, 2024

[9] Andersson, P. *Riskreducerande åtgärder för dödsbränder i bostäder*, **2018**, MSB 1241, ISBN 978-91-7383-852-8.

[10] Sundström, B., Bengtson, S., Olander, M., Larsson, I., Apell, A. *Brandskydd och lös inredning – en vägledning*, **2009**, SP Rapport 2009:30.

[11] Storesund, K., Amon, F., Steen-Hansen, A., Haghighatpanah, S., Larsson, I. *Fire safe, sustainable loose furnishing*, Fire and Materials, **2020**, 1-10.

[12] Ngo, T. Development of sustainable flame-retardant materials, Green Materials, **2020**, 8(3), 101-122.

[13] Costes, L., Laoutid, F., Brohez, S., Dubois, P. *Bio-based flame retardants: When nature meets fire protection*, Materials Science and Engineering R, **2017**, 117, 1-25.

[14] Malucelli, G. Biomacromolecules and Bio-Sourced Products for the Design of Flame Retarded Fabrics: Current State of the Art and Future Perspectives, Molecules, **2019**, 24, 3774.

[15] <u>https://www.niehs.nih.gov/health/topics/agents/flame_retardants/index.cfm</u>, accessed April 22, 2024

[16] <u>https://en.wikipedia.org/wiki/Tetrakis(hydroxymethyl)phosphonium_chloride</u>, accessed April 22, 2024

[17] https://en.wikipedia.org/wiki/Aramid, accessed April 22, 2024

[18] https://en.wikipedia.org/wiki/Polytetrafluoroethylene, accessed April 22, 2024

[19] <u>https://en.wikipedia.org/wiki/Per-_and_polyfluoroalkyl_substances</u>, accessed April 22, 2024

[20] <u>https://web.archive.org/web/20100328222236/http://www.fibersource.com/f-tutor/modacrylic.htm</u>, accessed April 22, 2024

[21] Johnston, P. K., Doyle, E., Orzel, R. A. Acrylics: A Literature Review of Thermal Decomposition Products and Toxicity, Journal of the American College of Toxicology, **1988**, 7, 139-200.

[22] <u>https://en.wikipedia.org/wiki/Polychlorinated_dibenzodioxins</u>, accessed April 22, 2024

[23] https://en.wikipedia.org/wiki/Downstream processing, accessed April 22, 2024

[24] <u>https://www.un.org/sustainabledevelopment/sustainable-development-goals/</u>, accessed April 22, 2024

[25] Salmeia, K. A., Gaan, S., Malucelli, G. *Recent Advances for Flame Retardancy of Textiles Based on Phosphorus Chemistry*, Polymers, **2016**, 8,319.

[26] Zhang, Z., Ma, Z., Leng, Q., Wang, Y. *Eco-friendly flame retardant coating deposited on cotton fabrics from bio-based chitosan, phytic acid and divalent metal ions*, International Journal of Biological Macromolecules, **2019**, 140, 303-310.

[27] Sonnier, R., Taguet, A., Ferry, L., Lopez-Cuesta, J.-M. *Biobased Flame Retardants*, in: *Towards Bio-based Flame Retardant Polymers*, **2018**, Springer International Publishing.

[28] Liu, X., Zhang, Q., Peng, B., Ren, Y., Cheng, B., Ding, C., Su, X., He, J., Lin, S. *Flame retardant cellulosic fabrics via layer-by-layer self-assembly double coating with egg protein and phytic acid*, Journal of Cleaner Production, **2020**, 243, 118641.

[29] Maqsood, M., Seide, G. Investigation of the Flammability and Thermal Stability of Halogen-Free Intumescent System in Biopolymer Composites Containing Biobased Carbonization Agent and Mechanism of Their Char Formation, Polymers, **2019**, 11, 48.

[30] Patra, A., Kjellin, S., Larsson, A.-C. *Phytic Acid Based Flame Retardants for Cotton*. Green Materials, **2020**, 8(3), 123-130.

[31] Larsson, A.-C., Patra, A. Environmentally friendly flame retardants for cellulose-based materials – Continuation, **2021**, Brandforsk 2021:5, <u>https://www.brandforsk.se/wp-content/uploads/2021/11/brandforsk-friendly-flame-retardants_report.pdf</u>

[32] He, S., Gao, Y.-Y., Zhao, Z.Y., Huang, S.-C., Chen, Z.-X., Deng, C., Wang, Y.-Z. Fully Bio-Based Phytic Acid-Basic Amino Acid Salt for Flame-Retardant Polypropylene, ACS Applied Polymer Materials, **2021**, 3, 1488-1498.

[33] Ginesy, M., Belotserkovsky, J., Enman, J., Isaksson, L., Rova, U. Metabolic Engineering of Escherichia coli for Enhanced Arginine Biosynthesis, Microbial Cell Factories, 2015, 14:29.
[34] LeVan, S. L. Chemistry of Fire Retardancy, in: Rowell, R. (Ed.), The Chemistry of Solid Wood, Advances in Chemistry, 1984, 207, 531-574.

[35] Schofield, K. *The Flame Chemistry of Alkali and Alkaline Earth Metals*, in: Fontijn, A. (Ed.), *Gas-Phase Metal Reactions*, Elsevier B. V., **1992**, 529-571.

[36] Laoutid, F., Bonnaud, L., Alexandre, M., Lopez-Cuesta, J.-M., Dubois, Ph. New prospects in flame retardant polymer materials: From fundamentals to nanocomposites,

Materials Science and Engineering R, **2009**, 63, 100-125.

[37] Hunger, S., Cho, H., Sims, J. T., Sparks, D. L. Direct Speciation of Phosphorus in Alum-Amended Poultry Litter: Solid-State ³¹P NMR Investigation, Environ. Sci. Technol., **2004**, 38, 674-681.

[38] Larsson, A.-C., Patra, A. *Studies on environmentally friendly flame retardants for cellulosebased materials*, **2020**, Brandforsk 2020:2, <u>https://www.brandforsk.se/wp-content/uploads/2020/04/Brandforsk Flamskyddsmedel rapport.pdf</u>

[39] Laufer, G. Kirkland, C., Morgan, A. B., Grunlan, J. C. *Intumescent Multilayer Nanocoating, Made with Renewable Polyelectrolytes, for Flame-Retardant Cotton,* Biomacromolecules, **2012**, 13, 2843-2848.Wang

[40] Wang, X., Romero, M. Q., Zhang, X. -Q., Wang, R., Wang, D. -Y. *Intumescent* multilayer hybrid coating for flame retardant cotton fabrics based on layer-by-layer assembly and sol-gel process, RSC Advances, **2015**, 5, 10647-10655.

[41] Li, Z.-F., Zhang, C.-J., Cui, L., Zhu, P., Yan, C., Liu, Y. *Fire retardant and thermal degradation properties of cotton fabrics based on APTES and sodium phytate through layer-by-layer assembly*, Journal of Analytical and Applied Pyrolysis, **2017**, 123, 216-223.

[42] Feng, Y., Zhou, Y., Li, D., He, S., Zhang, F., Zhang, G. *A plant-based reactive ammonium phytate for use as a flame-retardant for cotton fabric*, Carbohydrate Polymers, **2017**, 175, 636-644.

[43] Liu, X. -h., Zhang, Q. -y., Cheng, B. -w., Ren, Y. -l., Zhang, Y. -g., Ding, C. Durable flame retardant cellulosic fibers modified with novel, facile and efficient phytic acid-based finishing agent, Cellulose, **2018**, 25, 799-811.

[44] Liu, L., Huang, Z., Pan, Y., Wang, X., Song, L., Hu, Y. *Finishing of cotton fabrics by multi-layered coatings to improve their flame retardancy and water repellency*, Cellulose, **2018**, 25, 4791-4803.

[45] https://en.wikipedia.org/wiki/Purine, accessed April 22, 2024

[46] Sui, Y., Dai, X., Li, P., Zhang, C. Superior radical scavenging and catalytic carbonization capacities of bioderived assembly modified ammonium polyphosphate as a

mono-component intumescent flame retardant for epoxy resin, European Polymer Journal, 156, **2021**, 110601.

[47] Wang, Z., Liu, Y., Li, J. Regulating Effects of Nitrogenous Bases on the Char Structure and Flame Retardancy of Polypropylene/Intumescent Flame Retardant Composites, ACS Sustainable Chem Eng, **2017**, 5, 3, 2375-2383.

[48] Ke, S., Wang, C., Shu, Y., Yang, J., Liang, Q., Zhang, Q., Liu, Z. Biomass adenosine triphosphate filler for improving the fire resistance and smoke suppression of intumescent coatings, J Coatings Technol Res, 2024.

[49] Qi, J., Pan, Y., Luo, Z., Wang, B., *Facile and scalable fabrication of bioderived flame retardant based on adenine for enhancing fire safety of fully biodegradable PLA/PBAT/TPS ternary blends*, J Appl Polymer Sci, 138, 35, **2021**, 50877.

[50] Lowden, L. A., Hull, T. R. *Flammability behaviour of wood and a review of the methods for its reduction*, Fire Science Reviews, **2013**, 2, 1-19

[51] Qiang, X., Mensah, R. A., Jin, C., Jiang, L. A critical review of the methods and applications of microscale combustion calorimetry for material flammability assessment, **2021**, Journal of Thermal Analysis and Calorimetry, 147, 6001-6013.

[52] <u>https://www.nist.gov/laboratories/tools-instruments/cone-calorimeter</u>, accessed April 22, 2024

[53] ISO 5660-1:2015, Reaction-to-fire tests - Heat release, smoke production and mass loss rate - Part 1: Heat release rate (cone calorimeter method) and smoke production rate (dynamic measurement), ISO copyright office, Switzerland, **2015**

[54] <u>https://en.wikipedia.org/wiki/Thermogravimetric_analysis</u>, accessed April 22, 2024

[55] https://en.wikipedia.org/wiki/Differential scanning calorimetry, accessed April 22, 2024

[56] Polenova, T., Gupta, R., Goldbourt, A. *Magic Angle Spinning NMR Spectroscopy: A Versatile Technique for Structural and Dynamic Analysis of Solid-Phase Systems*, Analytical Chemistry, **2015**, 87, 5458-5469.

[57] <u>https://en.wikipedia.org/wiki/Scanning_electron_microscope</u>, accessed April 22, 2024
[58] <u>https://en.wikipedia.org/wiki/Energy-dispersive_X-ray_spectroscopy</u>, accessed April 22, 2024

[59] EN 1021-2:2014 Furniture - Assessment of the ignitability of upholstered furniture - Part 2: Ignition source match flame equivalent'. CEN-CENELEC, Brussels, **2014**.

[60] Price D, Horrocks, A. R., Combustion processes of textile fibres, Handbook of fire resistant textiles, Woodhead Publishing Limited, **2013**.

[61] Storesund, K., Steen-Hansen, A., Bergstrand, A. *Fire safe upholstered furniture – Alternative strategies to the use of chemical flame retardants*, SP Fire Research AS, Trondheim, Norway, SPFR report A15 20124:2, Dec. **2015**, <u>https://risefr.no/media/publikasjoner/upload/2015/rapport-spfr-a15-20124-2.pdf</u>, accessed

April 22, 2024

[62] Amiri, R., Steen-Hansen, A., Larsson, A-C., Patra, A., Melia, C. S. A Demonstration test of passive fire safety measures for upholstered furniture, **2022**, Nordic Fire & Safety Days, Lund, Sweden.

[63] Wang, Z-J., Liu, Y., Li, J. Regulating Effects of Nitrogenous Bases on the Char Structure and Flame Retardancy of Polypropylene/Intumescent Flame Retardant Composites, ACS Sustainable Chemistry & Engineering, **2017**, 5, 2375-2383.

[64] Jiang, H., Sun, L., Zhang, Y., Liu, Q., Ru, C., Zhang, W., Zhao, C. *Novel biobased epoxy resin thermosets derived from eugenol and vanillin*, Polymer Degradation and Stability, **2019** 160, 45-52.

[65] Zamboulis, A.; Papadopoulos, L.; Terzopoulou, Z.; Bikiaris, D.N.; Patsiaoura, D.; Chrissafis, K.; Gazzano, M.; Lotti, N.; Papageorgiou, G.Z. *Synthesis, Thermal Properties and Decomposition Mechanism of Poly(Ethylene Vanillate) Polyester*, Polymers, **2019**, 11, 1672

[66] Cao, X., Pignatello, J. J., Li, Y., Lattao, C., Chappell, M. A., Chen, N., Miller, L. F., Mao, J. *Characterization of Wood Chars Produced at Different Temperatures Using Advanced Solid-State* ¹³*C NMR Spectroscopic Techniques*, Energy&Fuels, **2012**, 26, 5983-5991.

[67] Baccile, N., Falco, C., Titirici, M. -M., *Characterization of biomass and its derived char using* ¹³*C*-solid state nuclear magnetic resonance, Green Chem, **2014**, 16, 4839.

[68] Griffiths, L., Root, A., Harris, R. K., Packer, K. J., Chippendale, A. M., Tromans, F. R. *Magic-angle Spinning Phosphorus-31 Nuclear Magnetic Resonance of Polycrystalline Sodium Phosphates*, Journal of the Chemical Society Dalton Transactions, **1986**, 2247-2251.

<u>Appendix</u>

Report from RISE

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Report

Furniture cover textile treated with natural fire inhibiting molecules

NS-EN 1021-2:2014

Author: Edvard Aamodt



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Furniture cover textile treated with natural fire inhibiting molecules

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SUMMARY:		
This report summarizes exp	eriments done in part 3 in	project "Inhibit fire with
molecules from nature – app	olication on textiles". The p	roject investigates if it is
possible to inhibit fire ignitio	on in furniture with the use	of natural occurring molecules.
Part 3 of the project demons	strates the fire inhibiting e	ffect of the molecules Adenine
and Phytic acid on polyester	and cotton textiles in a me	edium scale experimental set-
ap.		
The results indicates improv	red fire ignition inhibiting e	effect when polyester and cotton
are treated with the molecu	les. Moreover, it also indic	ates that the molecules
improves cotton more than	polyester.	
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1 Introduction

The following report describes a series of demonstration experiments performed by RISE Fire Research. The demonstration experiments were part 3 in the Brandforsk financed research project "Inhibit fire with molecules from nature - application on textiles" (ref.BF23-007). The project is led by Luleå Technical University.

Part 1 and 2 of the project performed studies and small scale screening experiments on different textiles and fire inhibitors to ascertain the most promising candidates. The candidates were then sent to RISE Fire Research to be studied in medium scale according to standard NS-EN 1021-2:2014 [1].

This report will in brief present the demonstration experiments performed, the results and conclusion. Supplementary materials from the study are pictures and videos from the demonstration experiments, and these are delivered to the project owner together with this report.

2 Purpose of study

In this study, the effect of adding a fire inhibitor to cotton and polyester textiles on their reaction to fire properties will be demonstrated experimentally.

3 Method description

The demonstration experiments were performed according to NS-EN 1021-2:2014 with some alterations:

- The upholstery filling was cut 100 mm thick as opposed to 75 mm thick in the standard.
- In the cases where the cover material (called "specimen" for the rest of the document) passed both tests with the standardized small flame ignition source application, an additional ignition source of wood crib number 5 (called "crib 5" for the rest of the document), specified in BS 5852:2006 [2], was utilized.

The experiments were conducted in a standardized small room (2.4 x 3.6 meters) defined in ISO 9705-1:2016 [3]. This assured wind still conditions during the experiments. In the room a timer clock was placed to keep track of experimental duration. The furniture mock-up, when assembled with upholstery filling and specimens, was placed inside the small room on a scale to monitor the mass loss. A board of non-combustible material was placed between the weight and mock-up to shield the weight from heat. The mock-up can be seen in Figure 1.

Two repetitions of each specimen were performed with the option of a third repetition if the two former were inconclusive. Samples were provided by Luleå Technical University, and were upon arrival placed into a conditioning chamber ($23 \pm 2^{\circ}$ C, relative humidity $50 \pm 5\%$), see Figure 2, and reached stabile weight according to NS-EN 1021-2:2014. More info on the specimens can be found in Table 1.

The experimental procedure was as follows: First the specimen was ignited. The small flame burner was turned on for 15 seconds, and then turned off (for standardized tests, if the specimen continues to burn

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after these 15 seconds, it has failed the test). For ignition using the "crib 5", these were positioned on top of the specimen, then ignited and allowed to burn freely. If ignited, the specimen was allowed to burn freely for a given time, and then extinguished with water according to the standard. Visual observations were made of the specimen after the end of the experiment.



Figure 1: The experimental set-up. The furniture mock-up is placed on a non-combustible board, on top of a scale. A timer clock was positioned behind the set-up.



Figure 2: The received specimens placed on a rack in the conditioning chamber.

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4 Received specimens

Table 1: Received specimens with description. The list includes the respective weights of the specimens upon arrival and stabilised weight after conditioning.

Specimen ID	Specimen description*	Weight on arrival [g]	Final weight [g]
P1	Untreated polyester textile	80.2	80.5
P2	Untreated polyester textile	83.2	83.5
P3	Untreated polyester textile	81.4	81.4
C1	Untreated cotton textile	160.9	164.9
C2	Untreated cotton textile	159.4	163.4
C3	Untreated cotton textile	160.6	165.5
P _{ad+pa} 1	Polyester textile treated with adenine and phytic acid	96.4	98.4
$P_{ad+pa}2$	Polyester textile treated with adenine and phytic acid	95.3	97.3
P _{ad+pa} 3	Polyester textile treated with adenine and phytic acid	95.8	97.9
$C_{ad+pa}1$	Cotton textile treated with adenine and phytic acid	179.4	184.4
$C_{ad+pa}2$	Cotton textile treated with adenine and phytic acid	180.0	185.2
C _{ad+pa} 3	Cotton textile treated with adenine and phytic acid	180.6	185.8

*All specimens were cut into $800 \pm 10 \text{ mm x } 650 \pm 10 \text{ mm}$ according to NS-EN 1021-2:2014.

5 Results and discussion

In this chapter, the results from the experiments are presented. The main purpose is to study whether the specimens support combustion after a given time interval. If the specimen self-extinguish before the given time is concluded the specimen is considered to have passed. All results are summarized in Table 2 on page 17.

5.1 Untreated polyester textile

5.1.1 Experiment 1 on specimen P1

P1 was the first untreated polyester textile. The specimen ignited within 15 seconds by the use of the small flame ignition source. The experiment was conducted for 3 minutes and 35 seconds, before extinguishing with water, and 228 grams of material mass was consumed. Figure 3 and Figure 4 present pictures taken during and after experiment. The supplementary material video shows fire behaviour details.



Figure 3: The fire propagation in experiment 1, with small flame ignition source, at 30 seconds, 1 minute, 1 minute and 30 seconds and 2 minutes time stamps.



Figure 4: The specimen, in experiment 1, after the fire was extinguished at 3 minutes and 35 seconds. 228 grams of material was consumed.

As the fire in this experiment propagated fairly quickly a lot of burnt and melted plastic was observed on the set-up after the experiment. To reduce cleaning needs, it was decided to reduce the burner time, keeping the small flame running for only 2 minutes after removal of ignition source (2 minutes and 15 seconds total), before extinguishing with water.

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5.1.2 Experiment 2 on textile specimen P2

P2 was the second untreated polyester textile. The specimen ignited within 15 seconds by the use of the small flame ignition source. The experiment was conducted for 2 minutes and 15 seconds, before extinguishing with water, and 55 grams of material was consumed. Figure 5 and Figure 6 present pictures taken during and after experiment. The supplementary material video shows fire behaviour details.



Figure 5: The fire propagation in experiment 2, with small flame ignition source, at 30 seconds, 1 minute, 1 minute and 30 seconds and 2 minutes time stamps.



Figure 6: The specimen, in experiment 2, after the fire was extinguished at 2 minutes and 15 seconds. 55 grams of material was consumed.

The fire propagation in experiment 2 was similar to that of experiment 1. The ignition started 2-3 seconds after application of the ignition source and the development of the flame continued past 2 minutes and 15 seconds. The difference in consumed material is due to the shorter duration time in experiment 2 than in experiment 1. The fire propagation was very similar for P1 and P2 and a third experiment was therefore not performed.

5.2 Untreated cotton textile

5.2.1 Experiment 3 on specimen C1

C1 was the first untreated cotton textile. The specimen ignited within 15 seconds by the use of the small flame ignition source. The experiment was conducted for 2 minutes and 15 seconds, before extinguished with water, and 15 grams of material was consumed. Figure 7 and Figure 8 present pictures taken during and after experiment. The supplementary material video shows fire behaviour details.



Figure 7: The fire propagation in experiment 3, with small flame ignition source, at 31 seconds, 1 minute, 1 minute and 30 seconds and 2 minutes time stamps.



Figure 8: The specimen, in experiment 3, after the fire was extinguished at 2 minutes and 15 seconds. 15 grams of material was consumed.

The untreated cotton continued to burn after the burner was turned off at 15 seconds (i.e., the specimen failed the criteria). However, the fire propagation was much slower and less intense than with the polyester textile as can be seen in Figure 7 and Figure 8. In the pictures in figure 8 a tear can be observed in the burned textile (indicated by an arrow).

5.2.2 Experiment 4 on specimen C2

C2 was the second untreated cotton textile. The specimen ignited within 15 seconds by the use of the small flame ignition source. The experiment was conducted for 2 minutes and 15 seconds, before extinguished with water, and 15 grams of material was consumed. Figure 9 and Figure 10 present pictures taken during and after experiment. The supplementary material video shows fire behaviour details



Figure 9: The fire propagation in experiment 4, with small flame ignition source, at 30 seconds, 1 minute, 1 minute and 30 seconds and 2 minutes time stamps.



Figure 10: The specimen, in experiment 4, after the fire was extinguished at 2 minutes and 15 seconds. 15 grams of material was consumed.

Similar to experiment 3 C2 did fail the criteria of igniting after 15 seconds of small flame exposure, but the fire propagation was much slower than with the polyester textile as can be seen in Figure 9 and the damage to the specimen was smaller (Figure 10). In Figure 10 a tear can be observed in the burned textile as with C1 (indicated by an arrow). The fire propagation was very similar for C1 and C2 and a third experiment was therefore not performed.

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5.3 Polyester textile treated with adenine and phytic acid

5.3.1 Experiment 5 on specimen $P_{ad+pa}1$

 $P_{ad+pa}1$ was the first polyester textile treated with adenine and phytic acid. The specimen did not ignite within 15 seconds by the use of the small flame ignition source. The experiment was conducted for 2 minutes and 15 seconds with no material mass consumed, see Figure 11. According to the test standard the experiment was repeated on the left side of the mock-up. This time the specimen ignited, and 38 grams of material was consumed, see Figure 12. Figure 13 present pictures taken after experiment. The supplementary material video shows fire behaviour details.



Figure 11: The fire propagation in experiment 5, 1. repetition with small flame ignition source, at 30 seconds, 1 minute and 1 minute and 30 seconds and 2 minutes time stamps.



Figure 12: The fire propagation in experiment 5, 2. repetition with small flame ignition source, at 30 seconds, 1 minute, 1 minute and 30 seconds and 2 minutes time stamps.



Figure 13: The specimen, in experiment 5, after two small flame ignition repetitions. The second repetition was extinguished with water at 2 minutes and 15 seconds. 38 grams of material was consumed.

The treated polyester passed the first repetition, and failed the second. Even though it failed one of two, the second repetition had a slower fire propagation than untreated polyester P1 and P2, thus it may be considered an improvement of the reaction to fire properties. The two specimens in this experiment were taken out of the conditioning chamber at the same time, which could potentially explain the differences in their behaviour, as the second specimen may have been drier, and therefore ignited more easily.

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5.3.2 Experiment 9 on specimen $P_{ad+pa}2$

 $P_{ad+pa}2$ was the second polyester textile treated with adenine and phytic acid. The specimen did ignite, within 15 seconds by the use of the small flame ignition source, although it almost self-extinguished around 30 seconds. The experiment was conducted for 2 minutes and 15 seconds, before extinguished with water, with 5 grams of material consumed, see Figure 14. Since the specimen had been close to self-extinguishment, the experiment was repeated on the left side of the mock-up. This time the specimen did not ignite, and only 1 grams of material was consumed, see Figure 15. Figure 16 present pictures taken after experiment. The supplementary material video shows fire behaviour details.



Figure 14: The fire propagation in experiment 9, 1. repetition with small flame ignition source, at 30 seconds, 1 minute and 1 minute and 30 seconds and 2 minutes time stamps.



Figure 15: The fire propagation in experiment 9, 2. repetition with small flame ignition source, at 30 seconds, 1 minute and 1 minute and 30 seconds and 2 minutes time stamps.



Figure 16: The specimen, in test 9, after two small flame ignition repetitions. The first repetition was extinguished with water at 2 minutes and 15 seconds. 5 grams of material was consumed.

The treated polyester did almost pass the first repetition of small flame and passed on the second repetition. The fire propagation was slower than the untreated polyester P1 and P2, and thus this may be considered an improvement of the reaction to fire properties (as in experiment 5). The fire propagation was very similar between $P_{ad+pa}1$ and $P_{ad+pa}2$, and third experiment was therefore not performed.

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5.4 Cotton textile treated with adenine and phytic acid

5.4.1 Experiment 6 on specimen Cad+pa1

 $C_{ad+pa}1$ was the first cotton textile treated with adenine and phytic acid. The specimen did not ignite within 15 seconds by the use of the small flame ignition source. The experiment was conducted for 2 minutes and 15 seconds with no material mass consumed, see Figure 17. According to the test standard the experiment was repeated on the left side of the mock-up. This experiment was conducted for 2 minutes and 15 seconds, with no ignition and no material mass consumed, see Figure 18.



Figure 17: The fire propagation in experiment 6, 1. repetition with small flame ignition source, at 30 seconds, 1 minute and 1 minute and 30 seconds and 2 minutes time stamps.



Figure 18: The fire propagation in experiment 6, 2. repetition with small flame ignition source, at 30 seconds, 1 minute and 1 minute and 30 seconds and 2 minutes time stamps.

A third experiment was then conducted with a "crib 5" ignition source. The experiment was conducted for 10 minutes and the specimen did not ignite, but 19 grams of material was consumed due to the fire from the "crib 5" itself. See Figure 19. Figure 20 present pictures taken after experiment. The supplementary material video shows fire behaviour details.



Figure 19: The fire propagation in experiment 6, with "crib 5" ignition source, at 1 minute, 2 minutes, 4 minutes and 8 minutes time stamps.

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Figure 20: The specimen, in experiment 6, after two small flame ignitions and one "crib 5" ignition. 19 grams of material was consumed by the "crib 5" ignition.

A tear was observed in the specimen after the "crib 5" fire (as indicated by an arrow in Figure 20). The treated cotton did pass the two repetitions of small flame, and the demonstration with "crib 5" ignition, thus this may be considered an improvement of the reaction to fire properties compared with the untreated cotton.

5.4.2 Experiment 7 on specimen C_{ad+pa} 2

 $C_{ad+pa}2$ was the second cotton textile treated with adenine and phytic acid. The specimen did not ignite within 15 seconds by the use of the small flame ignition source. The experiment was conducted for 2 minutes and 15 seconds with no mass of material consumed, see Figure 21. According to the test standard the experiment was repeated on the left side of the mock-up. This experiment was conducted for 2 minutes and 15 seconds, with no ignition and no mass of material consumed, see Figure 22.



Figure 21: The fire propagation in experiment 7, 1. repetition with small flame ignition source, at 30 seconds, 1 minute and 1 minute and 30 seconds and 2 minutes time stamps.



Figure 22: The fire propagation in experiment 7, 2. repetition with small flame ignition source, at 30 seconds, 1 minute and 1 minute and 30 seconds and 2 minutes time stamps.

A third experiment was then conducted with a "crib 5" ignition source. The experiment was conducted for 10 minutes before it was extinguished with water. In this experiment the specimen did ignite, consuming 88 grams of material. See Figure 23. Figure 24 present pictures taken after experiment. The supplementary material video shows fire behaviour details.



Figure 23: The specimen, in experiment 7, after two small flame ignition repetitions and one "crib 5" ignition. 88 grams of material was consumed.

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Figure 24: The specimen, in experiment 7, after two small flame ignition repetitions. The second repetition was extinguished with water at 2 minutes and 15 seconds. 88 grams of material was consumed.

A tear can be observed in the specimen after the "crib 5" fire (as indicated by an arrow in Figure 24). The treated cotton did pass the two repetitions of small flame ignition, but not the "crib 5" ignition. This may be considered an improvement of the reaction to fire properties compared with the untreated cotton.

For the small flame ignition method, the results were very similar between $C_{ad+pa}1$ and $C_{ad+pa}2$ (neither ignited), and a third experiment was therefore not performed.

For the wood "crib 5" ignition method, there was a large difference in the results between $C_{ad+pa}1$ and $C_{ad+pa}2$ (no ignition vs ignition), and it was decided to proceed with a third experiment (experiment 8).

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5.4.3 Experiment 8 on specimen C_{ad+pa} 3

 C_{ad+pa} 3 was the third cotton textile treated with adenine and phytic acid. The experiment was conducted for 10 minutes before extinguished with water. In this experiment the specimen did ignite, consuming 89 grams of material. Figure 25 and Figure 26 present pictures taken during and after experiment. The supplementary material video shows fire behaviour details.



Figure 25: The fire propagation in experiment 8, with "crib 5" ignition source, at 1 minute, 2 minutes and 2 minutes and 5 minutes time stamps.



Figure 26: The specimen, in experiment 8, after one "crib 5" ignition. 89 grams of material was consumed.

A tear can be observed in the specimen after the "crib 5" fire (as indicated by an arrow in Figure 26). The "crib 5" ignition source, similar to experiment 7, ignited the specimen. It was concluded that specimen $C_{ad+pa}3$, similar to $C_{ad+pa}2$, did not pass the "crib 5" ignition.

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5.5 Summary of results

Table 2 summarizes the results from the study. In addition to the tabulated results, there were also differences observed visually of the fire propagation behaviour between textiles, see details in sections 5.1 to 5.4.

		Self-extinguished within time limit?				
Specimen ID	Exp. no.	Small flame 1 [2min, 15	Small flame 2 [2min, 15	Crib 5 [10min]	Mass consumed, small flame [g]	Mass consumed, crib [g]
P1	1	No	NA	NA	228*	NA
P2	2	No	NA	NA	55	NA
C1	3	No	NA	NA	15	NA
C2	4	No	NA	NA	15	NA
$P_{ad+pa}1$	5	Yes	No	NA	38	NA
$P_{ad+pa}2$	9	No	Yes	NA	5	NA
C _{ad+pa} 1	6	Yes	Yes	Yes	0	19**
C _{ad+pa} 2	7	Yes	Yes	No	0	88
C _{ad+pa} 3	8	Yes	Yes	No	0	89

Table 2:	Summary of results, untreated and treated textiles, with two different methods of
	ignition (small flame and "crib 5").

NA = not applicable

* Longer test time than the others, therefore more material consumed.

** Mass consumed was mainly the burned away upholstery filling, not the specimen.

The visual observations showed that the untreated textiles burned more intensely than the corresponding treated textile, demonstrating an improvement in the reaction to fire properties when introducing the fire inhibitor.

All the untreated textiles continued to burn after the pilot ignition (small flame) was removed. For the polyester textiles, the treated textiles did start to burn in some cases, and self-extinguished in others, with small flame ignition. For the cotton textiles, the treated textiles did not start to burn with the smallest pilot ignition (small flame), and for the more intense ignition source (wooden "crib 5"), there was ignition for 2 of 3 cases. This demonstrates that fire inhibitor treatment of the polyester textile gave *some* improvement, and fire inhibitor treatment of the cotton gave a *clear* improvement of the reaction to fire properties.

To summarize, this study demonstrates experimentally that the addition of a fire inhibitor to cotton and polyester textiles may improve their reaction to fire properties, and that the effect was most clear for cotton

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6 Conclusions

The polyester textile (P1 and P2) is more ignitable than the cotton textile (C1 and C2).

The treatment of both the polyester and cotton textiles with adenine and phytic acid has been demonstrated to inhibit the ignitability of the textiles.

The combination of cotton textiles and the treatment with adenine and phytic acid was demonstrated to have the largest improving effect on the reaction to fire properties.

Bibliography

- [1] 'EN 1021-2:2014 Furniture Assessment of the ignitability of upholstered furniture Part 2: Ignition source match flame equivalent'. CEN-CENELEC, Brussels, 2014.
- [2] 'BS 5852:2006 Methods of test for assessment of the ignitability of upholstered seating by smouldering and flaming ignition sources'. BSI - British standards Institution, London, UK, 2006.
- [3] ISO, 'ISO 9705-1 Reaction to fire tests Room corner test for wall and ceiling lining products -Part 1: Test method for a small room configuration', International Organization for Standardisation (ISO), Switzerland, 2016.

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