Mitigation of environmental impact caused by flame retardant textile finishing chemicals

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Abstract. LIFE FLAREX project focuses on the mitigation of environmental and health impacts caused by toxic compounds that are contained in commonly used flame retardants (FRs) in home textiles which are based on halogenated-, antimony trioxide-, formaldehyde release related products. Conventionally used FRs in the home textile sector are decabromodiphenyl ethane, its combination with antimony trioxide and dialkyl phosphono carboxylic acid amides, respectively. The project evaluates alternative FRs and their feasibility at the industrial scale level. Among all the home textile applications, curtains, upholstery, mattress ticking and bedding sheets were selected as the most interesting products in terms of need for substitution. Within these applications, cotton, polyester and polyester/cotton blends were selected as most representatives. Technical performance, flame retardant resistance as well as washing durability was evaluated for up to eight different alternatives and compared to the conventional FRs. The alternative FRs included mixtures of phosphates, ammonium polyphosphate, expandable graphite, guanidine phosphate, ammonium sulphamate and other new patented technologies in the market. A toxicological assessment through skin- FRs contact measurements is being conducted for assessing their absorption and toxicological properties. Additionally, an environmental and health assessment is also being conducted as well as a life cycle assessment comprising environmental, economic and social considerations. The project has at the moment demonstrated the feasible substitution of the aforementioned toxic FRs for greener and safer FR alternatives.

1. Introduction
Flame retardants play an important role in reducing the incidence of fire on a global scale. Statistics that at least 94% of fire deaths occur in homes and buildings [1,2]. Flame retardants are used in home textiles for ensuring protection against the risk of fire by retarding or inhibiting propagation of flame. They are used in European countries in home textile contracting by legislation (i.e. theatres, hotels and public accommodations, public buildings and offices, hospitals and care homes, among others) while in more stricter countries like in the UK their use extends to houses.
Nowadays, current technologies used for obtaining flame retarded textiles are based on halogen, antimony trioxide and formaldehyde releasing compounds [3] which present health concerns and environmental impact [4].

Commercial and greener alternatives to current flame retardant compounds are based on phosphorous compounds, a combination of phosphorous and nitrogen compounds and inorganic materials among others. Phosphorous and their combination with nitrogen compounds have proven to be efficient. However, they are more expensive due to their lower volume production. In some cases, it is necessary to add a higher amount to the flame-retardant formulation in order to achieve good results/flame retardancy. In terms of environmental impact inorganic materials are the best alternatives for flame retardants, however higher amounts of inorganic material needed for achieving good efficiency. In addition to this, the lack of legislation and promotion of greener alternatives [5] lack of user awareness are also other key factors making more difficult.

With this regard, this project aims to demonstrate and evaluate the technical and industrial feasibility of the current flame retardant materials halogen and antimony-trioxide based compounds and formaldehyde releasing compounds greener alternatives. Additionally, an environmental and health assessment as well as a life cycle assessment will be also carried out.

2. Materials and methods

2.1. Selection of materials

Based on a survey and a workshop conducted with the main stakeholders (textile manufacturers, textile finishers, among other), three fabric compositions were selected, 100% PES, 100% CO and their blends thereof, PES/CO, as well as four home textile applications as most common and potentially interesting regarding their presence in home textile contracting but also regarding their substitution. The applications selected were curtains, upholstery, mattress ticking and bedding sheets. A screening and selection of the most promising alternatives was carried out.

Table 1 collects the conventional flame retardant compounds and the most promising and commercial alternatives selected. Among the conventional flame retardants are: 1) decabromodiphenyl ethane which has been the drop-in solution in industry of the recently restricted decabromodiphenyl ether 2) decabromodiphenyl ethane used with antimony trioxide used as synergist and 3) dialkyl phosphono carboxylic amide. Selected alternatives include cyclic phosphonate, expandable graphite, ammonium polyphosphate, ammonium, guanidine phosphate, and a new patented technology based on a combination of ammonium, urea and a phosphorus compound. A brominated polymer has also been chosen as a transitional alternative due to its industrial interest, being a bigger halogenated compound therefore presenting lower risk of migration from the fabric.

Table 1. Home textile applications, fabrics selected for each application, conventional, intermediate and alternative flame retardants evaluated.
2.2. Experimental part

The experimental part contains two steps. Firstly, the flame retardants were applied and tested at laboratory scale and based on these results the flame retardants were applied at industrial scale. This paper presents exclusively the results obtained at laboratory scale.

The fire-tests are carried out in part B1 of the laboratory-scale project for different textiles used in definite final applications (curtains, upholstery, mattress ticking and bed sheets). After the pre-industrial tests, the most promising applications are executed at the industrial level in the companies that showed interest in participating in the project. The procedure of the application at the industrial level is similar but with at least 50 m of fabric.

The selected flame retardants were applied to the materials depending on the application. Afterwards the flame retardancy of the treated textiles was tested according to the adequate for the application sector. Another part is to test the toxicity of the flame retardants in-vitro. Also, an LCA (Life Cycle Assessment) is conducted to evaluate different aspects such as raw materials, energy consumed during their application, cost of the products among others important parameters that have to be assessed when promoting substitution of the conventional FR products.

Foulard process is used for impregnation of textile substrates. In this process, after submersion in the aqueous finish solution the fabric is squeezed between 2 rolls with a pressure of 1.5 bar and a speed of 5 rpm to remove the excess of finish solution (Figure 1 Left). This is followed by a drying and curing process that occurs in the stenter machine at the specific drying and curing temperatures for each finish product (Figure 1 Right).

The wet pick-up (amount of wet finish solution absorbed on the textile) is determined after squeezing while the dry pick-up (amount of dry finish product absorb on the textile) is determined after drying and curing.

Coating of A4-samples is performed on stenter machine (see Figure 1). The fabric is mounted in the stenter frame and the coating thickness is adjusted by varying the distance between the blade and the roll (knife-over-roll coating). Afterwards the applied coating is thermally dried/cured in the oven; temperature and time depends on the used system. Here the add-on of the fabric is determined by weighting the sample before and after the coating.

Figure 1. Left) Foulard; Right) Stenter machine (Mathis coater).
The fire behavior of the applied products were conducted according to the EU for the application sectors. The efficiency of the flame retardants was detected by comparing and analyzing the results of the treated samples to the untreated samples.

The flammability of curtain fabrics was determined according to the standard UNE EN 13773:03 which consists of two parts, UNE EN 1101 and UNE EN 13772. It was decided to first conduct the part one (UNE EN 1101) and follow with the second part with the most promising alternatives in case of successful results. For upholstery the flame retardant treated textiles were tested according to the UNE-EN 1021-1:2015. The flammability of the mattress ticking is determined according to EN 597 (1994): Furniture – Assessment of the ignitability of mattresses and upholstered bed bases. Furthermore, the Crib 5-test as described in the BS6807 (methods of test for assessment of the ignitability of mattresses, upholstered divans and upholstered bed bases with flaming types of primary and secondary sources of ignition) was used as a screening method. To determine the flame retardancy of the products applied on bed linen it is performed the EN ISO 12952 Textiles – Assessment of the ignitability of bedding items.

3. Results and discussion

As there were two different PES curtain textiles screened according to UNE EN 1101, it can be said that textile A has better fire results than textile B because less dense material. Also, textile A has a higher absorption potential which means a better wet/dry pick up. Textile B has clearly a handicap for the warp direction. It is quite usual for woven textiles that the warp direction burns faster and more because the yarn is thicker than in weft direction.

Regarding conventional treatments for curtain the products are not meant to be washed. The treatment of DBDPE + MC was not successful for both curtain types at any concentration. Besides, the treatment of 50% DBDPE + ATO worked for the less dense textile A but for textile B it only worked in weft direction.

The results of the alternative cyclic phosphonate are that none of the studied concentrations passed the standard. However, it was noted that the samples passed the fire test if they were not washed. In this regard, a different cyclic phosphonate had to be screened and applied which worked successfully due to its washing resistance.

The samples treated with brominated polymer showed positive results as they were treated by impregnation. On the other hand, the samples treated with brominated polymer showed a high rigidity which is not suitable for curtain applications.

The results for the upholstery treatments are shown in figure 2 and 3. Figure 2 displays the results of UNE-EN 1021-2:2005 of the PES untreated textile (Figure 2 Left) compared to the halogenated products decabromodiphenyl ethane (Figure 2 Middle) and the application of brominated polymer (Figure 2 Right). It is clear to see that the coating worked successfully, as the burn marks of both samples are quite small and regular compared to the untreated sample (Figure 2 Left).

![Figure 2](image1.png)

**Figure 2** UNE-EN 1021-2:2005, Left) PES untreated, Middle) DBDPE + ATO, Right) brominated polymer.

As it is shown in Figure 3 the burn marks of the sample coated with expandable graphite are quite small, similar to the marks obtained when using halogenated compounds indicating similarity during the burning behavior (Figure 2 Middle and Right).
For mattress ticking the ignition of the untreated CO/PES mattress ticking results in an escalating fire. All FR treatments make the fabric pass the crib 5 test, nevertheless differences between the different treatments are noticeable. Lower concentrations of guanidine phosphate (11 wt%) and ammonium (5 wt%) are sufficient to make the CO/PES FR. The ammonium polyphosphate in higher concentrations (16 wt%) is more efficient than the lower concentration (7 wt%).

The PES 3D spacer fabric passes the crib 5 test without flame retardant treatment, but its performance can be improved by applying a flame retardant treatment. Also, in this case the lower concentrated guanidine phosphate (12 wt%) is more efficient. The higher concentration of ammonium polyphosphate (27 wt%) is significantly better than the concentration of 16 wt%. The difference between higher and lower concentration of ammonium is not decisive.

Conventional flame decabromodiphenyl ethane with antimony trioxide is not usually used in the industry for bed linen; this also reflected in the results. As the treatment is not wash resistant it cannot be used for this sector.

The treatment based on Pyrovatex, based on dialkyl phosphono carboxylic acid amide, on the other hand is durable and maintains its flame retardant effect after the washing cycles. Despite the flame retardant is only bound to cotton, the CO/PES 50/50 bed linen still passes the fire test. As the dry pick-up of the tested cotton bed linen was very low, only 0.4 wt%, the flame retardant effect was not great. The conventional Pyrovatex-like treatment has affinity for cotton which should result in a flame proof fabric.

As the alternatives to Pyrovatex only act on the cotton fraction of a CO/PES blend, non-halogenated alternative identified able to make a wash durable flame retardant CO/PES 50/50 fabric treatment with the polymeric FR resulted into a wash durable flame retardant blend. The treatment did have an influence on the touch of the fabric: it is stiffened.

The cotton bed linen can be made flame retardant with both the polymeric FR as the ammonium + urea + PO(OH)₂-R-PO(OH)₂ treatment-based FR. The polymeric FR had the most impact on both the color as the touch of the fabric.

Among all the alternatives tested at laboratory scale, the transitional alternative, brominated polymer, showed good efficiency conferred to the fabric for both curtains and upholstery achieving a passed fire test under the standard “UNE EN 13773, part 1: UNE EN 1101” and “UNE EN 1021-part2-match flame”, respectively. However, for curtains applications the treated textiles showed loss of flexibility. Fire tests are still being carried out with textile treated with the alternative based on a cyclic phosphonate for its application in curtains. Expandable graphite showed promising results being tested under the “UNE EN 1021-part2-match flame”, for upholstery applications compared to current alternatives based only on halogenated compounds. The new patented solution consisting of ammonium combined with urea and a phosphorus compound resulted in very promising results being tested under the “UNE EN ISO 12952-1for bedding sheets applications Guanidine phosphate, ammonium and ammonium polyphosphate
resulted to pass the fire test for mattress ticking under the standard “UNE EN 597-part1 cigarette and part2-match flame” as well as the crib 5 test.

The technical feasibility of the selected flame retardant alternatives has been demonstrated at laboratory scale. Current work is being performed on running industrial trials for their evaluation. Moreover, work is being conducted on the health and environmental assessment and life cycle assessment of the selected alternatives.

References

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