Non-halogen FR treatment of cellulosic textiles

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Review

A historical overview of the most commonly used textile flame retardants (FR) is given, with an emphasis on halogen-free FRs acting through their mechanism to slow down or prevent burning. Since a large number of halogen FRs are toxic, or potentially toxic, to the organisms and the environment, there is a need for them to be replaced by eco-friendly agents. The paper presents new alternative FRs that are trying to be put into practice, as well as different methods of their application onto textiles in comparison to one another. One of the possible ways of developing alternative FRs could be the application of bio-macromolecules such as chitosan, phytic acid, casein, whey, hydrophobins or DNA.

Key words: *FR treatment, non-halogen agents, textile*

1. Introduction

Cellulosic textile materials have always been prone to easy burning, and it has been a problem throughout the history of humankind. This was why the first systematic studies were started in the 19th and 20th centuries concerning the substances which could coat cotton, linen and jute fabrics, so as to prevent, or at least retard, burning. The substances tested were quite effective; however, their main disadvantage was they were not resistant to washing [1, 2]. So called golden period in the development of flame retardants and procedures started after the World War II, when two most important flame retardants for cellulosic fabrics were developed, both of them resistant to washing, and both of them used even today, with no important alternative [3]. Due to a number of environment-protection issues regarding the manufacture, use and disposal of textile materials treated with commercial flame retardants, a need arose to substitute them partially or completely with new alternative and more environment-friendly agents and/or technological solutions. As statistics show, the consumption of FRs globally was more than 2 million tons in 2013, with commercially outstanding sectors of building and construction, primarily in Asia, the USA and the European Union [4].

2. Flammability of cellulosic textiles and mechanisms of FRs functioning

Textile material flammability is affected by numerous physical and chemical factors, by the content and structure of the material, as well as by the environment, while fibre behaviour in burning depends upon the temperatures of thermal transitions and thermodynamic parameters: glass transition temperature (T_g), melting temperature (T_m), pyrolysis temperature (T_p), combustion (oxidation) temperature (T_c), limiting oxygen index (LOI) and heat of combustion (ΔH_c). The mechanism of burning as a feedback mechanism can be seen in Fig. 1 [5].

The heat that is transferred from the source of flame towards the polymer results in pyrolysis (at T_p specific for a particular fibre), where long-chain polymer molecules are split into low-molecular liquid condensates and tar, with char residue and non-flammable gases. Liquid condensates and tar (condensed phase) are further split into small molecules of flammable gases. The gases (gaseous phase) form, together with the air, a flammable mixture, where flammable gases are oxidised with the oxygen from the air (at T_c characteristic for a particular fibre). A part of the heat released by oxidation returns to the polymer and causes pyrolysis to continue. In this case, oxidation temperature is higher than pyrolysis temperature. The material burns, as can be seen, only if flammable gases are generated in the course of pyrolysis. Oxidation generates free radicals of high energy ($R^{\cdot}$, $O^{\cdot}$, $H^{\cdot}$, $OH^{\cdot}$), which stimulate further burning reaction of the gases. The product of ideal burning of cellulose should theoretically be water and carbon dioxide. However, in reality, carbon monoxide, polycyclic aromatic hydrocarbons, hydrogen cyanide, etc. [5] are created as well.

Thermal decomposition of cellulose occurs in a similar manner. When cellulose is heated in the air at the temperatures between 25 °C and 150 °C, water desorption occurs. At the temperatures between 150 °C and 240 °C two parallel chemical reactions are started. One is cellulose dehydration, which results in the generation of primary char residue, stable at the temperatures from 400 °C to 600 °C, with non-flammable gases (water, carbon monoxide, carbon dioxide), while the other is depolymerisation at the temperatures between 240 °C and 400 °C, due to which acetyl bonds are broken in glucoside units of the primary char residue, and levoglucosane is generated, which, at the temperatures between 400 °C and 700 °C yields flammable gases and initiates the generation of secondary char residue, stable at the temperatures below 800 °C [6].

Flame retardants with chemical and/or physical action retard or block the process of burning in particular phases of burning so that they stop the inflow of heat to the polymer, block the access of oxygen, increase the generation of non-flammable gases or reduce the generation of flammable

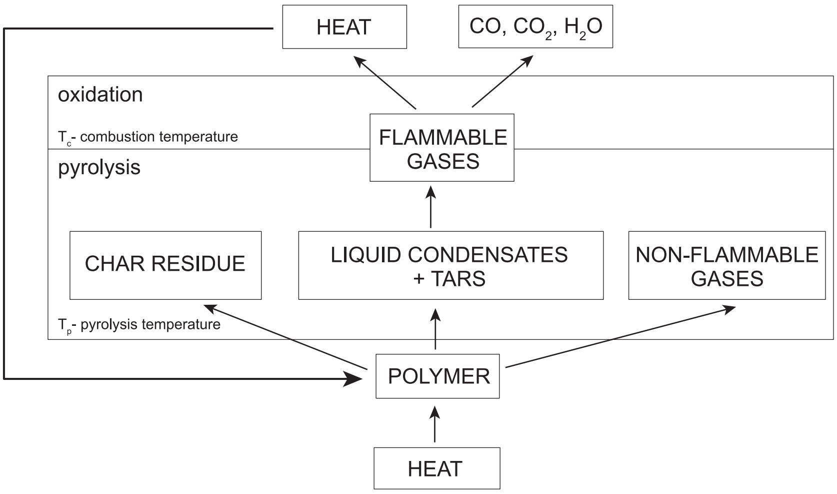

Fig.1 Mechanism of polymer burning

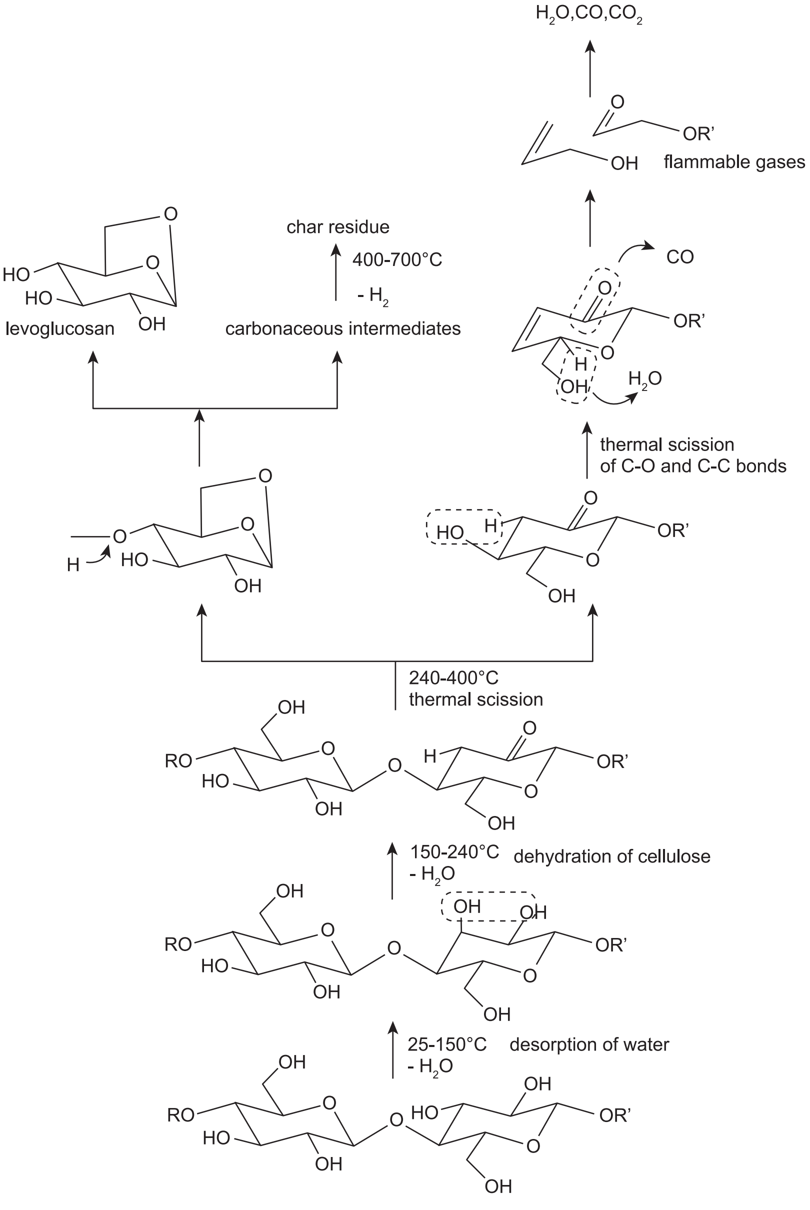

Fig.2 Thermal degradation of cellulose [6]

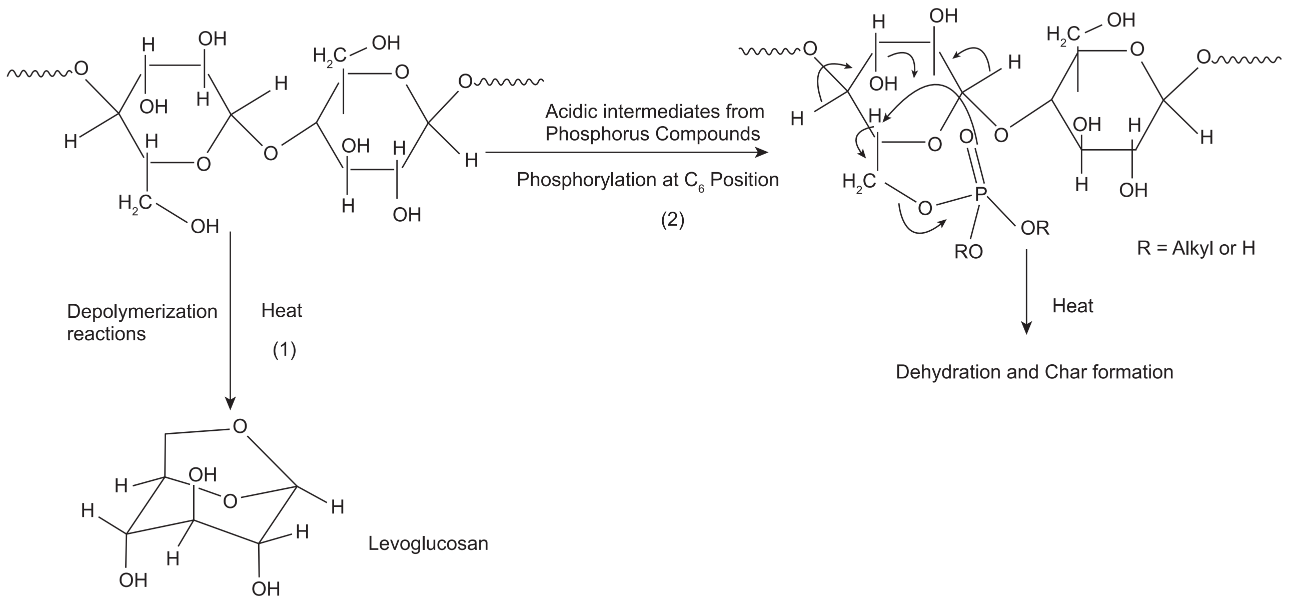

Fig.3 Thermal decomposition of cellulose without a phosphorus-based FR (1) and with it (2) [11]

ones and increase the content of char residue, acting in the gaseous and condensed phases. These mechanisms often cannot be clearly separated [7, 8]. Flame retardants that act in the gas phase, during the burning of flammable gases, are bonded to high-energy free radicals ($R^{\cdot}$, $O^{\cdot}$, $H^{\cdot}$, $OH^{\cdot}$), generated by oxidation, which results in non-flammable gases that extinguish the flame. Halogen FRs act in this manner, as well as metal hydroxides, phosphorus- or nitrogen-based FRs [9].

FR mechanism in the condensed phase can be seen in reaction of the polymer and flame retardant at the temperatures below the temperature of pyrolysis and is realised in two stages: dehydration and cross-linking, or the generation of char residue, which reduces the generation of flammable gases and limit the access of oxygen [10]. Phosphorus-based FRs, as well as silicone and silicon FRs act in this manner.

If cellulose is treated with phosphorus-based FRs (reaction 2, Fig.3), during decomposition at the temperature below T_c, phosphorilation of hydroxyl group occurs at the C_6 atom, caused by dehydration, which increases carbonisation and reduces the total amount of flammable gases. If no FR is used, levoglucosan is generated, which stimulates the generation of flammable gases at the temperatures above 400 °C [11].

Flame retardants with physical action are divided into:

1. inorganic salts which melt under the impact of high temperature and create a layer that protects the polymer surface from the heat source,
2. thermally unstable inorganic carbonates and hydrates which yield carbon dioxide when heated and/or water to cool down the polymer, forming a layer to protect the polymer surface from the heat source,
3. heat conductors (metals) and phase-change materials (PCM), which absorb huge amounts of heat when decomposing or evaporating, thus removing the heat from the polymer before the conditions for ignition are reached [12].

Inorganic FRs include metal oxides, zeolites, hydroxides, borates, stannates, inorganic phosphorus compounds (red phosphorus and ammonium polyphosphate) and graphite. They are usually combined with halogen FRs, as well as with phosphorus- and/or nitrogen-based ones [7, 8].

Phosphorus-based (P) FRs reach their maximum efficiency if they are combined with nitrogen (N) compounds, in so called N-P synergism [13]. There are more theories on N-P synergism:

1. nitrogen compounds (melamines, urea and their derivatives) release nitrogen which is bonded to high-energy free radicals, generated by oxidation, creating in the process stable non-flammable gases which quench the flame (NO – nitrous monoxide, NO_2 – nitrous dioxide) [14, 15]
2. nitrogen compounds make the reaction of phosphorilation of phosphorus-based FRs easier as they are bonded to phosphorus-based FRs, creating a link between phosphorus and nitrogen, of much better thermal stability than is the case with the link of phosphorus and oxygen, which increases the phosphorus and nitrogen content remaining in the carbonised residue [16].

Past decade has witnessed the development of so called intumescent FRs, intended primarily for the protection of wood, plastics and metals. They are applied to the material surface and expand under the influence of high temperature, forming an insulatory fire-resistant layer at the surface of the material, protecting it from further pyrolysis and burning. The char residue has a characteristic foamy appearance. These systems act in the condensed phase and involve some highly complex mutually dependent components. A phosphorous compound (phosphoric acid and their derivatives, polyphosphate) in the intumescent system cause the polymer to phosphorilate (with a C-O bond), stimulating its dehydration and carbonisation. Liquid polymer foams during carbonisation as it releases non-flammable gases (NO, NO_2) generated by the decomposition of nitrous compounds (melamine, urea, dicyandiamine etc.) [17].

3. Commercial flame retardants

The year 1783 is officially considered to be the year when the first FR was used on cotton. Brothers Montgolfier coated their air balloons with aluminium to prevent burning [18]. In early 20th century Perkin released the first systematic study of fire retardants for cellulosic materials, which was used until the fifties and included: ammonium chloride, ammonium phosphate, ammonium sulphate, zinc chloride, calcium chloride, magnesium chloride, aluminium hydroxide, zinc sulphate, sodium borate, boracic acid, magnesium sulphate, sodium chloride, sodium silicate, silicic acid, potassium chloride, sodium phosphate, aluminium borate, aluminium phosphate, calcium phosphate, magnesium phosphate, zinc borate, tungstic acid, sodium tungstate, ammonium tungstate and clay. A chief disadvantage of these agents is their poor resistance to washing [2].

The 1950s are noted as a start of so called golden period, which will last until the end of the 1980s. This was the period when resistant FRs for cellulosic materials were marketed, based on:

1. organophosphorous compounds created by cross-linking of tetraoxi(hydroxymethil)phosphonium salts (THPX) condensates and urea, under the trade name of Proban®,
2. derivatives of N-alkyl substituted phosphonopropionamides (e.g. MDPA - N-methyldimethylphosphonopropionamide), which were reactive compounds under the trade name of Pyrovatex CP®,
3. antimony-organo-halogen compounds: hexabromocyclododecan (HBCD) + antimony III oxide and decabromodipheniloxide (DECA) + antimony III oxide,
4. chlorinated paraffin waxes [3, 8, 18].

THPX- and MDPA-based FRs have been used until present days with no substantial alternative and are applied to textile materials by pad-dry method. Their chief disadvantage is that they release free formaldehyde during condensation, or impregnation of textile material, as well in use. As an alternative to formaldehyde-free flame retardants cross-linking agents based on polycarboxile acids were developed and launched in the market in the period from 1980 to 2010. However, their chief disadvantages were that treated fabrics treated experienced considerable strength reduction, they had a detrimental impact on the colouring shade, as well as on the pH value of the fabric treated [12]. The mechanism of polycarboxylic acid action in fire-resistant treatments for cotton fabrics has been described in literature in detail [19-25]. Table 1 shows some of the formaldehyde-free agents developed or experimented with in the period from 1980s until today [18, 26-29].

Future FRs for cellulosic material should:

1. be non-toxic,
2. be economically feasible,
3. not change the appearance, colour or shade of the fabric treated,
4. ensure pleasant feel (roughness), adequate strength (breaking strength, elongation at break) and be wear resistant,
5. be water-proof for at least 50 washing cycles in alkaline medium, at high temperatures, independent of water hardness,
6. not release free formaldehyde during processing or after it,
7. have high air-permeability after the treatment, regardless of the

Tab.1 FR agents developed in the period from 1980s until today

- N-methylol dimethylphosphonpropionamide (MDPA) and citric acid (CA);
- N-hydroxymethil-3-dimethylphosphonpropionamide and butanetetracarboxylic acid (BTCA)/ citric acid (CA);
- aminomethilphosphonic diamide;
- triethylamoinophosohonic oxides;
- phosphate-phosphonate oligomer;
- hydroxy-functionalise organophosphorous oligomer and multifunctional carboxylic acid;
- hydroxyalkilorganophosphorous oligomer (Fyroltex®)/ trimethylamine/ dimethiloldihydroxyethilene urea (DMDHEU);
- BTCA phosphated by hydroxyalkyl organophosphorous oligomer (Fyroltex®);
- BTCA phosphated hydroxyalkyl organophosphorous oligomer (Fyroltex®) – triethanolamin (TEA);
- maleic acid – sodium hypophosphite;
- succinic, mallic, racemic acid - sodium hypophosphite;
- oligomers of maleic acid which contain phosphorus.sodium hypophosphite – TEA;
- alkylphosphorusamidate stabilised as a salt product with ammonium chloride;
- diammmonium phosphape (DAP), phosphoric acid (PA), tributylphosphate (TBP), triallylphosphate (TAP) and triallylphosphoroustriamide (TPT);
- TBT – nitrogen-based compounds (urea, guanidinecarbonate, melaminformaldehyde);
- triethylphosphate (TEP) -diethylphosphorusamidate, -phosphorousamide acid, N(2-hydroxyethyl)diethylester -diethylethylphosphorusamidate or –diethyl 2-metoxiethylphosphorusamidate

high amount of the FR coating [30-33].

4. Alternative flame retardants

4.1. Biomacromolecules

Biomacromolecules or biopolymers are long-chain molecules essential for the functioning of every living being. They include nucleic acids – polymers of nucleotides (deoxyribonucleic acid – DNA and ribonucleic acid – RNA), and are used as genes and intermediates in transferring genetic information (biosynthesis of proteins), then proteins – polymers of peptides, which perform various functions in every living cell (enzymes, transferring oxygen and electrons, etc.), and finally polysaccharides – polymers of sugar, which serve as building blocks (e.g. cellulose, chitin) or to store energy in the organism (starch, glycogen) [34]. The biomacromolecules most frequently used in fire-resistant and fire-retardant treatments for textile materials in laboratory conditions are chitin derivatives, casein proteins, wheys, hydrophobins and DNA [35].

4.1.1. Chitosan

Chitosan is a linear polysaccharide consisting of randomly distributed β-(1→4)-linked D-glucosamine and N-acetyl-D-glucosamine. Chitosan is commercially obtained by alkali deacetylation of chitine, which is a building element of crustacean (crabs, lobsters) shells and of some mushrooms (button mushrooms). Varying the deacetylation degree various properties are obtained in chitosan, adequate for various applications. The amino group in chitosan has the pKa value of about 6.5, while the charge depends upon the solution pH and degree of deacetylation. Being a positively charged biopolymer in an acidic environment, chitosan is bioadhesive and is easily bonded to negatively charged surfaces [36, 37]. It is biocompatible and biodegradable, possesses good antibacterial properties, which makes it adequate for wide application in agriculture, for treatment of seeds, as a biopesticide, in wine production for fine filtration and wine clearing, in pharmacy for the production and transfer of insulin, as well as for reduced absorption of fats (dietary food). Chitosan is a polymer with thousand faces, as it can be chemically modified through estherification, etherification, graft polymerisation, phosphorylation, etc. [38]. Chitosan has proved to have good antibacterial and flame retardant properties and a number of research papers have been published in the last decade dealing with its application on polyurethane (PU) foams and in textiles, both by impregnation/exhaustion and by layer-by-layer (LbL) deposition.

Teli et al. have shown that adding chitosan to conventional multifunctional crease-proof, flame retardant and antibacterial treatments of cotton, results in lower free-formaldehyde release [39]. The treatment of phosphorilation in a bath of diammonium hydrogenphosphate (DAPH), sodium hypophosphite (SHP) and 1,2,3,4-butanetetracarboxylic acid (BTCA) as a cross-linking agent, yields chitosan phosphate, which, due to its nitrogen component, in synergy with phosphorus, offers good FR properties to cotton. Raising the DAPH concentration also raises resistance of cotton to washing [40]. El-Tahlawy et al. combined sodium stannate and chitosan in treating cotton against burning. They used chitosan (CH), citric acid (CA), sodium hipophosphite (SHP), diammonium hydrogenphosphate (DAHP) and sodium stannate ($NaSnO_3$). A reaction of phosphorilation occurs in the presence of DAHP with hydroxylic groups in cellulose and amino groups in chitosan, yielding phoshphorilised cellulose and chitosan phosphorus. Citric acid cross-links the chitosan phosphorus and cellulose, acting simultaneously as a crease-resistant agent. It also solutes chitosan into chitocan citric salts. Sodium stannate offers excellent FR properties. However it feels hard to touch, requires a high concentration of DAHP and ureas, as well a few phases of cross-linking [41]. El-Shafei et al. experimented with multifunctional FRs, antibacterial treatments and crease-resistant treatments of cotton using titanium dioxide (TiO_2) nanoparticles, chitosan phosphate, BTCA, and sodium hipophosphite (SHP) as a catalyst. Chitosan, as a derivative of chitin, exhibited good FR properties in combination with phosphorous compounds, due to the N-P synergy, with a simultaneous antibacterial activity. It can reduce the amount of commercial organophosphorous compounds, and experiments have shown it reduces the release of free formaldehyde in conventional recopies for flame retardant treatments [42].

4.1.2. Phytic acid

Phytic acid can be found in cereal bran, various seeds and vetch, as well as in various nuts in the form of phytin (Fig. 4). Human organism cannot digest it, while it can readily take various minerals important for life and link them to its OH groups, such as calcium, magnesium, iron and zinc. It can have a detrimental impact to health, as it inhibits enzymes necessary for digesting proteins and starch, which makes minerals and phosphorus inaccessible to human organism. However, it is still widely present in a manner in the organisms of mammals and is attributed with the

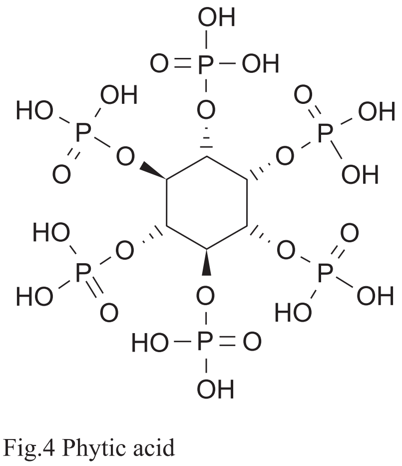

Fig.4 Phytic acid

ability to „repair" mutated DNA. Still, not much is known of the role of phytic acid in human organism. Phytic acid and its salts are obtained by extraction from the bran rich in phytin, using aqueous solutions of sulphonic or hydrochloric acids, precipitated by sodium hydrogen carbonate and purified by extracting in ether from the solution of hydrochloric acid. It is used as a preservative E391 in food industry [43]. As it contains phosphorus in its structure, together with OH groups which readily bond to metals and other organic compounds, it is an ideal FR agent, which could, in theory replace ammonium polyphosphates. Only a few papers have been published on the use of phytic acid in flame-retardant treatments. Laufer at al. used polyelectrolytic solutions of phytic acid and chitosan applied by LbL method on cotton [44]. Wang et al. treated cotton fabric with phytic acid and a silane hybrid [45].

4.1.3. Proteins – casein, hydrophobines and whey

Casein is a phosphorus-rich protein, a by-product in the manufacture of completely skimmed milk, containing about 80% of milk proteins. It consists of αs1-casein, αs2-casein, β-casein and Ҝ-casein [46]. Besides cheese manufacture, casein is traditionally used in the production of emulsifiers, binders, in paper manufacture, leather tanning, manufacture of fibres etc. [47]. Hydrophobines are natural surface active proteins of low molecular mass, rich in sulphur (cisteins) occurring as surface spew on some mushrooms and fungi, where they form monolayers. They exhibit amphiphilic properties, meaning that, depending upon the environment, they can have either hydrophobic or hydrophilic properties. It occurs in two different crystalline structures – class I and class II. Class I includes stable and hard to dissolve polymer monolayers, consisting of fibrillated rod-like structures which can only be dissolved in strong acids. The process is reversible, meaning that the rods, under favourable conditions, can be readily polymerised again. Class II hyrophobines includes polymer monolayers with no fibrillated rod-like structure, readily soluble in organic solvents and detergents. Hydrophobins reduce surface tension of the substrate where the mushroom grows, making its interaction with air and water easier. In other words, mushroom spores can be dissipated in the air and protected from moisture, embedded into favourable ground, while once they are stable in the ground the spore can take moisture/water, grow and further propagate. Hydrophobins are also considered to play a major role in deactivating the immune system of the host on which the mushrooms (or fungi) grow. Hydrophobic is very hard to make in the form adequate for laboratory or industrial use [48]. Hydrophobian have recently been applied in foaming agents and nanoencapsulating active substances in pharmaceutical and food industries [49]. Alongi et al. impregnated cotton fabrics with aqueous suspensions of casein and solution of hydrophobin, and compared thermogravimetric curves (TG) obtained with TG curves of untreated cotton and of cotton treated with ammonium polyphosphate (APP). Cotton samples treated with casein/hydrophobin exhibited good and almost identical FR properties, but considerably lower than the samples treated with APP [50]. Carosio et al. proved that casein has an impact on FR properties of pure cotton and pure polyester (PES); having at the same time no influence on cotton/PES blends [51].

Whey proteins make 20% of milk proteins, with the structure similar to α-helixes, with alternating acidic/basic and hydrophobic/hydrophilic aminoacids, with sulphur contained within the peptide chain (methionine, cysteine). Chief components of whey are β-lactoglobulin, α-lactalbumin, serum albumin and immunoglobulin. Due to their amphiphilic properties, these proteins are used in the manufacture of emulsifiers. Bosco et al. studied the impact of whey protein denaturation on cotton FR properties. Denaturation means disturbing secondary (tertiary) structure in proteins (and nucleic acids) by high temperature, irradiation, mechanical factors, heavy metal salts, or actions of strong acids and alkalis. They proved that denaturation of whey protein has no effect on FR properties of cotton treated with them [52].

4.1.4. Deoxyribonucleic acid (DNA)

DNA molecule consists of long chain nitrogen-based polymers – adenine, guanin, cytosine and thymine, with the backbone made of polysaccharide and phosphate groups linked with ester linkages. It could be said that DNA contains all three components of a swelling FR system in a single molecule – phosphate groups that can yield phosphoric acid, deoxyribose with C-O linkages which can be dehydrated and yield carbonised residue, and nitrogen compounds (adenine, guanin, cytosine and thymine) (Fig.5). When heated, phosphate groups in DNA yield phosphoric acid, which releases water, accompanied by dehydration and carbonisation. At the same time, nitrogen-rich bases yield ammonium, which retards burning and reacts with the liquid polymer to create a protecting layer on the material [54]. The sources for purified DNA are codfish and herring sperm and spawn. Alongi et al. were the first to impregnate cotton fabric with DNA, with the idea of using DNA as a FR [55]. Carosio et al. used chitosan/DNA in LbL layering on cotton [56]. Alongi et al. compared DNA flame retardant properties with casein and ammonium polyphosphate (APP), and the results obtained showed that APP offers much better results than the other agents, DNA being the second [54]. Chief disadvantage of all of these environment-friendly treatments is their poor fastness to washing, even at 30 °C with no detergent used [57].

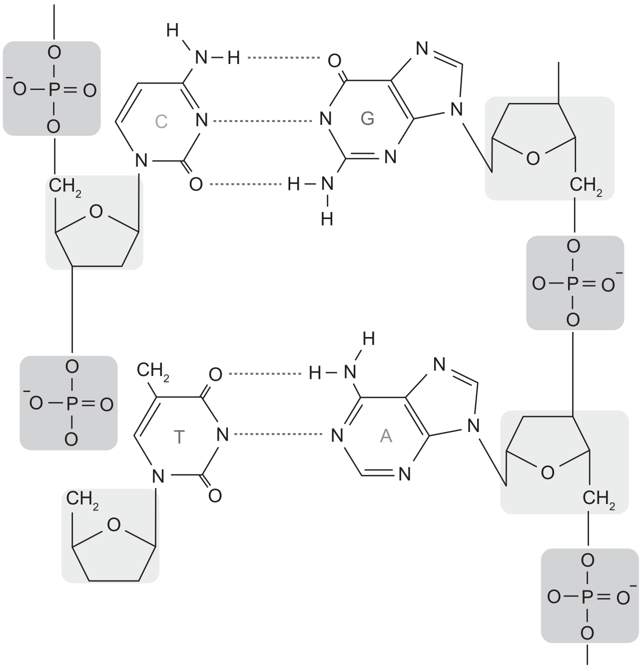

Fig.5 DNA structure [53]

5. Processes of applying FRs to cellulose textile fabrics

Flame retardants can be applied to textile fabrics using either the process of pad-drying or back-coating. Pad-drying consists in immersing the material in the bath containing a flame retardant, wringing it and drying. However, after such a treatment the fabric is often stiff, of unpleasant feel, and sometimes of reduced strength and no elastic recovery. Back-coating is the process in which FR is applied to the fabric surface, does not penetrate its structure, so that the material can retain its basic and favourable properties (in the case of cotton it means comfort, good absorption of moisture etc.). Back-coating has recently been classified as a single-layer coating. Pad-dry process and back coating are the only surface functionalisation techniques used for cellulose textile fabrics in industry, using non-intumescent FRs exclusively. Some other nanotechnologies have also been experimented with in the course of past few years:

1. nanoparticle adsorption,
2. sol-gel process,
3. plasma treatment and
4. layer-by-layer deposition [18, 58].

5.1. Nanoparticle adsorption

Nanoparticle adsorption is a simple, fast and cheap, but not permanent process, in which the fabric is impregnated in an aqueous suspension of nanoparticles, while bonding is based on ionic interaction of negatively charged textile substrate and positively charged nanoparticle. Nanoparticle adsorprion is classified as a single-layer coating. Literature references mention:

- natural and synthetic zeolites (montmorillonite, klinoptilolit),
- nanoclays (carbonate hydrotalcite, sulphonate bohemite),
- nanoparticles (zinc oxide, titanium dioxide, silicon dioxide, octapropylammonium polyhedral oligomeric silsesquioxane (POSS®) [18, 59-64].

5.2. Sol-gel process

Sol-gel process is a simple, inexpensive and environmentally friendly procedure of synthesizing homogenous metal oxides, or organic-inorganic hybrids (dual-cure sol-gel) of good mechanical, optical, electric and thermal properties, at the temperatures below 100 °C. The procedure includes hydrolisis and condensation reactions of metal alkoxides (precursors), which changes the colloidal solution (sol) into s solid gel with uninterrupted three-dimensional metaloxide network, with an acid or alkali as a catalyst [65]. The process of applying FR by sol-gel technique onto a textile material starts with precursor hydrolysis. Hydrolysed pre-

Tab.2 Precursor in different systems type in Sol-Gel process in flame retardant treatments

System type	Precursor
Inorganic meal alkoxides	– tetraethyl orthosilicate (TEOS), – tetramethyl orthosilicate (TMOS), – tetrabutyl orthosilicate (TBOS), – alkoxysilane with various numbers of hydrolysed groups, – tetraethyl ortho-titanate, – tetraethyl ortho-zirkonate – aluminium isopropylate, – TMOS + aluminium micro and nanoparticles
Inorganic--organic hybrids based on N-P systems	– TMOS + aluminium phosphinate – TMOS + aluminium phosphinate/melamine(poly)phosphate/zinc oxide/boron oxide, – TMOS + α-zirconium phosphate, – TEOS + H_3PO_4 or ethyl dichlorophosphate – diethylphosphatoethyltrioxysilan (DPTES), – DPTES + 3-aminopropyltriethoxylane (APTES) or APTES melamine-based resin, – DPTES + 1-hydroxyethanal 1,1-diphosphonic acid, – DPTES + N,N,N′,N′,N″,N″-hexametoxymethyl-[1,3,5]triazine-2,4,6-triamine, – DPTES + urea, – sodium metasilicate + urea/ammonium dihydrogen phosphate – DPTES/APTES (3-aminopropyiltrietoxysilane)+ melamine/urea

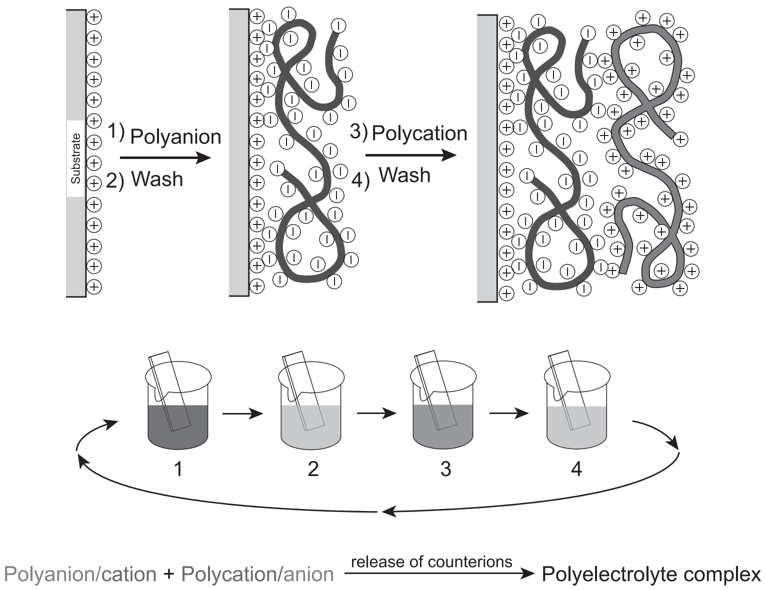

Fig.6 Schemes of the layer-by-layer deposition method (LbL) [72]

cursor is then added into the bath with organic FRs, which is then used to impregnate the textile fabric to be treated. Drying follows after impregnation, together with condensation, creating a solid gel on the fabric [66]. Tab. 2 lists some of the precursors used in these processes [18, 66-69].

5.3. Plasma treatment

Plasma treatment is a process in which functional groups and macromolecules are synthesised by grafting onto the surface of textile fabric, with no internal modification of the textile, through:

1. etching fabric surface and/or functionalisation with the help of non-polymerising gases (N_2, H_2, O_2, Ar, NH_3, CO_2 etc.)
2. polymer synthesis with the help of shoots from non-volatile kinds of phosphorus in cold plasma,
3. deposition of organosilicone compounds with the help of plasma polymerisation,
4. using cold N_2 plasma technique,
5. using acrylic monomers for graft polymerisation [58].

Cold plasma in flame retardant treatments of cellulosic fabrics offer satisfactory values of limiting oxygen index, even after 50 washing cycles (27%). However, the process has not been widely accepted by the industry, primarily due to high necessary investments, as compared to the conventional commercial FR processes, which results in too high a price for the final product [70, 71].

5.4. Layer-by-layer deposition

Layer-by-layer deposition (LbL) is a surface adsorption of long-chain polyelectrolyte molecules of one charge (+) on a solid substrate of the opposite charge (-), followed by rinsing with deionised water. The second phase consists in linking positively charged polyelectrolyte to negatively charged polyelectrolyte (Fig.6). The process is alternately repeated [72].

It is thus possible to arrange a few layers of the same or completely different electrolytes one on the other as a bilayer (BL), trilayer (TL) or quadlayer (QL).

LbL coating has been experimentally tested for FR treatments of textile fabrics, using various FR agents. Chief disadvantage of this method is again poor wash-fastness, as polyelectrolyte links are based on electrostatic bonds or H-bonds. Somewhat better results have been achieved by post-treatments of UV cross-linking. The advantage of this process is its simplicity, possibility to control the number, thickness and homogeneity of individual layers (which depends upon the choice and concentration of polyelectrolytes, solution pH, additional ultrasonicating etc.), as well as the usage of green solvent - water [58]. LbL coating is implemented in laboratories using the following techniques:

1. dipping and
2. horizontal or vertical spraying [73].

Only a few papers could be found dealing with possible commercial approaches to a continuous industrial LbL process of coating textile materials by dipping technique [74, 75]. LbL coating has until now been applied to the following cellulosic fibres: cotton, ramie and sisal. Cationic/anionic or anionic/cationic BL, TL, and/or QL systems used can be seen in Tab.3 [44, 45, 56, 74-91].

6. Toxicology

American National Academy of Science published a comprehensive study in 2000 on the toxicological risks in using commercial flame retardants. The study encompassed all the FRs known at the time, together with those used in textile industry. It proved that FRs to certain extent disturb the functioning of human immune system and endocrine system, cause neurological changes in the brain and physical malformation of foetus, disorders in child growth and development, skin depigmentation, they inhibit the workings of certain enzymes, can cause spontaneous miscarriage, gastroenterological problems, potentially are carcinogenic and can even damage the DNA structure. The toxicological study from 2000 also showed that most damaging agents used as FR on textiles were those halogen-based, organohalogen and anitimony organohalogen compounds. Commercial agents based on organophosphorus compounds were considered safe until 2000 [92]. Van der Veen and de Boer published a review in 2012 on toxicity of some organophosphorous FRs, where they stated the following:

1. bisphenol-A diphenilphosphate is not, for the time being, considered

toxic, due to insufficient data on its level of presence in the environment, based on in-vivo experiments. However, it can cause eye and skin irritation,

2. triphenilphosphate is more or less neurotoxic for aquatic organisms, can cause allergies, disturbs the workings of immune and endocrine systems, blocks the growth of algae,
3. diphenil cresyl phosphate can cause skin and eye irritation, is toxic for aquatic organisms, causes reproductive and development problems, but is considered safe for the time being due to insufficient data available,
4. melaminpolyphosphate can cause eye irritation, is toxic for algae, but is considered safe for the time being due to insufficient data available,
5. diethylphosphinic acid can cause eye irritation, it is toxic to algae, but is considered safe for the time being due to insufficient data available,
6. tricresyl phosphate is a neurotoxin, reproductive toxin and toxic for aquatic organisms [93].

Phosphorus, Inorganic and Nitrogen Flame Retardants Association, the member of which are Chemische Fabrik Budenheim, Ciba Inc. (a part of BASF now), Clariant Produkte (D) GmbH, Italmatch Chemicals S.p.A., Lanxess Deutschland GmbH and Nabaltec AG., published in 2009 a short report of non-halogen FRs, where they stated that non-halogen organophosporous compounds were completely safe to use, meaning they were not bioaccumulative, toxic, carcinogenic or mutagenic as phosphorus was a necessary chemical element for humans, animals and plants, being a major component of bones and DNA. The report even stated an example of a case-study in Japan where phosphorus was, in the form of phosphoric acid, recycled for mineral fertilisers. European Commission, as it is, has no official assessments of the risk of non-halogen FRs, as they have not been included into the so called list of priority chemicals to be a basis for risk assessment in Europe. [94].

Tab.3 LbL systems in flame retardant treatments

Cotton	
BPEI/CH/PSP	BPEI – branched polyethyleneimine; CH – chitosan; PSP – sodium polyphosphate
BPEI+urea+ DAP/kaolin	BPEI – branched polyethyleneimine; DAP – diammonium phosphate
BPEI/kaolin	BPEI – branched polyethyleneimine
BPEI/PAA-P/AA	BPEI – branched polyethyleneimine; PAA-P – phosphonate poly(allylamine); AA – oligoallylamine
CH/PA	CH – chitosan; PA – phytic acid
CH/APP	CH – chitosan; APP – ammonium polyphosphate
CH/PSP	CH – chitosan; PSP – sodium polyphosphate
FR-PAA/MMT	FR-PAA – aminoderived poly(acrylic acid); MMT – montmorillonite
FR-PAM/GO	FR-PAM – FR polyacrylamide derivative; GO – graphene oxide
BPEI/PSP/PAA	BPEI – branched polyethyleneimine; PSP – sodium polyphosphate; PAA – poly(allylamine);
SiN/PA	SiN – silane hybrid modified by nitrogen and obtained by sol-gel process; PA – phytic acid
CH/PT	CH – chitosan; PT – phosphorilated chitine
CH/PCL	CH – chitosan; PCL – phosphorilated cellulose
CH/DNA	CH – chitosan; DNA – deoxyribonucleic acid
AP/-POSS	AP – aminopropyil silsesquioxane -POSS – octakis(tetramethylammonium)pentacyclo[9.5.1.1.^{3,9}.1^{5,15}.1^{7,13}] octasiloxane1,3,5,7,9,11,13,15-octakis(cyloxide)hydrate
+POSS/-POSS	+POSS – octa(3-ammoniumpropyl)octasilsesquioxane octachloride -POSS – octakis(tetramethylammonium)pentacyclo[9.5.1.1.^{3,9}.1^{5,15}.1^{7,13}] octasiloxane1,3,5,7,9,11,13,15-octakis(cyloxide)hydrate
BPEI/MMT	BPEI – branched polyethyleneimine; MMT – montmorillonite
BPEI/-SiO_2	BPEI – branched polyethyleneimine -SiO_2 – negatively charged silicon dioxide nanoparticles
-Al_2O_3/+Al_2O_3, with cotton cationisation	-Al_2O_3 – anionic aluminium oxide colloidal solution +Al_2O_3 – cationic aluminium oxide colloidal solution
-Ag/PDDA	-Ag – anionic colloidal solution of silver nanoparticles PDDA – poly(diallyldimethylammonium chloride)
CH/TNT	CH – chitosan; TNT – titanium nanotubes
Ramie	
DMF + MWNT-NH_2/APP	DMF – N,N-dimethylformamide; MWNT-NH_2 – aminofunctionalised multilayered carbon nanotubes; APP – ammonium polyphosphate
BPEI-$CuSO_4$ /PVPA	BPEI – branched polyethyleneimine; CuSO4 – cupric sulfate; PVPA – poly(vinylphosphonic) acid
BPEI-$ZnCl_2$ /PVPA	BPEI – branched polyethyleneimine; ZnCl2 – zinc chloride; PVPA – poly(vinylphosphonic) acid

Another problem of FR treatments for primarily cellulosic fabrics is the release of free formaldehyde in processing and use. As the technology goes, in order to bond an organophosphorous compound-based FRs more permanently to a cellulosic fibre, a formaldehyde-based cross-linking agent is necessary (phenolformaldehyde, ureaformaldehyde, melaminformaldehyde), which is gradually released in the course of processing and use. International Agency for Research on Cancer, of the World Health Organisation, classified formaldehyde as a carcinogenic chemical (causes nasopharynx cancer and leukaemia) [95]. Because of its potential or proved toxicity, intensive research has been done with new alternative agents and/or technological solutions, which could partially or completely replace all the existing commercial FRs.

7. Conclusion

The ease with which textile fabrics caught flame and burned was a problem which faced people from prehistoric time. As early as the end of 18th century a detailed study was made on the substances to coat cotton, linen and generally cellulose fabrics used in the manufacture of balloons, stage curtains in theatres etc., which would prevent, or at least retard, burning. These were natural substances, mostly based on mineral salts and clay, highly efficient, but completely nonfast to washing. After the World War II chemical industry developed at a fast pace and some promising substances were created, based on halogen and halogenphosphorus compounds of excellent FR properties, resistant to washing. After a few decades of commercial use doubts appeared of their potential detrimental impact on the environment. Some 15 years ago, their extreme toxicity was proved (disturbing the workings of immune and endocrine systems, neurotoxicity, carcinogenicity, inhibiting the function of enzymes, spontaneous miscarriages, foetus malformations, physical and mental retardation etc.). Some countries banned these substances while some limited their use. Organophosporous compounds are for the time being considered safe. Past decade or so has witnessed intensive experimenting with new alternative and environment-friendly agents and/or technological solutions, which could partially or completely replace all the existing commercial FRs. One of the solutions could be the implementation of biomacromolecules, such as chitosan, phytic acid, casein whey, hydrophobins and DNA.

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