Guidelines for improving the formulation of detergents for washing flame-retardant textiles

Tea Kaurin, mag. ing. techn. text.
Prof. **Tanja Pušić**, Ph.D.
University of Zagreb
Faculty of Textile Technology
Zagreb, Croatia
e-mail: tea.kaurin@ttf.unizg.hr
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Review

The resistance of flame-retardant (FR) textiles to washing depends on processing conditions, maintenance, use, wearing and storage. Sustainability imposes the need to extend their life cycle while maintaining technological characteristics, degree and level of FR protection, shape, dimensions, comfort and appearance. In the washing process of these textiles, it is necessary to remove stains and ensure a sufficient level of hygiene. In many cases, the use of high temperatures, excessive amounts of detergent and air treatments to remove soil, stains and odours can significantly impair their functional and aesthetic properties. Additionally, detergents containing surfactants, alkalis, bleaches, fragrances, softeners and other additives can leave residues on the surface of treated textiles, which in some cases are a potential cause of user skin irritation. This paper is focused on the significance of Sinner's circle factors in the washing process of FR textiles, where the emphasis was placed on the significance of detergents, which makes it possible to maintain durability,

Keywords: *textiles, fire protection, washing, detergent*

1. Introduction

The guidelines for the rationalization of processes in the textile industry had impact on the improvement of the existing ones and introduction of more economically favourable finishes in order to achieve certain durability and/or resistance. Taking into account this review, focused on processing of textiles treated with flame retardants (FR), in recent decades it has been aimed [1]:

- reduction of process water consumption (less bath ratios),
- reduction and/or complete removal of formaldehyde released during the processing and use of FR textiles,
- reducing the load of process wastewaters,
- analysis of potential environmental risks associated with halogen content in FR products.

In accordance with this, the development of FR agents is focused on improving the functionality, ecological and economic features of the products, whereby new products should meet the criteria of prominent features [1]:

- equivalent or better method of application,
- without releasing formaldehyde (FF - formaldehyde free)
    - the current requirement for formaldehyde emissions into the atmosphere, especially during curing, is ≤ 20 ppm
- high durability, improved touch and tensile properties
- comparable or better economy than the existing ones

- equivalent or better toxicological and environmental impacts
  - the requirement for emission of volatile organic compounds is ≤ 50 ppm
  - release of unbound FR agent substances in washing

The emission of harmful substances and the release of unbound substances depends on the reaction mechanism of flame retardants - FR agents with textiles. The stability of the textile system - FR agent against various influences in the processing, use and care can be monitored by analysing the technological and use permanence.

The technological stability of textiles includes their properties after certain stages of the finishing process, and they depend on the conditions of dry and wet processing. When FR finish of textiles is performed, it is important to harmonize the process parameters with the properties of dyed or undyed textiles. Process parameters include, among other things, auxiliaries, procedures (impregnation, spraying, coating - classic or layer by layer (LbL), thermal treatments (drying, curing / UV curing etc) [2-8].

The durability of FR textiles includes their properties in dry (friction, rubbing, wear, ironing without steam, light -UV, tearing) and wet (exposure to moisture, washing, sweat and other solvents media) which are related to use, wear and care. The choice of FR agents and additives should be coordinated with the process parameters in order to reduce the degree of textiles damage and prolong their life time [9].

In accordance with all the mentioned aspects, it is important to reduce the risks affecting [10]:

- level of protection
- shape and dimensions
- comfort.

The composition, structural and construction features of materials, degree of pretreatment and processing, and environmental conditions (humidity, heat, air flow, oxygen concentration) affect their fire resistance [8].

Cellulosic textiles are acceptable due to comfort, but due to their easy flammability, processing procedures try to achieve flame suppression, reduction and dilution of combustible and non-combustible gaseous decomposition products. Most FR treatments of cellulosic materials are non-permanent or semi-permanent and as such have limited application because they are not resistant to washing [11, 12].

FR treatments according to washing fastness are evaluated as:

- non-durable
- semi-durable
- durable.

Non-durable treatments are those whose FR effect is lost through one washing cycle; semi-durable treatments ensure a degree of protection through multiple washing cycles, and their effect is expected from two to 25 cycles; the effect of durable FR treatment is satisfactory even after 25 washing cycles.

It is clear that the number of washing cycles has a direct impact on the FR properties of protective clothing, which in some cases are lost after several cycles, which indicates the fact that it is necessary to keep records of the number of cycles and conditions.

It is necessary to optimize complex systems of FR treatment and the textile washing process in order to achieve efficiency, retain FR properties and environmental acceptability.

Criteria for the selection of FR agents include the analysis of the risk of mucosal and skin irritation and the monitoring of potential mutagenic and carcinogenic effects [13].

Tab.1 Advantages and disadvantages of THPX and MDPA for cotton [1]

FR agent	Advantages	Disadvantages
THPX condensates (Proban®) Tetrakis-hydroxymethyl phosphonium salts	– durability > 100 washing cycles in hospital conditions (temperature: 75°C) – minimal loss of strength and good tear resistance – there are no recorded emissions (releases) of formaldehyde in use	– requires a special gas chamber for curing – reacts with some types of dyes, e.g. sulfur dyes – requires the use of a softener to improve the touch
MDPA derivative N-methylol dimethyl phosphonopropionamide	– durability > 100 washing cycles without the presence of bleach in hospital conditions (temperature: 75°C) – applicable in impregnation and curing procedures – compatible with all types of dyes and excellent compatibility with printing pigments – applicable with other finishing agents, eg soil release agents	– significant drop in strength (typically ≤ 20%) and tear resistance (≤ 50%) – often forms tar deposits in the curing chamber – poor wear resistance – release of formaldehyde during processing and application – formaldehyde is released by autocatalytic hydrolysis during storage – cannot be used for delicate products, e.g. children's pyjamas

A comprehensive control system can indicate the advantages and disadvantages of novel agents and innovative FR processing procedures compared to classic ones [14].
Table 1 lists the advantages and disadvantages of two selected FR condensates, THPX (tetrakis-hydroxymethyl phosphonium salt) and MDPA (N-methylol N,N' dimethyl phosphonopropionamide derivative) for cotton textiles, where, in addition to other properties, the durability FR textiles treated in this way to washing is highlighted [15].
In this review, the durability of FR textiles is considered, primarily the influence of washing through the factors of the Sinner's circle, which must be considered in addition to technological permanence and ecological features.

2. The influence of Sinner's circle factors on the properties of FR textiles

The washing process is theoretically presented and practically considered by the circuit set up in 1959 by the tenside chemist Dr. Herbert Sinner [16]. The Sinner cycle of the washing process takes place through four factors: chemistry, mechanics, time and temperature. Theoretically, according to Fig.1, their share is equal. However, in real systems, a change in one factor is compensated by a change in at least one or more of them [17, 18]

Fig.1 Sinner's circle of the washing process [19]

The combined effect of mechanics, chemicals, heat and time associated with water that transmits kinetic and thermal energy can affect the properties of functionnal textiles, which can cause changes and damage, which are difficult or impossible to subsequently remove [20, 21].
Guidelines in the modern technology of the washing process, in addition to the need to reduce energy and water consumption, require the extension of the life time of textiles. The share of factors in these conditions changes in accordance with the technological requirements and settings of sustainable development through [22]:
- energy saving
- saving water
- saving chemicals
- extended life time of textiles
- reduced level of waste water load.

The representation of the share of individual factors is reflected in the quality of FR washed textiles, which can be viewed on the basis of different criteria and systems. The level of quality should be aligned with production and cost requirements. However, in many cases, the use of high washing temperatures, excessive amounts of detergent, the use of chlorine-based chemical bleaches and other stain, stain and odor removers can affect the durability of FR properties.

2.1. Detergent as a factor in the Sinner's cycle of the washing process

Universal detergents intended for washing at different temperatures are formulated with the aim of meeting the above requirements [20]:
- remove various types of stains
- applicability for different types of textiles
- pleasant smell
- remove a wide range of different water hardnesses
- after washing, do not form any deposits on the parts of the washing machine and deposits on textiles
- low foaming, i.e. have a regulated foam
- environmentally friendly and harmless to health
- flawless granular or powdery form, if they are not liquid
- expedient packaging
- good aging stability
- meet the washing success with the highest set requirements
- extend the life cycle of textile products.

In order for textile washing detergents to be able to meet these requirements, they are composed of several groups of components, each of which individually or in combination has a role in washing, and some can act synergy on each other. Individual components can consist of several subtypes, for example two or three surfactants, considering the removal of different types of dirt and preservation of textile properties as long as possible.
Innovative surfactants, advanced enzyme systems, highly effective bleaches and activators in detergents and their synergistic action with other factors of the Sinner's circle affect the properties of washed textiles.
Research on the washing resistance of FR textiles treated with alternative FR means compared to classic ones is often linked to certain norms or in-house developed methods, which prescribe the washing agent and machine, and the temperature and number of cycles are determined depending on the type of FR means, the type of textile and durability requirements. Accordingly, in most scientific publication, standard protocols are applied, usually through 15 cycles, using a washing device, Launder-Ometer or Linitest.

Tab.2 Composition of standard detergent (IEC - *The International Electro-technical Commission*)

Component	w (%)
A linear sodium alkylbenzenesulfonate of average chain length 11.5	9.7
Ethoxylated fatty alcohol, C_{12-18} (7 EO)	5.2
Sodium soap (C_{12-17}: 46%, C_{18-20}: 54%)	3.6
Foam inhibitor in a concentration of 8% on an inorganic carrier	6.5
Sodium aluminosilicate (Zeolite 4A)	32.5
Sodium carbonate	11.8
Sodium salt of acrylic and methacrylic acid copolymer	5.2
Sodium silicate (SiO_2:Na_2O = 3.3:1)	3.4
Carboxymethylcellulose	1.3
Diethylenetriamine penta(methylene phosphonic acid)	0.8
Optical brightener for cotton (stilbene type)	0.3
Sodium sulfate	7.5
Water	12.2
Σ	**100.0**

Tab.3 Composition of standard detergent IEC A*

Component	w (%)
Linear sodium alkylbenzenesulfonate with an average chain length of 11.5	8.8
Ethoxylated fatty alcohol C_{12-14} (7 EO)	4.7
Sodium soap *(tallow)*	3.2
Foam inhibitor	3.9
Sodium aluminosilicate, Zeolite 4A (80% active substances)	28.3
Sodium carbonate	11.6
Sodium salt of acrylic and maleic acid copolymer (granulate)	2.4
Sodium silicate (SiO_2:Na_2O = 3.3:1)	3.0
Carboxymethylcellulose	1.2
Sodium phosphonate/Dequest 2066, 25% active substance)	2.8
Optical brightener for cotton (stilbene type)	0.2
Sodium sulfate	6.5
Protease enzyme (*Savinase* 8.0)	0.4
Sodium perborate tetrahydrate (active oxygen 10.0-10.4%)	20.0
Tetra Acetyl Ethylene Diamine, TAED (active substance 90.0-94.0%)	3.0
Σ	**100.0**

Tab.4 Composition of standard IEC B detergent

Component	w (%)
Linear sodium alkylbenzenesulfonate with an average chain length of 11.5	8.0
Ethoxylated fatty alcohol C_{12-18} (14 EO)	2.9
Sodium soap (C_{12-16}: 13-26%, C_{18-22}: 74-87%)	3.5
Sodium triphosphate	43.7
Sodium silicate (SiO_2:Na_2O = 3.3:1)	7.5
Magnesium silicate	1.9
Carboxymethylcellulose (CMC)	1.2
Tetra Acetyl Ethylene Diamine (TAED)	0.2
Sodium sulfate	21.0
Optical brightener (diaminostilbene type)	0.2
Water	9.9
Σ	**100.0**

Different formulations of standard detergents are used within the protocols, and the biggest differences are manifested through the type of builder and the presence of optical brighteners. The presence of certain types of builders along with other components affects the alkalinity of the detergent solution, and indirectly the durability of the FR effects.

Standard detergents that do not contain optical brighteners are:

– AATCC – WOB
– ECE A
– ECE B

while detergents containing optical brighteners are:

– AATCC – OB
– IEC A
– IEC A*
– IEC B.

In short, IEC detergents contain optical brighteners (OB); ECE detergents are without optical brighteners (WOB); A indicates non-phosphate detergents, and B indicates phosphate detergents; AATCC – American Association of Textile Chemists and Colorists.

The composition of the mentioned detergents with and without optical brighteners are shown in tables 2-8 [23].

The IEC A* standard detergent replaces the previous IEC A formulation, and its composition is shown in Table 3.

This standard detergent, in addition to the base composition, also includes a foam inhibitor and enzyme in a total proportion of 77%, sodium perborate tetrahydrate in a proportion of 20% and a bleach activator, TAED in a proportion of 3% [24].

This IEC B standard detergent contains sodium perborate tetrahydrate in the proportion of 20% in addition to the base composition in the proportion of 80%. In some standards, the ratios of the base composition and sodium perborate are modified, for example, the Australian standard AS/NZS 2040.1 [25] refers to the IEC B standard detergent with the note that a reduced amount of sodium perborate in the proportion of 5% is added to the IEC B base formulation.

Tab.5 Composition of standard detergent ECE A (ECE, *European Colourfastness Establishment*)

Component	w (%)
A linear sodium alkylbenzenesulfonate of average chain length 11.5	9.7
Ethoxylated fatty alcohol, C_{12-18} (7 EO)	5.2
Sodium soap (C_{12-17}: 46%, C_{18-20}: 54%)	3.6
Antifoam (DC2-4248S)	4.5
Sodium aluminosilicate (Zeolit 4A)	32.5
Sodium carbonate	11.8
Sodium salt of acrylic and maleic acid copolymer (Sokalan CP5)	5.2
Sodium silicate (SiO_2:Na_2O = 3.3:1)	3.4
Carboxymethylcellulose	1.3
Diethylenetriamine penta(methylene phosphonic acid)	0.8
Sodium sulfate	9.8
Water	12.2
Σ	**100.0**

Tab.6 Composition of standard ECE B detergent

Component	w (%)
A linear sodium alkylbenzenesulfonate of average chain length 11.5	8.0
Ethoxylated fatty alcohol, C_{12-18} (14 EO)	2.9
Sodium soap (C_{12-16}: 13-26%, C_{18-22}: 74-87%)	3.5
Sodium triphosphate	43.7
Sodium silicate (SiO_2:Na_2O = 3.3:1)	7.5
Magnesium silicate	1.9
Carboxymethylcellulose	1.2
Tetra Acetyl Ethylene Diamine (TAED)	0.2
Sodium sulfate	21.2
Water	9.9
Σ	**100.0**

Tab.7 Standard soap without optical brighteners

Component	w (%)
Salts of fatty acids (PAT)	≥ 85.0
Moisture	< 5.0
Σ	**100**
Requirements (mass of dry matter)	
Free alkalis, Na_2CO_3	max 0.3%
Free alkalis, NaOH	max 0.1%
Titer of fatty acid mixture from soap	30 °C
Iodine number	max 50.0

Some standard protocols include the application of a standard soap that is used to wash textiles through a certain number of cycles. This type of treatment is usually done manually by soaking textiles in a bath for a short time. A solution of standard soap is not acceptable for washes in machines or laboratory devices, primarily to generate foam. The composition of standard soap and its features are shown in tab.7.

Despite the number of available standard detergents, in some studies detergents for general consumption are applied [5, 25].

A comparison of their efficiency compared to standard detergents in washing confirmed that generate more foam, which affects the efficiency of FR processing, reduces the resistance of textiles to washing and shortens their use cycle [10, 25].

The development, height and properties of foam can be attributed to the influence of surfactants and hydrodynamics in washing. An insight into the compositions of standard detergents, shown in tables 2-6, shows that their surface active substance (SAS) consists of anionic and nonionic surfactants.

All formulations contain the anionic surfactant, sodium alkylbenzenesulfonate, whose proportion varies from 8.0 to 9.7%, while the nonionic surfactant, ethoxylated fatty alcohol, is represented in the proportion from 2.9 to 5.2%. The hydrophobic and hydrophilic parts of nonionic surfactants are different, whereby the length of the hydrophobic chain occurs in two variations (C_{12-14} and C_{12-18}), and the number of hydrophilic, ethylene oxide groups (EO) varies from 7 to 14. Anionic surfactant, sodium alkylbenzenesulfonate is classifies as strong foaming agents, and ethoxylated fatty alcohol as medium foaming agents. Nonionic surfactants are characterized by a cloud point, above which this surfactant is classified as low-foaming surfactants, i.e. antifoams.

The development of foam in washing also has some favorable properties, for example, the friction of textiles against textiles, as well as textiles against metal parts of the drum, is reduced. However, at the end of the process it is important that it is completely removed from and from the textile. This depends on the properties of the foam, of which the following stand out: height, stability, structure and shape of bubbles, Fig.2 [26].

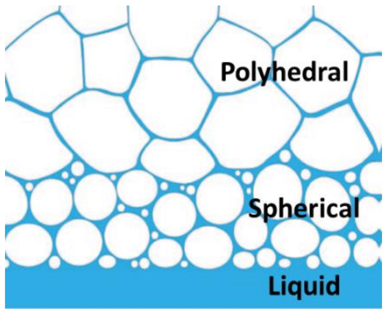


Fig.2 Structure and characteristics of the foam in the column [26]

Tab.8 Overview of standard washing agents and application in standard procedures

Detergent	Bilder	Optical brightener	Representation in the standard
IEC A	Zeolite 4A Sodium carbonate	+	EN ISO 6330: 2000 [27]
IEC A*	Zeolit 4A Sodium carbonate	+	EN ISO 6330: 2000 [27] IEC 60456 [28]
IEC B	Sodium triphosphate	+	BS 5651: 1989 [29] EN ISO 10525: 1995 [30] EN ISO 26330: 1994 (ISO 6330: 1984) [27]
ECE A	Zeolit 4A Sodium carbonate	-	EN ISO 6330: 2000 [27] EN ISO 12138 [31] EN ISO 10528: 1995 [32] EN 26330:1994 (ISO 6330: 1984) [27] EN ISO 105 C08 [33] EN ISO 105 C09 [34]
ECE B	Sodium triphosphate	-	EN ISO 105 C06: 1997 [35] BS 5651: 1989 [29] EN ISO 10528: 1995 [32] EN 26330:1994 (ISO 6330: 1984) [27]
Standard soap	-	-	EN ISO 105 C01-C05 withdrawn and replaced by EN ISO 105 C10 [36]

Through the drainage or draining of the bath, the spherical shape of the bubbles gradually changes to a polyhedral one, which is easier to remove from surfaces during the washing process. The greatest difficulties arise with liquid viscous foam, which, due to its pronounced ability to adhere to solid surfaces, is more difficult to break and remove. The presence of soap in all standard formulations regulates the foam during washing. Foam generation is also related to the hardness of the water, so it is important to look at the type of builder in the detergent formulation.

Separated formulations of powdered standard detergents have three types of builders: aluminosilicate (Zeolite 4A), sodium triphosphate and sodium carbonate, which can be seen from tab.8. In this table, where builders are highlighted, the presence of an optical brightener and the application of a certain formulation of the agent in certain standard procedures are indicated.

It is important that the pH value of the solution, as well as the shelf life of the product under appropriate storage conditions, are indicated along with the standard detergent applied in a certain concentration. If the composition of the standard detergent contains more thermally unstable components, such as sodium perborate tetrahydrate or sodium perborate monohydrate, it is important to analyze the content of active oxygen, and accordingly compensate for any loss of activity by increasing the concentration of the detergent.

3. Durability and sustainability of the FR properties of textiles through the design of the washing process

Despite the application and development of numerous means in the development of FR textiles, standard detergents and protocols in research and testing the persistence of effects, in some cases commercial protocols, powder and liquid detergents for general consumption and some softeners are applied [5, 37-39].

It is recommended to apply industrial washing for professional protective clothing, which is based on means and equipment that meet technical-safety conditions and engineering-development components. Manufacturers provide a guarantee for a certain number of washing cycles, however, in real conditions, the usage cycle is much shorter. Independent tests have confirmed the high level of resistance of Proban® cellulose textiles to washing, which, depending on the conditions, satisfies 100 to 150 washing cycles. However, the FR properties of processed textiles in the extreme conditions of the washing process can be lost even after several cycles. Therefore, it is necessary to use specific and targeted formulated detergents and procedures that contribute to the sustainability of FR effects and the durability of these functional textiles [40, 41]. Such product is the specialized liquid detergent Derval Rent, which contains three types of nonionic surfactants produced by the German manufacturer, Chemische Fabrik Kreussler & Co. GmbH, It is important to point out that the product formulation contains a nonionic surfactant, an alkylpolyglycoside, which is characterized by mild-

Tab.9 Composition of specialized liquid detergent Derval Rent [42]

Derval Rent		w (%)
ethoxylated alcohols, C_{13}-C_{15}, branched and linear		15-30
ethoxylated propyl alcohols, C_{12}-C_{18}		5-15
alkyl polyglycoside		1-5
polycarboxylates		1-5
potassium hydroxide		1-5
ethanol		1-5
fragrance		< 1

ness and ecological advantages, from raw materials from renewable sources to biodegradebility in waste water compared to other nonionic surfactants [20]. Table 9 shows the ingredients of this detergent and the mass fraction of its ingredients.

According to the manufacturer's specifications, Derval Rent:

- excellent at removing pigments and other dirt
- good at removing oil, grease and greasy dirt
- effective in the temperature range from 40 to 60°C
- particularly suitable for firefighter clothing, high visibility clothing, cleanroom clothing, outerwear
- mild due to low alkalinity
- has antistatic properties
- protects color and retro-reflection (RR) of high-visibility clothing
- it contains potassium-based raw materials.

The product has additional certificates:

- list of VAH (*Der Verbund für Angewandte Hygiene*) / DGHM (*Die Deutsche Gesellschaft für Hygiene und Mikrobiologie*) disinfection effect – applicable in a concentration of 2 ml/L Derval Rent with Ottalin Peracet (bleach based on peracetic acid) at a temperature of 60 °C with OK 1:4 in 10 minutes,
- DuPont personal protective textiles
- Nomex®
- HuPF (*German abbreviation for Manufacturing and Testing Description for a Universal Fire- Resistant Clothing*) for clothing for firefighters [43].

There are several standards that prescribe care and maintenance procedures for different types of FR protective clothing, whose fire resistance has been achieved through treatment with FR means or the choice of raw materials (inherent), tab.10 [40].

NFPA 2112 is applied to test the durability of FR textiles before and after 100 washing and drying cycles. The washing protocol according to this standard is used for heavily soiled clothes and an extremely alkaline washing medium is used, tab. 11 [40].

The specificity of some detergent formulations is manifested in a highly alkaline medium (pH 12.6) which originates mainly from sodium metasilicate (Na_2SiO_3) and sodium triphosphate ($Na_5P_3O_{10}$). In the tabular representation of the washing protocol after alkali, a nonionic surfactant, TergitolTM-15-S-9, is added. This surfactant belongs to the group of secondary alcohol ethoxylates or secondary ethoxylated alcohols, the properties of which are detailed in tab.12.

Tab.10 Selected norms for the care and maintenance of FR protective clothing [40]

Norm	Field of application
ASTM F1449 – 08 [41]	Standard guide for industrial laundering of flame, thermal, and arc-resistant clothing.
ASTM F2757 – 09 [44]	Standard guide for home laundering care and the maintenance of flame, thermal and arc-resistant clothing.
CEN/TR 14560: 2003 [45]	Guidance for selection, use, care and maintenance of protective clothing against heat and flame.
ISO/TR 2801: 2007 (AS/NZS 2801: 2008) [46]	Clothing for protection against heat and flame - General recommendations for selection, care and use of protective clothing.
NFPA 1851 [47]	Standard on selection, care, and maintenance of protective ensembles for structural fire-fighting and proximity fire-fighting.
NFPA 1855 [48]	Standard on selection, care, and maintenance of protective ensembles for technical rescue incidents.
NFPA 2112 [49]	Standard on flame-resistant garments for protection of industrial personnel against flash fire.
NFPA 2113 [50]	Standard on selection, care, use, and maintenance of flame-resistant garments for protection of industrial personnel against short-duration thermal exposures.
EN ISO 15797 [51]	Textiles - Industrial washing and finishing procedures for testing of workwear.

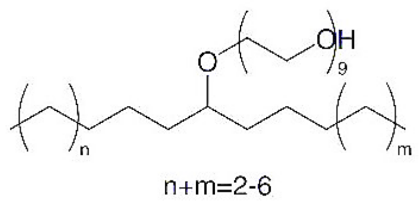
ASTM (*American Society for Testing and Materials*)
AS/NZS (*The Joint Australian Standard/New Zealand Standards*)
NFPA (*National Fire Protection Association*)

Tab.11 Specifications for industrial washing according to NFPA 2112 for testing the fastness of FR textiles [40]

Operation	T (°C)	t (min)	Water level	Amount/weight of dry laundry (g/kg)
Break	66	10	Low	
Sodium metasilicate, Na_2SiO_3 or equivalent				17
Sodium triphosphate				11
Tergitol™-15.S.9* or equivalent				
Drain		1		
Carry-over	66	5	Low	
Drain		1		
Rinse	57	2	High	
Drain		1		
Rinse	48	2	High	
Drain		1		
Rinse	38	2	High	
Drain		1		
Sour	38	5	Low	
Sodium silicofluoride				6
Drain		1		
Extract		5		

Tab.12 Properties of the nonionic surfactant Tergitol™-15-S-9 (secondary alcohol ethoxylate, synonym: nonyl phenol polyethylene glycol, commercial product: Triton)

EO (mol)	9
Surface tension (mN/m) 1%, 25 °C	30
Cloud point (°C)	60
HLB	13.3 (good washing power)
cmc (ppm)	52
Foam height, according to *Ross-Miles* (mm), solution 0.1%, 25 °C Initial/5 minutes	124/43
Biodegradability (OECD)	good



EO *(number of ethylene oxide groups)*
OECD *(The Organisation for Economic Co-operation and Development)*

The properties of the nonionic surfactant shown in tab.12 fully meet the technical and application requirements for maintaining the FR properties. Environmental acceptability, which is manifested through good biodegradability, is its additional advantage compared to some other less biodegradable surfactants. The cloud point is 60 °C, which indicates the approx. working temperature, at which good washing power can be achieved, expressed through the hydrophilic/lipophilic balance, HLB 13.3.

Table 13 highlights some features of the EN ISO 15797 standard for work protective clothing, which also includes FR products [51]. This standard is related to the ISO 30023 standard [52], which includes graphic symbols used to mark work and protective clothing and provides information on the acceptability of professional industrial washing in accordance with the EN ISO 15797 standard. The symbol specifies the application in the classification of textiles potentially acceptable for industrial washing, which includes procedures: washing, bleaching, tunnel refining (finisher) and drying in a drum after washing, Fig.3.

Norm EN ISO 15797 defines:

- washing machines
- filling ratio
- water quality
- detergent, bleaches
- programs, process parameters.

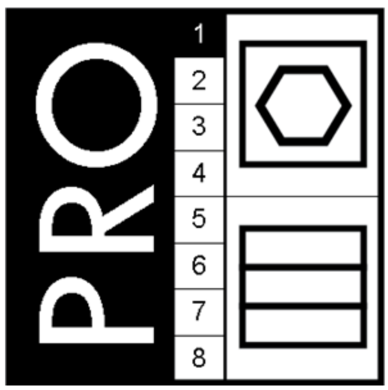


Fig.3 Graphic symbols according to ISO 30023

Tab.13 Washing machines, means and procedures according to EN ISO 15797

Machinery	Resources
for **washing** with a drum/centrifuge – V = 220 to 250 L – charging 15-25 kg	– **standard detergent** (with optical bleach) – **standard detergent** (without optical brightener) – **bleaching agents** (chlorine-based, oxygen-based) – **water** (°DH, pH, c $_{Fe/Mn/Cu}$, T)
drying	
A) drum dryer OP 1:25 – 1:35 T = 90°C	
B) tunnel dryer T = 155°C t = 4 min p* = 2-5 bars **spray steam*	

Within the scope of the standard, 8 washing procedures are defined, 4 procedures for cotton textiles and 4 for textiles in a polyester/cotton blend.

This standard includes a specially formulated standard detergent, which is qualitatively and quantitatively specified in tab.14 and 15.

Insight into the composition of the detergent, tab.14 and 15, shows that the proportion of surfactant (SAS), in which anionic surfactant is in an extremely low surfactant in a relatively high proportion (6%). The presence of metasilicate and sodium carbonate may imply increase in alkalinity of this formulation, value pH 12-13.

Bleaching agents are not included in the composition of the detergent, but according to EN ISO 15797 are dosed as separate components within the 8 described procedures, tab.16.

The norm also prescribes water quality, tab. 17, as a significant parameter in the durability test, which is an important process parameter for FR textiles.

The most common number of cycles for the stability test is 10, whereby after the 1st, 5th and 10th cycles, samples are taken out and analyzed by comparison with an unwashed (0) sample.

Tab.14 Composition of standard detergent with optical brightener

Component	w (%)
Sodium alkylbenzenesulfonate (C-12), ABS-Na	0.42
Nonionic surfactant ($C_{13/15}$ 7 EO ili $C_{12/14}$ 7 EO)	6.0
Sodium citrate dihydrate	5.0
Hydroxyethanediphosphonic acid sodium salt (HEDP)	1.0
Metasilicate (anhydrous)	42.3
Polymer (polymaleic acid)	2.0
Foam inhibitor (phosphoric acid ester)	3.0
Sodium carbonate (Na_2CO_3)	39.5
Optical brightener	0.3
Water	0.48
Σ	**100.00**

Tab.15 Composition of standard detergent without optical brightener

Component	w (%)
Sodium alkylbenzenesulfonate (C-12), ABS-Na	0.43
Nonionic surfactant ($C_{13/15}$ 7 EO ili $C_{12/14}$ 7 EO)	6.0
Sodium citrate dihydrate	5.0
Hydroxyethanediphosphonic acid sodium salt (HEDP)	1.0
Metasilicate (anhydrous)	42.6
Polymer (polymaleic acid)	2.0
Foam inhibitor (phosphoric acid ester)	3.0
Sodium carbonate (Na_2CO_3)	39.5
Water	0.48
Σ	**100.00**

4. Extending the life cycle of FR textiles in washing

Detergents contain numerous organic and inorganic substances that can leave, deposits or residues, which can result in clogging of the pores in the fabric. Most detergent solutions are alkaline (pH 9-13), which is necessary to remove stains and other contaminants from textiles. Considering the high alkalinity of the washing baths, it is necessary to completely neutralize residual alkalis, which can cause skin irritations and other secondary problems [53, 54]. Complete neutralization of all alkaline traces in commercial washing is carried out by the addition of acid, which must be monitored by analysing the pH and conductivity of the aqueous extract [5, 55-57]. The potential irritating effect of surfactants and other components can be reduced by the addition of special collagen-based bio-polymers, Fig.4 [57, 58]. The interaction of biopolymers with surfactant mole-

Tab.16 Bleach active agents

Bleaching agents	Concentration
Peracetic acid	4 g/L Acetic acid (4-5%) Hydrogen peroxide (20-30%)
Sodium hypochlorite	2 g/L (150 g/L)
Hydrogen peroxide	4 g/L (20-30%)

Tab.17 Requirements for water quality

Parameter	Values
Hardness mg/L or ppm $CaCO_3$	≤ 100
pH	6.0-7.5
Fe (mg/L)	0.1
Mn (mg/L)	0.03
Cu (mg/L)	0.05
T (°C)	15 ± 5

cules and their micelles can affect the non-specific adsorption of anionic surfactants on the textile surface. Such a specifically oriented polymer reduces the tendency to deposit inorganic and organic deposits, which can affect the reduction of FR properties.

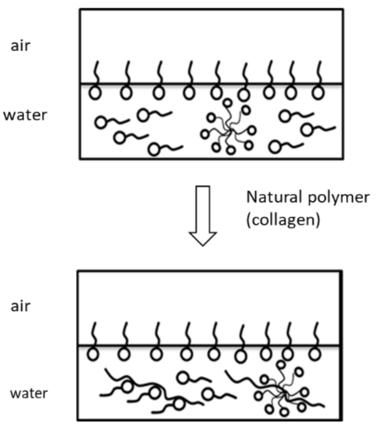


Fig.4 Interaction of anionic surfactant and collagen-based biopolymer in solution [58]

Builders, such as soda ash, which act on the basis of precipitation in washing, can precipitate insoluble Ca and Mg salts within or on the surface of the fiber. Such deposits, depending on the concentration, position and chemical constitution, can cause various unwanted effects such as:

– obvious changes in tone
– decrease in use value
– loss or reduction of FR properties
– unfavourable changes in mechanical properties and feel.
– Standard IEC B and ECE B detergents contain sodium triphosphate ($Na_5P_3O_{10}$) as a builder, which forms a stable water-soluble complex ($CaNa_3P_3O_{10}$) with calcium ions, showing excellent sequestration properties.

When cotton textiles are washed in cycles with low concentrations of detergent, and consequently with a small proportion of builder - sodium triphosphate, a significant amount of insoluble calcium phosphate precipitate, $Ca_5(P_3O_{10})_2$, can be deposited on the material [20].

The results of the conducted research showed that in some cases as much as 25% of the mass of the fabric belongs to phosphate ash [10]. When cotton fabric with a high phosphate ash content is examined microscopically, little or no inorganic deposits are observed on the surface of the fiber. However, the analysis of ash indicates a complete inorganic skeleton of the fiber structure, based on which it can be concluded that insoluble phosphates are deposited inside the fiber, more often than they are deposited on the surface of the fiber, Fig.5.


Fig.5 SEM image of alkaline earth fine crystalline sediment from a bath that does not contain carbonates, magnification 1000x [59]

The process of repeated rinsing with cold water and rewetting in a washing bath containing phosphate ions causes their accumulation on cotton fibers. The increased dispersion of these inorganic deposits can cause a change in the tone of colored fabrics.
Unlike calcium phosphate, calcium carbonate is deposited by accumulation on the surface with a tendency to form crystalline forms of calcite (limescales) the fiber surface, Fig.6.

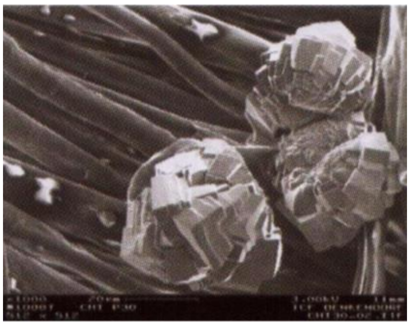


Fig.6 SEM images of alkaline earth deposits - microcrystals of calcium and magnesium (mass ratio 1:1) from a bath containing carbonates, magnification 1000x [59]

Relatively small amounts (below 5%) can be seen under the microscope as crystalline forms of calcite ($CaCO_3$), which gives an unpleasant sticky feel. Calcite is slightly abrasive, which has the effect that the utility value of textiles regularly washed in products containing carbonates compared to phosphates is significantly reduced. Calcite growth on the surface of the fiber is more likely than inside the fiber, which can be explained by the fact that the growth of calcite crystals is relatively slow and is slightly contaminated by other ionic species in the washing solution. The initially high concentration of calcium ions in the dry fiber is significantly reduced by dilution and ion exchange with sodium ions, before calcite precipitation occurs. The slow growth of calcite and the consequent slow lowering of the concentration of free calcium ions in the washing solution makes sodium carbonate a weaker builder in washing agents.

There is a danger of precipitation of Ca/Mg ions with surfactants and soaps, and the tendency to generate hard-to-dissolve precipitates with soaps is a more common problem. Therefore, it is important to incorporate a quality builder into the detergent formulation, which will prevent the generation of calcium or magnesium soaps, which can form flammable deposits [10]. Precipitation of calcium and magnesium soaps is present in systems poor in builders, because soaps and other anionic surfactants are irreversibly deposited before the builder works. The consequence of the deposition of these substances on the large active surface of cellulose textiles is hydrophobicity, a tendency to yellowing and an unpleasant smell. A large amount of soap deposits reduces the effect of anti-flame treatment and increases the flammability of textiles. The additional advantage of quality builder is justified by the fact that soap is included in the majority of qualitatively and quantitatively specified standard, tab.2-8, and detergents for general consumption.

The effectiveness of surfactants decreases in hard water. Anionic surfactants still dominate in detergent formulations due to easy availability, low cost and excellent properties. Three anionic surfactants were investigated: sodium lauryl benzene sulfonate (low price and the most widely used), methyl ester sulfonate (MES, a newer generation of "green" surfactants) and alcohol ether sulfate (AES, which has good properties in application) in combination with nonionic surfactant and oxalate builder. Considering the well-known synergistic effect of the combination of anionic and nonionic surfactants, ethoxylated alcohol with 9 EO groups, which is widely used, was used in this research. Sodium oxalate ($Na_2C_2O_4$) as an organic salt is used as a chelate, reducing agent and metal binding agent in the preparatory processes of textile finishing [60, 61]. An additional advantage of this organic salt compared to conventional builders (triphosphate, aluminosilicate) is a good synergistic effect with enzymes (especially lipase) and some surfactants on which modern washing chemistry is based. Research has shown that sodium oxalate is effective in binding calcium from textiles and dirt, and that it also has excellent synergistic properties with different surfactants in different washing conditions [62]. These facts open the possibility that this particular builder can be incorporated into standard detergents, which can reduce the influence of soap and surfactant deposits on the reduction of FR effects.

5. Conclusion

In the review, the features of standard detergents and standard protocols for the analysis of durability with an emphasis on FR textiles are highlighted through the importance of Sinner's circle factors in the washing process. Potential risks in washing these textiles using existing standard detergents are indicated. Guidelines are given for the composition of detergent formulations to ensure the durability of FR effects through multiple washing cycles and to increase their life time.

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