New approaches to the analysis of the influence of washing agents for delicate textiles

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The study is focused to the influence of the washing agents on the properties of delicate textiles, two black coloured wool knitwear, a blue cotton fabric and an orange linen-silk blended fabric through 10 cycles at 30 °C. The bath was varied by selecting four washing media: three liquid detergents (P, M, O), which were used in the recommended concentrations, and water. The washing process was preceded by an analysis of the detergents by determining the total surface-active substances and the pH value. Results of analysis showed differences between detergents.The secondary washing effect of liquid detergents and water of selected textiles was compared by analysing the spectral values of washed versus unwashed textiles, the degree of hydrophilicity and the surface analysis of all textiles. The effect of the washing process on the properties of textiles was checked by residual amounts of anionic and nonionic surfactants in an aqueous extract of textiles that had been washed 10 times and coloration of effluent after each washing cycle. The results of the parameters, the evaluation of colour fastness to washing and the total colour difference (dE) of washed compared to unwashed textiles, confirmed insignificant differences in the impact of liquid detergents on materials through 10 wash cycles at 30 °C. The greatest differences within the tested detergent series were achieved by the content of residual substances, nonionic and anionic surfactants in an aqueous extract of the washed materials. The content of nonionic surfactants in the extract of the wool knitwear with a more compact structure (VP1) is above the limit value according to the RAL-GZ 992 quality system, while it is below the limit values in the extract of the other materials (wool knitwear with a lower surface mass, cotton fabric and linen/silk fabric). The content of anionic surfactants in the aqueous extract depends on the type of textiles and the liquid detergent. Values above the limit value were obtained in an aqueous extract of knitwear (VP1, washed with detergent M), woollen knitwear VP2, washed with detergent M and fabrics LST, washed with detergent P. According to this environmental criterion, the best washing agent for all materials is detergent O. The results confirmed the justification of analysis of an aqueous extract on the surface substance content, which can have a negative effect to the skin.

Keywords: *textiles, liquid detergent, washing, secondary effect, colour fastness, surfactants*

1. Introduction

The process of textile care implementation is aimed at improving the existing and introducing new eco-friendly processes and means that can ensure the sustainability and functionality of textiles. The main objective of the washing process is to improve the touch of the fabrics in terms of their characteristics, surface, whiteness, shade, tint, print, shine, dimensional and application stability, stitch ability and other specific features of the product. The textile materials are represented by a number of substances which, apart from the degree and stains homogeneity, are distinguished by their physic-chemical composition and subdivision. They can interact with textiles from the edges of the yarns, fibers of the yarn, the pore and the surface of the textiles [1, 2]. The power of stain removal is related to the properties of the textiles (raw material composition, structural elements, degree and type of finishing, humidity), soil (physic-chemical composition), their interaction (time of aging, influence of heat and chemicals) and the factors of the washing process specified by the Sinner's circle [3].
The mentioned factors during the process of washing colored textiles can affect the desorption and/or migration of weakly fixed dye particles or pigment particles from the surface of the textile into the bath [4]. This transition is conditioned by the share of Sinner's cycle factors (detergent composition, hydrodynamics, time and temperature), pH value and water hardness [5]. If colored textiles of poor fastness were washed in the same bath with white textiles, the desorbed or migrated dye particles will consequently transfer to the white textiles [6, 7]. The desorption can be stabilized by surface-active substances, water-soluble detergent components and special additives, dye transfer inhibitors (DTI) polymers.
Dyes that are difficult to dissolve in water are accepted in molecular form in the hydrophobic parts of surface-active substances where they are stably dissolved, solubilized. For solubilization to be successful, the concentration of the surface-active substance must be higher than the critical micellar concentration (cmc), because particles of poorly soluble dyes are retained in the micelles. However, in complex matrices it is important to optimize the amount of surfactants for their impact on the environment [8]. The stabilizing effect of surfactants on dyes in the washing process is increased by special polymers, which are compatible with anionic, cationic and amphoteric surfactants [9]. Polymeric substances have in common that they can interact with both dyes and surface-active substances [6].
According to Schwuger, the mechanisms of dye stabilization in the washing bath are [6]:
– interactions of surfactant/dye,
– interfacial surfactant/polymer/adhesive interactions,
– inter-cooperative operations with water-insoluble detergent compounds.

Powdered detergents contain water-insoluble ingredients such as sodium aluminosilicate (zeolite A), whose effectiveness is determined by the capacity and kinetics of ion exchange. Experiments have confirmed that dyes are adsorbed on zeolite A depending on the surface properties of the adsorbent and the type of dissolved dye particles [2, 9, 10].
Intensive fading of some dyed textiles (cotton, wool) in most cases stops after 7 to 8 cycles of the washing process. Color transfer can be prevented or reduced with dye transfer inhibitors (DTI agents) or color fixing agents, which can be detergent ingredients or post-treatment agents [4].
Existing agents are polymers based on polyvinylpyrrolidone, polyvinyl alcohol, cationic polycondensation products, cationic polysaccharides, minerals, oxidase enzymes, oxidants, quaternary ammonium compounds.
Fig.1 shows two ways of color preservation: by wrapping the fibers (passive protection) and by the action of cellulases on the surface (active protection) [11].

a)

b)

Fig.1 Mechanisms of color preservation: a) passive protection; b) active protection [11]

The inclusion of (macro) molecules in detergent formulations for textiles that inhibit the undesired adsorption of dyes on fabrics can be used as a useful way of inhibiting dye transfer [12].
N-heterocyclic polymers, e.g. polyacrylamidopropyl trimethylammonium chloride or Polymer 100, Fig.2, inhibit the dye transfer and graying, and act synergistically with cellulases, which improves the brilliance of shades [13].

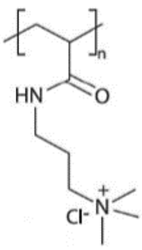


Fig.2 Polymer 100® [13]

Color retention is provided by a nonionic surfactant in combination with Polymer A, while this synergy is not realized in combination with an anionic surfactant.

Through Turbo Color Protect technology, Ecolab has developed innovative solutions that act on 3 levels:

- preventing and/or slowing down the graying of textiles - excellent suspension efficiency in washing conditions with a high degree of soiling,
- stopping polyquaternium stains - specific residues of cosmetic and personal hygiene products that cannot be removed, the new Ecolab technology protects textiles and prevents the appearance of polyquaternium stains [14],
- stopping the transfer of dyes - protecting the whiteness of white cotton textiles or mixtures with polyester, as well as the transfer of dyes from dyed textiles to the washing bath.

The advantages of this technology are longer lifetime of textiles, reduced procurement costs and increased productivity due to reduced repetition of the washing cycle (re-wash) [15].

In this study, three liquid detergents for washing colored textiles (P, M, O) and water (V) were analyzed as a comparative agent with the aim of insight into changes in the properties of textiles. Their influence was monitored in the washing process of two black-colored wool knits, a blue cotton fabric and an orange linen-silk blend fabric through 10 cycles at 30 °C. The washing process was preceded by an analysis of the washing agents by determining the total surface-active substance and pH value.

The secondary effect of liquid detergents and water in the washing process of selected textiles was monitored through the analysis of spectral values of washed versus unwashed textiles, degree of hydrophilicity and surface analysis of washed versus unwashed textiles. The state of the surface of washed knitwear and fabrics after 10 washing cycles was analyzed by determining the pH value and the content of anionic and nonionic surfactants in the aqueous extract in order to check the effect of the washing process and the residue content of these substances on the washed textiles.

2. Experimental part

Selected textiles were analyzed in the washing process with four agents, three liquid detergents for washing delicate laundry (P, M, O) and water (V), which was also used to prepare the bath.

2.1. Materials

In the research, four different textiles were used, two knits of the same color tone and different surface mass, and two fabrics, of a different color and different surface mass, whose markings and basic technical features are shown in Tab.1.

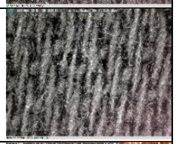
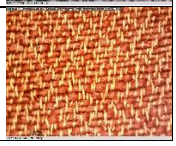
2.2. Washing agents

Three liquid detergents for delicate textiles are classified within the group [16], two of which belong to the group of liquid color detergents for general consumption (P, M), while the third is a liquid detergent for professional use (O). Their designations, descriptions and dosage for low soiling in the hard water washing process are contained in Tab.2.

Liquid detergent (P) intended for machine and hand washing of dark tones at temperatures of 20–60°C contains:

- 5–15% anionic surfactants
- <5% nonionic surfactants, soap
- enzymes
- fragrances – *benzisothiazolinone, methylisothiazolinone*.

Tab.1 Characteristics of the analyzed knitted fabrics and fabrics

Material	Label	Material composition (%)		Surface per unit area (g/m^2)	Density row/wale (stitches/cm) warp/weft (threads/cm)	Micrograph, 50x
Knit-more compact	VP1	Wool	100	285	20/18	
Knit	VP2	Wool	100	196	21/18	
Fabric	PT	Cotton	100	229	24/13	
Fabric	LST	Linen/ Silk	N/A	126	72/36	

Tab.2 Labels, description and recommended dosage of the analyzed detergents

Label	Description	Dosage* (mL/3 kg)
P	*color* detergent for delicate laundry (*black*)	75
M	*color* detergent for delicate laundry (*black*)	75
O	detergent for washing delicate textiles	30
V	tap water	-

The second detergent (M) intended for machine and hand washing of black and dark textiles at temperatures of 30–60°C contains:
- 5–15% anionic surfactant
- <5% nonionic surfactants, soap, phosphonate
- color protector
- fragrances.

The third detergent (O) intended for machine washing of all delicate washable textiles at temperature of 30–60 °C contains:
- 10–25% ethoxylated fatty alcohol (nonionic surfactant)
- 2.5–10% alkylbenzene sulfonate (anionic surfactant)
- 2.5–10% polypropylene glycol
- up to 100% water.

2.3. Washing process

The washing process of textiles weighing 5 g with liquid detergents (P, M, O) and water (V) was carried out in a laboratory apparatus Turbomat, P 4502, Mathis, through 10 cycles in a ratio of 1:20 at a temperature of 30°C for 30 minutes. After the washing process, the samples were washed with tap water through four cycles and air-dried.

2.4. Methods

The hardness of the water used for the preparation of detergent solutions and for the washing process (V) was analyzed using the complexometric titration method. In the research, physic-chemical methods were applied for the analysis of detergents (determining the pH value and total surface-active substances), washing bath (color), textiles before and after the washing process (hydrophilicity, spectral properties, surface) and water extract (pH value and surfactant content).

Detergents

The pH value of the detergent solution (1 %) was determined potentiometrically using a pH meter Metrel, Iskra. The total surfactant content of the analyzed detergents is determined gravimetrically at the end of the extraction in ethanol [17].

Washing bath (coloration)

Before and after each washing cycle (1st, 2nd, 3rd, 4th, 5th, 6th, 7th, 8th, 9th and 10th) of all textiles, the color of the bath was monitored.

Textiles

The hydrophilicity of all textiles before and after 10 washing cycles was tested by dropping of distilled water from a burette (height 10 cm) on the surface, in order to determine the time of complete penetration into the material.

The spectral characteristics of the analyzed textiles were measured at four locations using a spectrophotometer Spectraflash SF300, DataColor, selecting an aperture of 20 mm, standard light D_{65} and geometry d/8. The results are expressed as differences in brightness (dL*), hue (dH*), saturation (dC*) and total difference in color (dE) of washed versus unwashed samples. Color fastness was evaluated according to the ISO A05 and AATCC systems, where a score of 5 corresponds to excellent color fastness and a score of 1 to poor color fastness [18].

The surface of the textiles before and after the washing process was determined using a digital microscope, Dino-Lite, type Premier with a magnification of 50x.

The pH value of the aqueous extract of the analyzed textiles before and after the washing process was determined according to [19].

The amounts of anionic and nonionic surface active species, and the content of their residues on textiles are determined by in house/internal potentiometric titration on a Metrohm Autotitrator 736 GP Titrino. Ion-selective surfactant electrodes, High Sense Surfactant Electrode (6.0504.150) in combination with the reference Ag/AgCl electrode (6.0733.100) are used for the determination of anionic surfactant. The ion-selective electrode NIO electrode (6.0507.010) and the same reference electrode, all from Metrohm, were used to determine nonionic surface active species from the solution.

The calibration curves are prepared for each surfactant by determining their quantity in the solution. The anionic surfactant, sodium dodecyl sulphate (NLS), is titrated at pH 3 with Hyamine 1622 as the solvent, and the nonionic surfactant, Triton X-100, is titrated with sodium tetraphenyl borate (STFB) in addition to $BaCl_2$ [20, 21].

The content of anionic surfactant in the solution (X) is calculated from the equation of the calibration curve::

$$X=(V-0.001)/0.0008 \qquad (1)$$

X – content of anionic surfactant in the solution (μg)
V – volume of Hyamine 1622 (mL)

The content of nonionic surfactant in the solution (X) is calculated from the equation of the calibration line:

$$X=(V+0.0636)/0.004 \qquad (2)$$

X – content of nonionic surfactant in the solution (μg)
V – volume of STFB (mL)

3. Results and discussion

It is known that the properties of textiles change during the washing process, and the intensity of the changes depends on factors related to their construction features, raw material composition, finishing degree and conditions of the washing process, which are described by Sinner's circle [1-3].

In this research, liquid formulations of detergents for washing delicate textiles were selected. According to the specification, color detergent P "improves color intensity, smoothers sharp fibers, ensures better light reflection and helps strengthen fibers to maintain dimensions and shape".

Detergent M is a liquid color detergent specialized for machine and hand washing of black and dark laundry, and according to the specification "preserves colors, maintains elasticity, restores fibers and has a long-lasting effect - new formulas, making laundry look like new after 25 washing cycles".

Detergent O is a concentrated mild product suitable for washing all sensitive, washable textiles in professional conditions, and according to the specification "refreshes color, prevents redeposition and gives a pleasant, refreshing smell to washed textiles".

The fourth washing agent is tap water (V) with a hardness of 385 ppm $CaCO_3$.

The pH values of the washing agents are shown in Tab.3, and the total amount of surfactant in detergents in Tab.4.

Tab.3 pH values of the washing agent

Washing agent	pH	T (°C)
P	9.0	22.2
M	8.2	
O	7.8	
V	7.0	

From the results of the pH value of the solution of liquid detergents and the water from which the solutions were prepared, it is evident that detergent P has the highest value (pH 9), which is higher than the pH value of liquid detergents [2]. Detergent M has a lower value (pH 8.2) than detergent P and is similar to the pH value of most liquid detergents. The lowest pH value is detergent O (pH 7.8), and even lower is hard water (pH 7.0).

The total active surface substance (SAS) is an important parameter of detergent quality (Tab.4) even though it is not a key parameter in achieving good primary and secondary performance in the washing process. Based on the data extracted from the declaration of detergents mentioned in the description of the experimental part, it is evident that the three analyzed detergents contain anionic and nonionic surfactants, and detergents P and M also contain soaps. The proportion of declared nonionic surfactants in detergents P and M is less than 5%, and the proportion of anionic surfactants in the proportion is 5-15%. Detergent for professional purposes O has a smaller proportion of anionic (2.5-10%) compared to nonionic surface-active substances, which have 10-25%. Experimentally determined average values of SAS are shown in Table 4.

Tab.4 The average values of SAS of the analyzed detergents

Detergent	SAS (%)
P	12.3
M	24.1
O	16.1

From the SAS results obtained, it is evident that the analyzed detergents differ, with detergent M having the highest content, followed by detergent O and detergent P with the lowest proportion of SAS. Despite the mentioned differences in the share of surfactants, through analysis and comparison, it is not possible to predict the primary and secondary effect of individual detergents in the washing process, i.e. their quality and efficiency. It is known that the washing process takes place through the factors of Sinner's circle, where the chemical factor (detergent effect) takes place in synergy with temperature, mechanical action and time [10].

By analyzing the hydrophilicity of textiles before and after 10 washing cycles using the droplet penetration method, the influence of washing agents on this property was determined.

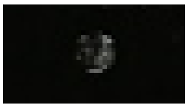
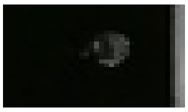
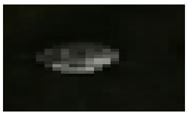
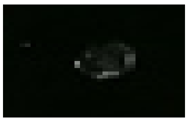
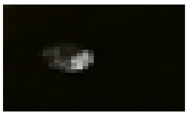
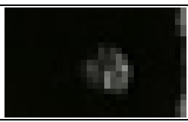
The hydrophilicity of cotton fabric (PT) and linen/silk blend fabric (LST) before and after washing are different. Complete penetration of water drops into unwashed cotton fabric occurred after 8 s, while penetration into textiles washed with detergents and water was instantaneous.

Full penetration of water drops into the unwashed LST fabric occurred after 155 s, while into the fabric washed with the analyzed detergents through 10 cycles, the penetration was instantaneous, and after washing with water through 10 cycles after 6 s.

Wool knits (VP1 and VP2) before and after the washing process with detergent and water showed a worse degree of hydrophilicity compared to PT and LST fabrics, Tab.5. The wool fabrics (VP1 and VP2) tested before and after 10 washing cycles showed weak hydrophilicity, which was manifested in the temporal stability of the water drop placed on the surface, Tab.5. The resolution of the images is not high, but despite this, a firmly localized drop of water is visible on the surface of unwashed and washed knitwear. The reason for this is the hydrophobicity of wool textiles in relation to PT and LST, as well as the low washing temperature (30°C) adapted to the type of textiles, rather than the full effect of anionic surfactants.

Spectral characteristics of textiles, black-colored wool knits, blue cotton fabrics and orange linen/silk blend fabrics were analyzed through differences in lightness (dL*), saturation (dC*), hue (dH*) and overall color difference (dE) of the face and the reverse sides of washed versus unwashed textiles, and color fastness ratings to washing according to the ISO and AATCC scale.

Tab.5. Appearance of drops on wool knits VP1 and VP2 before and after 10 washing cycles

Detergent	VP1	VP2
P		
M		
O		
V		
Unwashed		

Tab.6. Differences in the spectral characteristics of the face and back of the VP1 sample washed with detergent compared to the unwashed one and the rating of color fastness (ISO, AATCC)

Detergent	Fabric side	dE	dL*	dC*	dH*	ISO	AATCC
P	Face	0.350	-0.195	0.166	-0.237	5	5
	Back	0.762	-0.724	0.096	-0.154	4-5	4-5
M	Face	0.293	0.081	0.141	-0.167	5	5
	Back	0.396	-0.353	0.104	-0.132	5	5
O	Face	0.420	-0.161	0.087	-0.154	4-5	4-5
	Back	0.284	-0223	0.051	-0.145	5	5
V	Face	0.740	-0.701	0.091	-0.198	4-5	4-5
	Back	0.576	-0.532	0.051	-0.207	4-5	4-5

Tab.7. Differences in the spectral characteristics of the front and back of the VP2 sample washed with detergent compared to the unwashed one and the evaluation of color fastness (ISO, AATCC)

Detergent	Fabric side	dE	dL*	dC*	dH*	ISO	AATCC
P	Face	0.626	-0.616	0.089	-0.042	4-5	4-5
	Back	0.948	-0.942	0.099	0.006	4-5	4-5
M	Face	0.549	-0.529	0.137	-0.019	4-5	4-5
	Back	0.791	-0.750	0.187	0.085	4-5	4-5
O	Face	0.778	-0.767	0.045	-0.107	4-5	4-5
	Back	1.072	-1.060	0.102	0.068	4-5	4-5
V	Face	1.076	-1.069	-0.059	-0.108	4	4
	Back	1.112	-1.106	-0.013	0.045	4	4

Tab.8. Differences in the spectral characteristics of the face and back of the PT sample washed with detergent compared to the unwashed one and the rating of color fastness (ISO, AATCC)

Detergent	Fabric side	dE	dL*	dC*	dH*	ISO	AATCC
P	Face	0.627	-0.494	0.367	0.089	4-5	4-5
	Back	0.520	-0.181	0.296	0.041	5	5
M	Face	0.797	-0.709	0.251	0.140	4-5	4-5
	Back	0.398	-0.241	0.260	0.053	5	5
O	Face	0.802	-0.666	0.408	0.506	4-5	4-5
	Back	0.408	-0.231	0.296	0.041	5	5
V	Face	0.908	-0.864	0.215	0.170	4-5	4-5
	Back	0.514	0.440	0.232	0.044	5	5

Tab.6 shows the average values of the differences in the spectral characteristics of the black-toned wool knit (VP1) washed with detergents P, M, O and water, while Figs. 3 and 4 show the total difference in the color of the face and back of all washed textiles compared to unwashed ones.

The fastness ratings (ISO, AATCC) coloration of the face and back of wool knitwear in black tone VP1 when washed at 30°C indicates a slight influence of the agents in which the knitwear was washed. Black wool knit (VP1) has the best fastness to washing with agent M (grade 5 front and back). After the VP1 washing process with other agents (detergents and water), a high level of color fastness was maintained (grades 5 and 4-5), which confirms the good fixity of the dye and the good technological stability of this textile.

Ratings of fastness (ISO, AATCC) of the coloration of the face and back side of the wool knitwear in the black VP2 to washing at 30°C indicate the identical influence of the detergents in which the knitwear was washed (grades 4–5), Tab.7. The black wool knitwear (VP2) has a worse color fastness of the face and back when washed with water (grade 4). The composition of detergents adapted to preserve darker shades is hereby confirmed.

Ratings of color fastness (ISO, AATCC) of the face and back side of PT blue tone cotton fabric to washing at 30°C in Tab.8 indicate the identical influence of detergents and water in which the knit was washed, ratings 5 (face) and 4–5 (back side), which confirms good stability to the conditions of the washing process.

Color fastness grades (ISO, AATCC) of the front and back of the orange linen/silk fabric LST to washing at 30°C in Tab.9 indicate the identical influence of detergents P, M, O and water in which

Tab.9 Differences in spectral characteristics of the front and back of the LST sample washed with detergent compared to the unwashed one and the rating of color fastness (ISO, AATCC)

Detergent	Fabric side	dE	dL*	dC*	dH*	ISO	AATCC
P	Face	0.931	0.289	0.579	-0.568	4-5	4
	Back	1.834	-1.606	-0.387	-0.786	4	4
M	Face	1.155	0.459	0.520	-0.914	4-5	4
	Back	1.948	-1.496	-0.428	-1.164	4	4
O	Face	0.708	-0.134	0.624	-0.279	4-5	4-5
	Back	1.595	-1.525	0.089	-0.358	4	4
V	Face	1.111	-0.003	1.083	-0.121	4-5	4-5
	Back	1.517	-1.423	0.334	-0.368	4	4

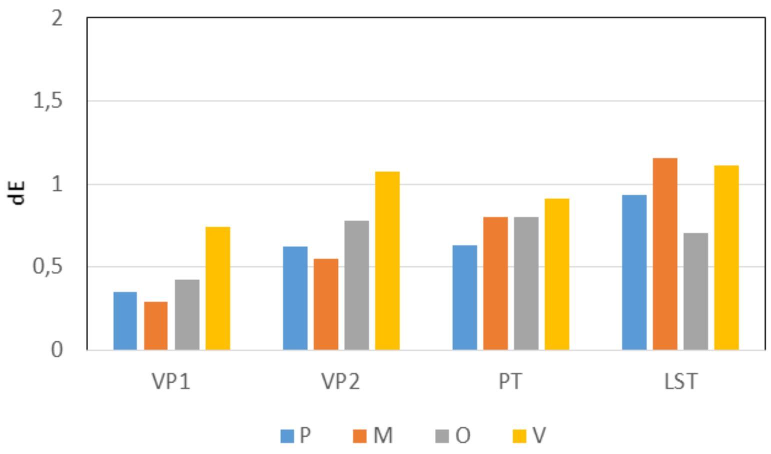


Fig.3 The total difference in color (dE) of the front of washed textiles (VP1, VP2, PT and LST) through 10 cycles compared to unwashed

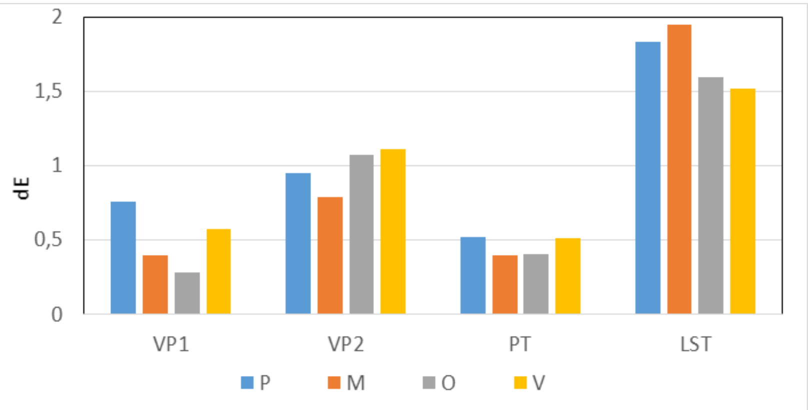


Fig.4 The total difference in color (dE) of the back side of washed textiles through 10 cycles compared to unwashed ones

the fabric was washed, ratings 4-5 (face) and 4 (back side), which confirms good resistance to the conditions of the washing process.

Fig.3 shows the total differences in the front color of washed textiles compared to unwashed ones. The total differences in color (dE) of the front of all washed textiles after 10 washing cycles compared to unwashed ones confirm the greatest influence of water on this spectral quantity.

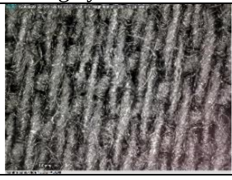
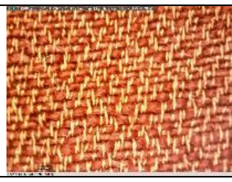
Fig.4 shows the total differences in the color of the back side of washed textiles compared to unwashed ones. The total color differences (dE) of the back side of all washed textiles after 10 washing cycles compared to unwashed ones confirm the greatest sensitivity of linen/silk fabric to orange hue in the washing process. The reason for this may be the "exotic" linen/silk mixture as well as the orange color of the LST fabric. It can be assumed that an acid dye was used for the dyeing of this mixture, which requires a neutral or slightly acidic wash bath medium. Within the series of tested detergents, detergent O has the least influence on changes in spectral characteristics, which in the applied concentration has the lowest alkalinity, pH 7.8. In addition to the lowest pH value, this detergent contains polyvinyl-pyrrolidone, PVP, a polymer – protector of color tones, as well as an increased proportion of non-ionic surfactants compared to anionic surfactants.

The determined differences in the spectral size of the total color difference (dE) of the front and back of the analyzed textiles can be attributed to the differences in the structural features of the analyzed textiles. The LST fabric is specifically designed, and has effective threads, whose thickness differences can affect the light reflection during measurement.

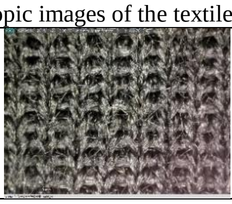
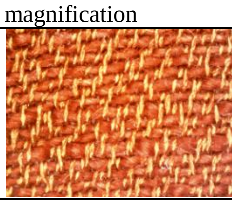
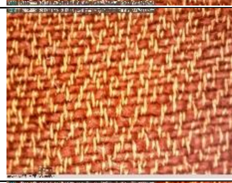
The surface of the analyzed textiles (face and back) before and after 10 washing cycles was recorded with a digital microscope, using a magnification of 50x, tabs. 10 and 11. Microscopic images of the textile surface (face side) before and after 10 washing cycles with 50x magnification in table 10 show certain changes in the textile surface washed with detergents (P, M, O) and water (V). Protruding fibers are observed after 10 cycles of washing with water. Within the examined series of textiles, the biggest difference can be seen on VP1 and PT, and the reason for this may be the compactness of these textiles.

Microscopic analyzes of the back side of the examined fabrics (VP1,

Tab.10 Microscopic images of the textile surface (face) before and after 10 washing cycles with 50x magnification

Unwashed				
Detergent	VP1	VP2	PT	LST
P				
M				
O				
V				

Tab.11 Microscopic images of the textile surface (back side) before and after 10 washing cycles with 50x magnification

Unwashed				
Detergent	VP1	VP2	PT	LST
P				
M				
O				
V				

VP2, PT and LST) in Tab.11 indicate a slightly higher degree of change, especially in VP1 and TP compared to the front of washed textiles. The smallest difference is in the surface of textiles LST (face/back) after 10 washing cycles with all means. The reason for this can be the extremely fine yarn (silk), as well as the high density, especially of the basic threads of the yarn (72 threads/cm) compared to the fabric PT, which is made of coarse yarn, and knits VP1 and VP2, which are characterized by a much lower density.

Analysis of the aqueous extract

Control of the process phases of washing and neutralization is an important criterion in the quality control of the washing process, where it is important to determine the pH value of washed textiles. If they are insufficiently washed and neutralized, irritation may occur during wearing [2, 22, 23]. The recommendation according to the RAL-GZ 992 system for the pH value of washed laundry should be between 4.5 and 8.3 [24, 25].

From the results of the pH value of liquid detergent solutions and water in Tab.12, it is confirmed that the highest pH value is the solution of detergent P. Detergent M has a lower pH value (pH 8.2) than P (pH 9), and detergent O has the lowest pH value, pH 7.8, while water has a pH value of 7.0. Table 12 shows the pH values of the aqueous extract of the tested textiles after 10 washing cycles in detergent solutions and in water.

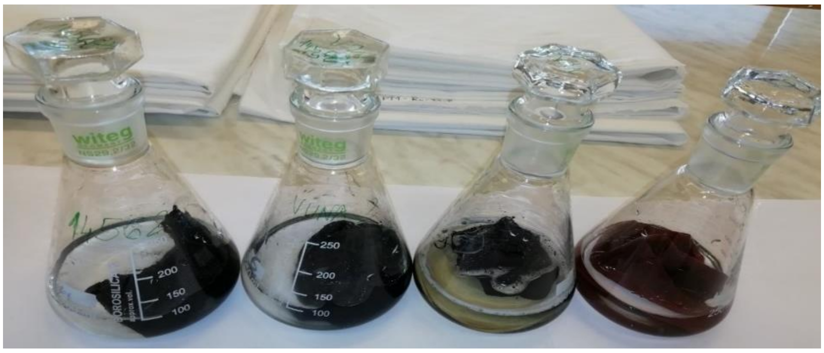
A comparison of the pH value of the aqueous extract of the VP1 fabric after 10 cycles of washing with the means in Tab.12 confirms the differences in values. VP1 washed in water has the highest pH value of 8.5. This value is high considering the fact that the material has been washed in water (pH 7.0) for 10 cycles, and still let out alkaline substances. The aqueous extract of VP1 after washing with detergents P and O has the same pH value of 7.2, which is only 0.2 pH units higher than the pH of water, confirming that the washing process is complete. The high pH of the aqueous extract of VP1 after washing with detergent M shows that 4 washing cycles are not sufficient to neutralize residual alkali on VP1.

Analysis of the aqueous extract of the VP2 mesh after 10 washing cycles with detergent P, M and O confirmed neutrality (pH 7.3 and pH 7.4), and the alkaline aqueous extract of VP2 washed in water (pH 8.6), Tab.12. The pH values of the aqueous extracts of the blue cotton fabric, PT after 10 washing cycles with all detergents in Tab.12 indicate a weak rinsing effect of residual alkalis. High pH values of the PT water extract indicate possible migration or alkaline residues of unknown origin that are present in this fabric. The surface unit area of the PT fabric is 228.8 g/m^2, which may be an additional reason for the difficulties in the washing process.

The results of the pH of the aqueous extract of fabric LST shown in Tab.12 differ from the previously described pH values of textiles VP1, VP2 and PT. The most favorable pH of the aqueous extract of LST fabric was obtained on a sample washed with detergent M (pH 7.7). Other pH values of the aqueous extract of LST washed with P (pH 8.0), O (pH 8.3) and water (8.4) confirm the alkaline extract and insufficient rinsing effect. The color of the water extract was checked, which was visually evaluated after soaking for one hour while shaking samples VP1, VP2, PT and LST, Fig.5 and Tab.13. Tab.13 shows the color (+) and coloration of the water extract of unwashed VP1, VP2, PT and LST in water after stirring for 1 hour. The results show that the aqueous extracts of PT and LST fabrics are colored, while those of VP1 and VP2 are uncolored. The color of the water extract PT is yellowish, while the color of LST is reddish, which is expected considering the orange color of these samples.

Tab.12 pH values of the aqueous extract

Detergent	pH value of the aqueous extract			
	VP1	VP2	PT	LST
P	7.2	7.3	9.3	8.0
M	8.2	7.4	8.8	7.7
O	7.2	7.4	9.4	8.3
V	8.5	8.6	9.1	8.4



VP1 VP2 PT LST

Fig.5 The color of the water extract of textiles after soaking with shaking in distilled water for 1 hour

Tab.13 The color of the aqueous extract after processing textiles of a certain mass in 100 mL of water

Material	Coloration	Color tone
VP1	-	-
VP2	-	-
PT	+	yellowish
LST	+	reddish

In accordance with the obtained results, it can be confirmed that the dyes are not completely fixed and their migration is expected, as well as the action of polymers in the composition of liquid detergents to prevent this.

The color of the bath after certain washing cycles

Visual evaluation of the coloration of the baths after individually performed washing cycles (1^{st}, 2^{nd}, 3^{rd}, 4^{th}, 5^{th}, 6^{th}, 7^{th}, 8^{th}, 9^{th} and 10^{th}) of textiles with liquid detergents and water within a series of 10 cycles is shown in Tab.14.

By viewing the results related to the evaluation of the color of the baths after individual washes, differences in the effect of the agents on individual types of textiles can be observed.

The bath after washing the VP1 and VP2 black knits with all agents from the 1st to the 10th individual cycle is not colored, which shows that there is no dye migration from the knits. The coloring is stable thanks to the quality of the technologically implemented dyeing process, in this case the yarn from which the knits were later made. Analyzing the results, it is clear that after washing the PT fabric by all agents, the baths are colored, even though there are differences within individual agents and the number of cycles. Detergents P and M affected dye migration through 4 cycles, and after the 5^{th} cycle, the wash bath with these agents was not colored. The bath from washing the PT fabric with agent O and water is colored. The bath from washing the sample with PT detergent O is brownish colored through 8 cycles, and after washing with water and after the 9^{th} cycle. Considering this condition, it can be concluded that the technological stability of the blue PT fabric is weak, i.e. that the color is not completely fixed.

The bath from washing the linen/ silk mixture (LST) in washing with all detergents was colored, whereby the color tone of the LST bath was visually assessed as reddish, with detergent P (after the 1^{st} to 8^{th} cycle), with detergent M (after the 1^{st} to 8^{th} cycle) and detergent O (after the 1^{st} to 10^{th} cycle), and the bath grade after washing with water is colorless. Despite the composition of the formulations of liquid detergents, the explanation for the coloration of the baths may be their alkalinity, which could affect the migration of dyes in the wash, while water did not affect the migration of the dyes in the wash. It is known that a lower pH is more favorable for washing silk and silk blends.

Results of determining the content of anionic and nonionic surfactants in the aqueous extract

After multiple cycles of washing and rinsing, an analysis of the residues of surface active substances on the washed textiles was carried out - which, considering the composition of the detergents, most often include anionic and non-ionic surface-active substances. Limit values of residues of surface-active substances on textiles after multiple washing and rinsing cycles are prescribed by the control system RAL-GZ 992 [25, 26], which for nonionic surface active substances is 200 μg/g, and for anionic surface active substances 400 μg/g.

Nonionic surfactant

The aqueous extract of wool knit VP1 after washing with detergent P contains 223.3 μg/g of nonionic surfactant, Tab.15, which exceeds the limit value, 200 μg/g. The aqueous extract of wool knitwear VP1 after washing with detergent M contained 111.1 μg/g of nonionic surfactant, which is almost twice less than VP1 after washing with detergent P, tab.15.

Tab.14 The color of the bath at the end of each washing cycle

Detergent	Sample	Washing cycle									
		1	2	3	4	5	6	7	8	9	10
P	VP1										
	VP2										
	PT	Brown	Brown	Brown	Grey						
	LST	Red	Red	Red	Red	Red	Red	Red	Red	Red	
M	VP1										
	VP2										
	PT	Brown	Brown	Brown	Grey						
	LST	Red	Red	Red	Red	Red	Red	Red	Red	Red	
O	VP1										
	VP2										
	PT	Brown	Brown	Brown	Brown	Brown	Brown	Brown	Brown		
	LST	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red
V	VP1										
	VP2										
	PT	Brown	Brown	Brown	Brown	Brown	Brown	Brown	Brown	Brown	
	LST										

The aqueous extract of VP2 washed with detergent M also contained a low amount of 31.8 μg/g, and the aqueous extract of washed PT and LST fabrics did not contain nonionic surfactants.
The aqueous extract of textiles VP1, VP2, PT and LST after washing with detergent O did not contain nonionic surfactants, despite the fact that detergent O contains a significantly higher proportion of nonionic surfactants compared to P and M, therefore the washing effect is excellent.

Anionic surfactant
The aqueous extract of textiles VP1, VP2, PT and LST after washing with detergent P contained anionic surfactants, Tab.16. The aqueous extract of LST washed with detergent P contains 423.5 μg/g, which is more than the limit value of 400 μg/g. Amounts of anionic surfactants below the threshold value were found in the aqueous extract of VP1, VP2 and PT, with PT having the lowest value. The aqueous extract of all textiles VP1, VP2, PT and LST after washing with detergent M contains anionic surfactants, tab.16.
Knitwear, VP1 and VP2 washed with detergent M in the aqueous extract contain high amounts of anionic surfactants, of which VP1 614.0 μg/g, and VP2 574.3 μg/g, which is more than the limit value of 400 μg/g. Detergent M has the highest content of SAS, and therefore higher values are to be expected compared to deter-gents P and O. Such an increased amount of anionic surfactant requires additional rinsing cycles.
The aqueous extract of textiles VP1, VP2, PT and LST after washing with detergent O also contained anionic surfactants, and they are below the threshold value for anionic surfactants, Tab.16. The values found in the extract of all textiles after 10 cycles of washing with detergent O are uniform.

Tab.15 Nonionic surfactant content in the water extract of 10 cycles of washed textiles

Detergent	Nonionic surfactant (μg/g)			
	VP1	VP2	PT	LST
P	223.3	-	-	-
M	111.1	31.8	-	-
O	-	-	-	-
Limit value	200.0			

Tab.16 Anionic surfactant content in the water extract of 10 cycles of washed textiles

Detergent	Anioic surfactant (μg/g)			
	VP1	VP2	PT	LST
P	385.8	336.4	102.1	423.5
M	614.0	574.3	187.8	335.9
O	148.6	152.9	66.7	180.2
Limit value	400.0			

4. Conclusions

The aim of the study was deter-mine the influence of washing agents on the properties of un-soiled textiles, two black knits (VP1 and VP2) and two fabrics, blue (PT) and orange (LST), washed through 10 cycles at 30°C. The variation was made through the choice of four agents: three liquid detergents for washing deli-cate textiles (P, M, O) in recommended concentrations, and water (V).
The analysis carried out indicated differences in the composition of liquid detergents, which were manifested in the pH values of the solutions of the agents:

P (pH 9.0) > M (pH 8.2) >
> O (pH 7.8) > V (pH 7.0)

and the share of the total surface active substances in detergents differs, whereby:

M (24.1%) > O (16.1%) >
> P (12.3%)

The total difference in color (dE) of washed textiles compared to unwashed ones is a parameter on the basis of which no significant differences in the influence of liquid detergents were determined through 10 washing cycles.
The comparison of color fastness scores also did not give significant differences within the series of tested detergents, which implies that this criterion is not completely acceptable for comparing the influence of washing agents.
The content of nonionic and anionic surfactants in the aqueous extract of textiles washed with detergents through 10 cycles is different. According to the quality system RAL-GZ 992, the content of nonionic surfactants in the water extract of woolen knit (VP1) is above the limit value, while in the extract of other textiles (VP2, PT, LST) they are below the limit value.
The content of anionic surfactants in the aqueous extract depends on the type of textile and detergent. The aqueous extract of knits VP1 and VP2 washed with detergent M and fabric LST washed with detergent P exceed the limit value of 400 μg/g. According to this criterion, the best agent for all analyzed materials is liquid deter-gent O.

In conclusion, the presented results refer exclusively to applied unstained textiles and used samples of liquid detergents and water in the specified washing conditions, and cannot be the basis for a complete evaluation and categorization of the selected detergents. The justification of the implementation of the method of analysis of the aqueous extract for the content of alkaline and surface-active substances, which can have a potentially irritating effect on the skin during wear, has been confirmed.

It is important to emphasize that anionic and nonionic surfactants as ingredients of liquid detergents in the washing process were not used to remove soiling, and their presence in the aqueous extract is partly conditioned by this fact. Despite this, the determined differences in residual surface active substances and alkaline substances in the aqueous extract confirm the differences between the analyzed detergents.

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