

REZUMAT – ABSTRACT

Calitatea spălării casnice cu ozon

În cadrul acestui studiu au fost investigate diferite proceduri de spălare casnică. După efectuarea procedurilor combinate clasice și cu ozon, au fost evaluate efectele de spălare primară și secundară, cum ar fi performanța de spălare, eficiența eliminării murdăriei, modificarea dimensională, scăderea rezistenței la rupere, reziduurile de incinerare și caracteristicile de culoare. Rezultatele finale au indicat faptul că spălarea casnică cu ozon oferă o calitate superioară a spălării în comparație cu procedura clasică și asigură reducerea consumului de apă și de energie.

Cuvinte-cheie: ozon, spălarea materialelor textile, mașină de spălat de uz casnic, generator de ozon, efecte de spălare

Quality of the household ozone laundering

Different household laundering procedures were investigated in this research. After performing classical and with ozone combined procedures, the primary and secondary laundering effects were evaluated, as washing performance, soil removal efficiency, dimensional change, decrease in breaking strength, incineration residue and colour characteristics. The end results indicate that household ozone laundering provides higher laundering quality compared to the classical procedure, and ensures reduction of water and energy consumption.

Keywords: ozone, textile laundering, household washing machine, ozone generator, laundering effects

INTRODUCTION

The main purpose for textile laundering is the removal of impurities, unpleasant odours and microorganisms, but with consideration that, at the same time, the fabric surface or structure must remain undamaged as much as possible. Household laundering is a complex process, where the synergy of physical and chemical factors in the aqueous medium influence the final results of textile cleaning. According to Sinner, the factors which determine the laundering quality are: chemical action, mechanical action, temperature and time. There is also a fifth quality parameter, water, which was added by Stamminger later, in order to expose its significance [1]. Water enables wetting with superseding air from fibres; it is a transportation system for heat and kinetic energy, a dispersing agent which, with help of detergent, absorbs inorganic and organic impurities and micro-organisms, thus preventing their re-deposition onto a textile's surface or onto parts of the washing machine [2–3].

Textile laundering is the most frequent household occupation, important to assure hygiene, reduce infection risk and, thus, protect the health and safety of household members. In the last decade, significant improvements in energy efficiency and also energy consumption have been achieved in home appliances. But, annual statistics and studies reveal a further wasteful consumption of water and energy in the EU27 household sector, where, amongst the largest energy consumers are washing machines [4–7]. Heightened environmental legislation demands producers to focus on the application and development

of new textile care technologies and processes for household laundering machines. The introduction of ozone in the industrial laundries has increased significantly in the last decades. Yet, on the other hand, the use of ozone for textile washing is still almost unknown. In the past, rare research reports have been published referring to industrial ozone laundering. Reports expose mainly the economic benefits, such as water, energy, chemicals and detergents reduction and the disinfection effects [8–11]. At the same time, in published reports, there have been no results referring to primary and secondary laundering effects and related laundering quality.

This paper evaluates the influences of classical and newly developed household ozone laundering procedures on the laundering quality using a household washing machine and ozone-generator. The first goal was to examine and evaluate the soil removal efficiency of each laundering procedure. After analysing the acquired results, there followed a selection of the most appropriate ozone procedure based on the efficiency and environmental impact factors. The next goal was to carry out and evaluate the influence of laundering repetitions on the properties of fabrics. After 25 laundering cycles (classical or with addition of ozone) of standard cotton fabrics, the secondary laundering effects were determined: Dimensional change, decrease in breaking strength, incineration residue and colour characteristics. All parameters (duration, water, electricity) were collected and analysed of each examined laundering procedure.

EXPERIMENTAL PART

The one-bath household classical and two-bath ozone laundering procedures were performed with the aim of evaluating the soil removal efficiency and the impacts on the fabric's properties. The primary and secondary effects were determined under laboratory conditions. A household washing machine, ozone-generator, ballast fabrics, stain test strips, standard fabrics and detergent were used. The laundering effects were measured and evaluated in accordance with ISO, EN, SIST or CIE requirements, specifications or guidelines. All experiments were repeated three times.

Materials

In the research of primary laundering effects, we used 4.5 kg of ballast load (consisting of cotton sheets IEC T11, pillow cases IEC T13 and towels IEC T12), and stain strips. The characteristics of the stains used for evaluation of soil removal efficiency are presented in table 1. When secondary laundering effects were determined, two pieces of standard cotton fabrics (SC) [12] (100% cotton, 295 dtex in warp and weft direction, 170 g/m², plain wave) and ballast load were laundered 25 times.

In the main-washing phases of all laundering procedures the IEC 60456 standard detergent A* was added, composed of 77% basic powder, 20% bleaching agent Sodium Perborate Tetrahydrate (SPT) and 3% bleach activator (TAED). The main ingredients of the basic powder are: Surfactants for soil removal (linear sodium alkyl benzene sulfonate, ethoxylated fatty alcohol C_{12/14} (7 EO), sodium soap), scale

inhibitors (phosphonate Dequest 2066 (diethylenetriamine penta (methylenephosphonic) acid, sodium salt, sodium chloride), sodium aluminium silicate zeolite 4A), sodium carbonate, sodium sulphate, carboxymethyl cellulose and anti-redeposition agent, coagulant sodium silicate, enzyme protease (hydrolysing insoluble protein stains into soluble peptides and amino acids, which can be removed from fabrics easily already at 20–40 °C) and stilbene type optical whitener.

All used textile materials and laundering detergents were supplied from WFK Testgewebe GmbH (D).

The characteristics of the ballast load, SC fabrics, stain strips and amounts of added laundering detergent meet the Standards [12–13].

Laundry equipment and procedures

In our research, five different laundering procedures were carried out. Their structure, regarding laundering phases' sequences, laundering temperatures, amounts of detergent and added ozone, are shown in table 2. The first procedure was a classical (CL) laundering procedure consisting of main-washing at 40 °C, two phases of rinsing with cold water, and final spinning (1200 rpm⁻¹). It followed two procedures where ozone was added to the inlet water. During the latter procedure (CO_{MR}), ozone was added in the main-washing and rinsing phases, and in the third performed laundering procedure CO_{RI} ozone was added only in two rinsing phases. The laundering temperatures (40°) and spinning conditions (1200 rpm⁻¹) were equal in both cases.

Two-bath ozone procedures were also performed in the scope of the first part of the research. They con-

Table 1

Soil type	Composition of soil [13]	Colour Characteristics CIELAB (D65/10)				
		R ₄₆₀	Y	L*	C*	h
Unsoiled	100% cotton, 200 g·m ² , desized, scoured, calandered	80.90	81.46	92.34	1.17	111.16
Sebum	Cows` and wool fat, free fatty acid, cholesterol, squalen, coconut oil, hard paraffin, carbon black, kaoline, iron oxide	47.21	49.35	75.56	2.99	97.60
Carbon	Carbon black, paraffin oil	20.81	22.01	53.98	2.53	74.47
Blood	Fresh pig's blood, stabilised with ammonium citrate	16.65	21.88	53.88	17.99	57.06
Cocoa	Unsweet. cocoa (22 % fat), sugar, full-cream cow's milk, water	22.81	33.75	64.76	21.05	58.05
Red wine	Red wine, treated with hot air	39.23	40.74	69.99	12.18	11.37

Table 2

Proc. code	Pre-washing		Main-washing			Rinsing 1		Rinsing 2	
	Oz	T	Det	Oz	T	Oz	T	Oz	T
CL	—	—	94	—	40	—	Col	—	Col
CO _{MR}	—	—	94	1	40	1	Col	1	Col
CO _{RI}	—	—	94	—	40	1	Col	1	Col
PO ₃₀	1	30	94	—	30	1	Col	—	—
PO ₄₀	1	30	94	—	40	1	Col	—	—

Note: Det – Laundering detergent IEC A (94g/cycle), Oz – Ozone (1 mg/L), T – Laundering temperature (°C), Col – Rinsing with a cold water

sisted of four phases: Pre-washing in a laundering bath heated to 30° with the addition of ozone, main-washing, cold rinsing with added ozone and final spinning (1200 rpm⁻¹). In the case of a two-bath ozone procedure, PO₃₀, the main-washing laundering bath was heated to 30°C, and, in case of the PO₄₀ procedure, it was heated to 40°C.

During the second part of the research, evaluation of secondary laundering effects was carried out only on two laundering procedures. Initially, 25 cycles of the classical procedure CL were performed, followed by 25 cycles of the two-bath ozone procedure PO₄₀. The structures and the conditions of 25 times performed washing procedures CL and PO₄₀ were identical to those in the first part of the research (table 2).

All laundering procedures were performed in a household washing machine SensoCare W8665K Gorenje d.d. (SLO), with a capacity of 9.0 kg and a drum volume of 64 L. The inlet water characteristics met the Standard [13]: conductivity < 10 µS/cm, total water hardness 2.5±0.2 mmol/L, pH = 7.3–7.7, T = 15±2°C.

Ozone was generated with a commercial ozone-generator OVK-W01 Eco Laundry (CN) at room atmosphere. In the laundering procedures, a concentration of 1.0 mg/L of ozone was used with a water flow rate of 4.5 L/min. Ozone is produced under the corona discharge principle. The surrounding air is pumped through the filter into the oxidizing module with a very strong electric field. That splits the molecules of oxygen into highly excited negatively charged oxygen atoms which react with other unstable oxygen molecules and, thus, form highly reactive and chemically unstable ozone gas [14–15]. The produced ozone is injected into water under negative pressure, which is generated in a venture injector, pulling the ozone into the inlet water stream [16].

The amounts of water, as well as their temperatures, total water hardness, conductivity and pH values, were measured using digital meters, WFH36 DVN Qvedis GmbH (D), at the inlet pipes. Power consumption was measured using an EMU Check electricity metre, EMU Elektronik AG (CH).

Determination of primary laundering effects – soil removal efficiency

Non-laundered and laundered stain strips were measured with the spectrophotometer Datacolor SF600 (CH) (d/8 measurement geometry, with measurement wavelength range from 400 nm to 700 nm and measurement area of 20 mm). Reflection measurements were calculated with the help of Datacolor Datamaster (CH) Software resulting in CIE tristimulus values XYZ, L*a*b* CIELAB 1976 and colour differences dE* according to [17].

The washing performance *q* was calculated in accordance with [13]. The reference laundering procedure was performed in a Wascator FOM 71CLS Electrolux (S) under the following conditions: 5 kg cotton ballast load, stain strips, “Cotton Normal” washing programme

(main washing, four rinsing phases), laundering temperature 40°C, bath ratio 1:5.

The Cleaning performance index CPI_{dE}^* was calculated based on [18].

Determination of secondary laundering effects

The ballast load and SC fabric were laundered 25 times in a household washing machine according to the selected laundering procedure. Dimensional change, stiffness, decrease in breaking strength, incineration residue and colour characteristics were determined later.

The conditioned unwashed and 25 times washed standard fabrics were subjected to dimensional change and stiffness measurements, which were evaluated according to [19–20] methods. The breaking strength and incineration residue of unwashed and washed samples of standard fabric were determined by the [21–22] methods, respectively. The colour characteristics were determined by measuring reflection values and calculations of CIELAB values and CIE whiteness indexes WI_{CIE} .

The methodology for determining the secondary laundering effects has been described briefly in earlier studies [23–24].

RESULTS AND DISCUSSION

Five different household laundering procedures, the classical and with ozone combined procedure, were carried out regarding primary and secondary laundering effects. The characteristics of the used stain test strips and the structure of tested procedures are shown in tables 1 and 2. The measured parameters of the performed one- and two-bath laundering procedures are presented in table 3, whilst the results of the primary and secondary laundering effects are shown in figures 1 and 2.

It is evident from table 3 that the washing performance indices are equal for procedures CO_{RI} and CL ($q = 1.097$), while somewhat higher washing performance differences occur for the procedure CO_{MR} (diff. 0.0042 units) compared to the classical laundering procedure CL. The lower washing performance index of procedure CO_{MR} can be explained by the reaction between the ozone in the inlet water and detergent ingredients starting in the dosing vessel of the household laundering machine. It is known that ozone is an unstable molecule that decomposes spontaneously by a complex mechanism, thus generating hydroxyl free radicals which react with organic and inorganic compounds [16]. Dissolution of detergent in water raises the pH of the laundering bath, and, consequently, accelerates the generation of free radicals and, thus, decomposition and lower ozone concentration in the water. [25] found that the simultaneous use of ozone and some surfactants can even cause a decrease in detergency compared to the one achieved with the surfactant alone. This observation was attributed to the degradation of this surfactant in the presence of ozone.

Parameter	Unit	Laundering procedure					
		CL	CO _{MR}	CO _{RI}	PO ₃₀	PO ₄₀	
WPI <i>q</i>	—	1.097	1.093	1.097	1.022	1.100	
Cycle duration	min	111	117	119	105	119	
Water	PW	L	—	—	—	13.69	13.74
	MW	L	22.18	21.73	22.06	7.32	7.26
	RI1	L	19.97	20.14	20.54	16.17	15.39
	RI2	L	20.32	21.30	20.90	—	—
	SUM	L	62.47	63.17	63.50	37.18	36.40
BR	PW	—	—	—	1:3	1:3	
	MW	1:5	1:5	1:5	1:5	1:5	
RWC	%	63.66	64.40	66.33	63.25	66.59	
Energy	kWh/kg	1.054	1.050	1.026	0.406	0.867	

Note: WPI – Washing Performance Index, PW – Pre-Washing, MW – Main-Washing, RI1, RI2 – Rinsing, BR – Bath Ratio, RWC – Remaining Water Content

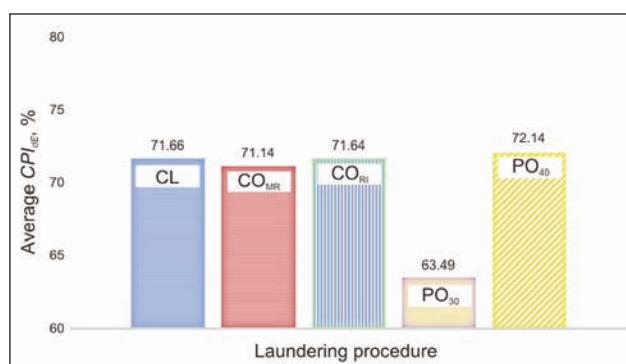


Fig. 1. Average Cleaning Performance Indices CPI_{dE^*} of laundering procedures

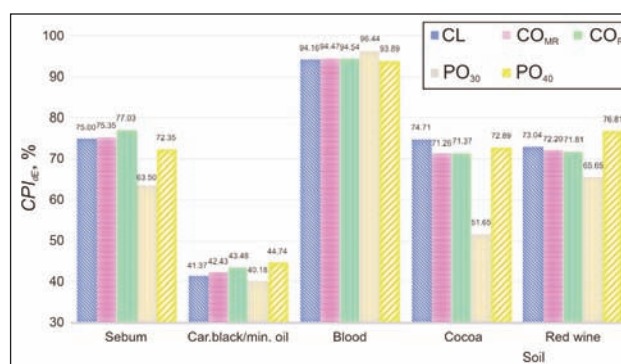


Fig. 2. Soil removal efficiency as CPI_{dE^*} of laundering treatments

From the results shown in table 3, it can be noticed that the CO_{MR} and CO_{RI} laundering cycles last longer (6 and 8 min); concurrently the increased water consumption, whereas the electricity consumption declined compared to the classical procedure CL. Increased total water consumption in ozone laundering procedures is accordant with [26]. It has been reported that the increase in water absorbency of the ozonised samples is assumed to occur as a result of the oxidation of the hydrophobic impurities by ozonation [27]. Another hypothesis is that this phenomenon happens due to oxidation, which weakens the amorphous regions of the fibres, hence the liquid can find its way to be easily transported through [15].

In terms of efficiency as well as environmental impact, the two-bath ozone laundering PO₃₀ and PO₄₀ procedures (table 3) are in the foreground. With regard to the CL process, the washing performance of the low temperature procedure PO₃₀ is noticeably lower (6.83%), while for procedure P₄₀ it is surprisingly even higher in absolute values. Realization of the PO₃₀ procedure demands 40.49% less water and 61.50 less energy compared to the classical laundering procedure, whilst the one of procedure PO₄₀ demands 41.74% less water and 17.75% less electric energy. The cause for the lower energy efficiency

of procedure PO₄₀ is the laundering bath heating in the main-washing phase, which influences lower electricity saving and longer duration (119 min) of the procedure PO₄₀.

From the results of soil removal efficiency shown in figure 1, one can summarise that the two-bath ozone laundering procedure PO₄₀ removes, on average, the highest amount of stains (72.14%), followed by procedures CL (71.66%), CO_{RI} (71.64%), CO_{MR} (71.14%), and, at the end, the procedure PO₃₀ with the lowest average CPI_{dE^*} (63.49%). It was found that the most efficient removal (figure 2) for all ozone procedures, on average, was noted for pig's blood (94.83%), followed by moderate soil removal of synthetic sebum (72.06%), red wine (71.62%) and cocoa (66.79%), while for carbon black and paraffin oil soil the removal efficiency was noticeably lower (42.71%). The low soil removal efficiency of the mentioned procedure could be attributed to the low temperature during the main-washing phase (30 °C) and the after-effect of inactivation of the system of bleaching agent SPB and bleach activator TAED [28].

Analyses of the primary laundering show that the household ozone laundering procedure PO₄₀ provides the best results: highest washing performance and, at the same time, the lowest water and energy

Parameter		Unwashed standard fabric	Laundering procedure	
			Classical (CL)	Ozone (PO ₄₀)
Dimensional change (%)		—	-13.35	-10.25
Stiffness (cN·cm ²)		6.14	4.86	5.08
Breaking strength	F_{25} (N)	999.41	909.57	932.91
	Z_{25} (%)	—	8.99	6.65
Incineration residue (%)		0.0219	0.1158	0.1044
Colour characteristics (D65/10)	R_{460}	76.57	88.22	90.57
	Y	78.74	82.95	83.57
	L^*	91.11	92.99	93.26
	C^*	2.90	2.37	3.05
	h	104.66	278.55	266.64
WI_{CIE}		65.51	93.55	97.55

consumption. These were the deciding factors in the ozone PO₄₀ procedure being selected and carried out in investigation of secondary laundering effects. Table 4 shows the characteristics of standard cotton fabric washed 25 times in the classical or ozone procedures.

The results show that the dimensional change of fabric laundered in the classical procedure was noticeably higher (13.35% shrinking) compared to ozone laundering PO₄₀ (10.25% shrinking). Classical laundering caused a higher change in fabric stiffness values (by 20.84%) than laundering with ozone (by 17.28%), compared to the un-washed fabric. Moreover, the breaking strength F_{25} of a fabric laundered classically 25-times was lower (diff. 89.84 N) than ozone laundering (diff. 66.5 N) compared to the breaking strength of the un-washed fabric. This also reflected in a decrease in breaking strength Z_{25} and, thus, mechanical damage. In the case of ozone treatment, the value Z_{25} was considerably lower (6.65%) than in the classical procedure (8.99%). These results can be explained by the fact that, after a certain amount of time, the ozone treatment deteriorates yarn tensile properties drastically, while the wickability increases simultaneously. The phenomena could be attributed to the weak links introduced in the fibre's amorphous region and their damage [15].

The results indicate a small difference in incineration residue between classically and ozone treated standard cotton fabric. However, the ash content of classical laundering was 5.2 times higher, and of ozone laundering 4.7 times higher, compared to the ash content of un-washed fabric. It is known that incrustation is caused by precipitation of calcium salts from hard water, together with the detergent ingredients, textile structure, washing and rinsing conditions (temperature, duration, bath ratio). During the laundering process accumulated incrustations in the textiles lead to soil retention, greying, fabric handle (higher stiffness values), mechanical damages, reduced absorbency, etc. [23, 29]. From the results of incineration residue we can conclude that repetition of

ozone treatments obstructs the mineralization process of textiles during the laundering process.

Ozone oxidation potential and reduction of accumulated incrustations probably contribute to the colour characteristics and higher whiteness WI_{CIE} of the PO₄₀ process compared to the classical treatment CL.

CONCLUSIONS

Evaluation of the primary and secondary effects of classical and different household ozone laundering procedures was the main subject of the presented research. Procedures were performed with the help of a household laundering machine and commercial ozone-generator, while the laundering effect was evaluated with measuring equipment and methods which meet suitable Standards.

Results show that household ozone laundering provides higher soil removal efficiency and appreciable consumption of water and electricity, compared to the classical washing process.

The common characteristics of 25 time laundered standard cotton fabrics with ozone proved to be surprisingly good. We can conclude that laundering with ozone in a household drum washing machine causes lower damages to cotton fabric than the classical procedure.

However, the scope of further investigations will be the development of new ozone laundering processes, introduction of powerful ozone-generator and disinfection efficiency, but the first and foremost priority will be the improvement of additional security systems to prevent ozone escaping from the household machine into the surroundings.

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