

University of Ljubljana,
Faculty of Natural Sciences and Engineering,
Department of Textiles,
Graphic Arts and Design,
Snežniška 5, 1000 Ljubljana, Slovenia,
e-mail: petra.forte@ntf.uni-lj.si

Abstract

The influence of adding Sodium Perborate Tetrahydrate (NaPB) and tetraacetylenediamine (TAED) on the efficiency of removing soils from cotton fabric was evaluated in the study. NaPB as inorganic peroxide and TAED as a bleach activator were added to a commercial washing powder agent. Four standard soils applied on cotton fabric (EMPA standard soiled fabrics) were used in the study, i.e. 101 – carbon black/olive oil, 114 – red wine, 116 – blood/milk/ink and 160 – chocolate. The washing of fabrics was conducted in accordance with the SIST EN ISO 105-C06 standard at 40, 60 and 90 °C in Launder-Ometer apparatus. The washing efficiency was evaluated by determining the CIE L* colour coordinates of the unwashed and washed fabric samples, and the difference in ΔL^* colour coordinates among them. The results showed that NaPB and TAED improve the efficiency of washing for two standard soils, have no effect on one, and deteriorate the washing results of one standard soil.

Key words: sodium perborate, soil removal, cotton, oxidation.

Introduction

Sodium perborate tetrahydrate (NaPB), with the chemical formula $\text{Na}_2\text{B}_2\text{O}_4(\text{OH})_4$, is a white, odourless, water-soluble chemical compound in the form of crystalline powder. NaPB hydrolyses in water into hydrogen peroxide, tetrahydroxoborate anions and different peroxoborate components. NaPB is an important ingredient of washing powder agents, laundry additives and dishwasher powders [1, 2, 3]. It has the ability to decolourise unsaturated compounds. Conjugated double bonds, which give colour to such compounds, epoxide and consequently decolourise. The chemical bonds between the fabric and soil can also be destroyed during bleaching.

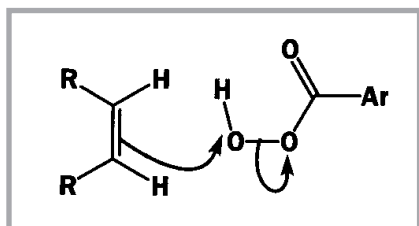


Figure 1. Oxidation of double bond with peroxyacid.

It can be used in the textile industry to bleach textile fibres, especially raw natural cellulosic fibres [4]. Reports on using NaPB to decolourise teeth have been published as well [5].

The addition of NaPB to washing agents should therefore improve the effects of washing. In previous research, it was established that the peroxide released improves the washing effect to a certain extent, but it cannot reveal its full power as its highest activity is at 100 °C and pH 12 [6]. In domestic laundry washing, the conditions are far below these. The washing temperatures preferred in the last 20 years have been from 30 to 60 °C [7-10]. Sustainability of laundering, antimicrobial efficacy and higher hygiene could be achieved by using bleach activators [11, 12].

Peracids are more active oxidants than peroxides and have been confirmed to bleach cellulosic fibres effectively at low temperatures and in mild media. Peracetic acid (PAA) is a powerful oxidant with excellent bactericidal, anti-microbial, fungicidal, and anti-viral properties, even at low concentrations [13, 14].

PAA and other peracids are efficient oxidising agents and are relatively environmentally benign. Typically, peracids are more reactive bleaches than hydrogen peroxide itself due to their stronger oxidising potential and are, therefore, effective at lower temperatures [6]. The main advantage of using PAA is that a satisfactory degree of whiteness is obtained at 50-70 °C and a pH value of around 7 with no addition of auxiliary agents. It has been proved that considerably less damage is caused to cotton, regenerated cellulose fibres, e.g. bamboo fibres, and also to polylactic acid and soy protein fibres when using PAA instead of HP for bleaching [15].

PAA functions as an oxidiser to destroy the colouring substances at low temperature (about 60 °C). The oxidation mechanism is shown in Figure 1 [16].

Bleach activators are peracid precursors which generate peracids *in situ* in an aqueous hydrogen peroxide solution [17-19]. Bleach activators were originally developed for industrial and home laundry use. The most common peracid bleach activator currently used is tetraacetylenediamine (TAED),

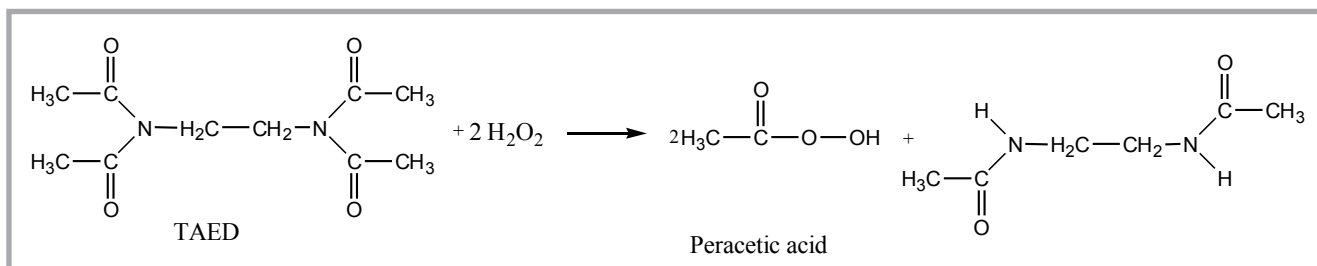


Figure 2. Formation of PAA in the reaction of TAED with hydrogen peroxide.

which is cost-effective and relatively environmentally benign, and it provides effective bleaching at temperatures as low as 40 °C [13]. The second most commonly used bleach activator is nonanoxylbenzene sulphonate (NOBS), while several other bleach activators are being studied for the bleaching of fibres in the textile industry and in laundry washing: N-[4-(triethylammoniomethyl) benzoyl] caprolactam chloride (TBCC) and N-[4-(triethylammoniomethyl) benzoyl] butyrolactam chloride (TBBC) [18, 20, 21], pentaacetyl glucose (PAG) [25], and others [3].

The activation of TAED is revealed in **Figure 2**. One molecule of TAED reacts with two molecules of HO₂⁻ in a nucleophilic manner to generate one molecule of diacetylenethylenediamine (DAED) with the release of two molecules of PAA. Peracid formation depends on pH, temperature and concentrations of peroxide and the activator in the bleaching bath [23].

The goal of our study was to check if the addition of Sodium Perborate (NaPB) and TAED to a washing powder agent can improve washing effects in domestic laundry washing for different soils and temperatures. Four different standard soils applied on cotton fabric were used in the study. They were washed by standardised procedures at 40, 60 and 90 °C. The washing efficiency was evaluated by determining the lightness, L*, of unwashed and washed fabric samples.

Experimental

Materials

Four standard soils applied on cotton fabric were used in the study. Standard stained samples and their initial CIE lightness (CIE L*) are listed in **Table 1**. All fabrics studied were EMPA standard soiled fabrics from Switzerland. Sodium Perborate Tetrahydrate was kindly supplied by Belinka Perkemija, Slovenia, and tetraacetylenethylenediamine (TAED) was purchased from Sigma Aldrich.

Treatment process

The washing of fabrics was conducted in accordance with the SISTENISO 105-C06 standard at 40 °C, 60 °C and 90 °C for 30 min in one washing cycle. Launder-Ometer apparatus was used for washing. The dimensions of the test specimen were 100 mm x 40 mm. No adjacent fab-

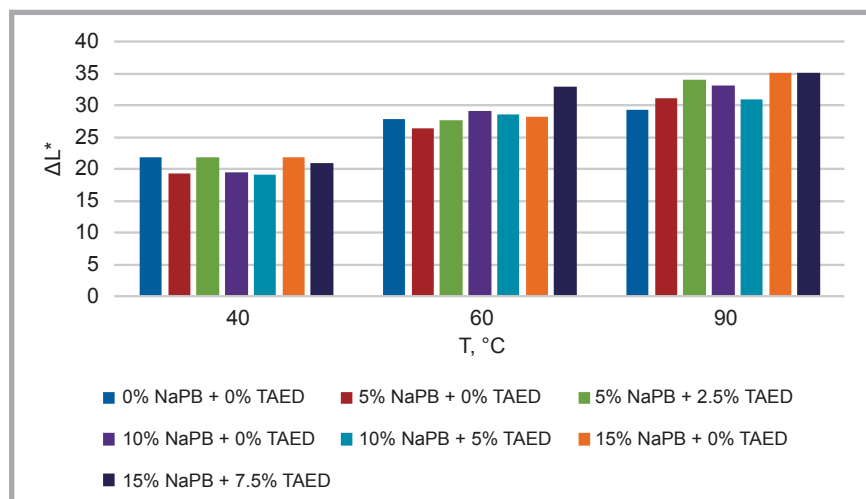


Figure 3. Lightness difference, ΔL^* , between unwashed 101 EMPA standard fabric soiled by carbon black/olive oil and samples washed in the presence of different NaPB and TAED concentrations and at different temperatures.

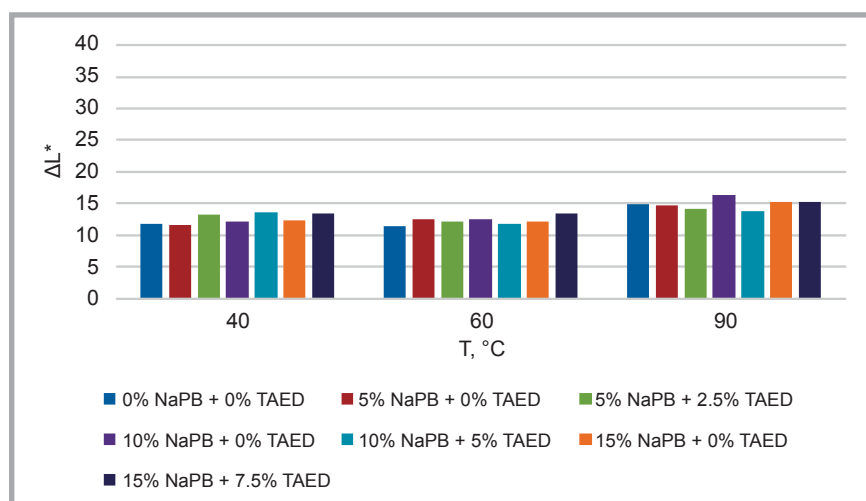


Figure 4. Lightness difference, ΔL^* , between unwashed 114 EMPA standard fabric soiled by red wine and samples washed in the presence of different NaPB and TAED concentrations and at different temperatures.

rics were used. 10 steel balls were added into each washing container.

The wash liquor contained 4 g of washing powder agent per litre of water. The washing agent was composed of borax – 50%, sodium stearate – 20%, sodium carbonate – 4%, carboxymethylcellulose – 1%, anionic surfactants – 1%, and a non-ionic active substance+moister – up to 100%.

0, 5, 10 or 15% NaPB was added to the washing powder agent according to the weight of the washing powder agent. Additionally, 0, 2.5, 5 and 7.5% TAED was added to the washing powder agent and NaPB mixture. The names of the experiments and compositions of the washing mixture are presented in **Table 2**.

Table 1. Standard soils and initial lightness values, L_s^* of unwashed EMPA standard soiled fabrics.

Soil No.	Soil	L_s^*
101	carbon black/olive oil	45.41
114	red wine	75.53
116	blood/milk/ink	43.25
160	chocolate	76.21

Table 2. Amount of NaPB and TAED added to washing powder agent.

Experiment No.	NaPB, %	TAED, %
1	5	0
2	5	2.5
3	10	0
4	10	5
5	15	0
6	15	7.5
7	0	0

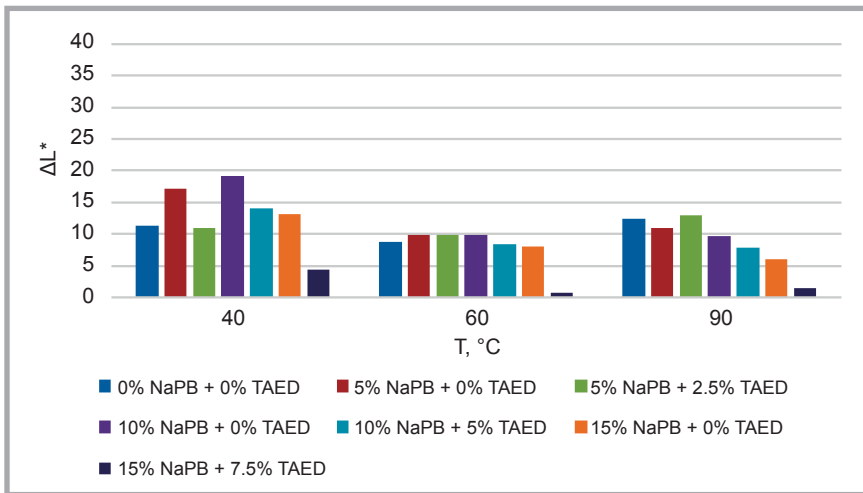


Figure 5. Lightness difference, ΔL^* , between unwashed 116 EMPA standard fabric soiled by blood/milk/ink and samples washed in the presence of different NaPB and TAED concentrations and at different temperatures.

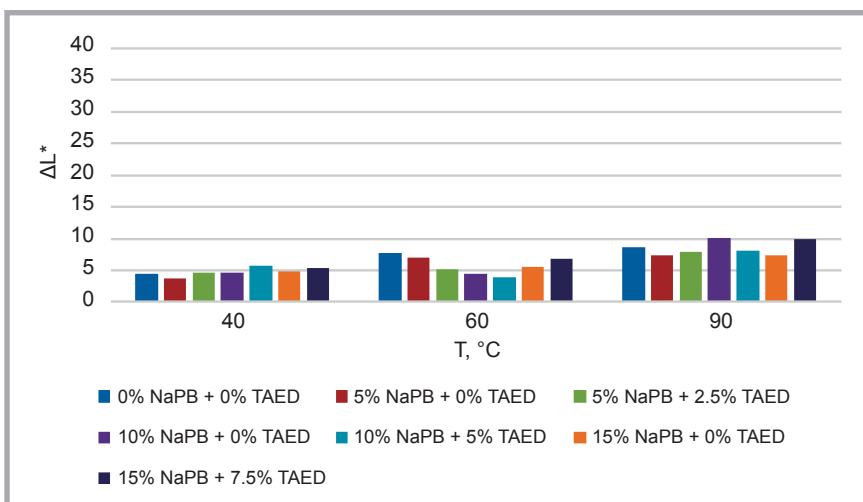


Figure 6. Lightness difference, ΔL^* , between unwashed 160 EMPA standard fabric soiled by chocolate and samples washed in the presence of different NaPB and TAED concentrations and at different temperatures.

Measurements

CIE L^* colour coordinate

The washing efficiency was evaluated by determining the CIE L^* color coordinate (lightness) of the unwashed and washed fabric samples on a spectrophotometer – Datacolor Spectraflash 600 Plus-CT (Datacolor International) with the following settings: illuminant D65, large area view, specular excluded, UV included and 10 degree standard observer. 10 measurements per sample were made on the spectrophotometer.

Before the measurements, the samples were conditioned for 24 h at 20 °C and 65% relative humidity.

The difference in lightness between the unwashed and washed samples, ΔL^* ,

was calculated with *Equation (1)*, where L_w^* means the lightness value of washed EMPA standard soiled fabrics and L_s^* that of an unwashed EMPA standard soiled sample.

$$\Delta L^* = L_w^* - L_s^* \quad (1)$$

Results and discussion

Figures 3-6 represent the lightness differences, ΔL^* , between the washed and unwashed EMPA standard soiled fabrics with the addition of different concentrations of NaPB and TAED to the washing powder agent at different temperatures. The lightness difference between the unwashed and washed sample, ΔL^* , is a measure of washing efficiency.

The higher the difference, the more soil was removed from the fabric. Photos of all unwashed and washed samples are shown in *Figure 6*.

Figure 3 represents the lightness differences, ΔL^* , between the washed and unwashed EMPA standard soiled fabrics 101 with 0, 5 & 10 in 15% of NaPB and 0, 2.5 and 5% of TAED added to the washing powder agent at 40 °C, 60 °C & 90 °C.

The best washing results among all soils were obtained for soil 101 (carbon black/olive oil). Even at 40 °C ΔL^* is around 20, whereas higher temperatures markedly improve the washing results, i.e. by about 5 units of ΔL^* at 60 and 90 °C, respectively. At 40 °C there is no improvement of the washing effect by the addition of bleach activators, while at 90 and 60 °C the addition of NaPB improves the lightness. The addition of TAED does not further improve the lightness.

Figure 4 represents the lightness differences, ΔL^* , between the washed and unwashed EMPA standard soiled fabrics 114 with 0, 5, 10 & 15% of NaPB and 0, 2.5 and 5% of TAED added to the washing powder agent at 40 °C, 60 °C & 90 °C.

The addition of bleach activators should be most expressed for soil 114 (red wine), as the oxidants primarily degrade colour (*Figure 4*).

At 40 °C the addition of NaPB slightly increases ΔL^* , which is additionally increased when TAED is added to the solution. During the washing, NaPB releases hydrogen peroxide, which improves the lightness to a small degree, since it has very low activity at low temperatures. When TAED is added, the hydrogen peroxide transforms into peracetic acid, which is also active at low temperatures, and the washing effects are improved.

A similar picture can be seen at 60 °C (highest lightness is at 15% NaPB + 7.5% TAED). The improvement in lightness caused by TAED is lower, as hydrogen peroxide is more active at 60 °C than at 40 °C.

At 90 °C we can see no improvement with the addition of TAED, since hydrogen peroxide is active at 90 °C and oxidises the coloured compounds, while the peracetic acid decomposes very fast

and cannot act successfully. In all cases, lightness is higher at 90 °C than at 40 and 60 °C.

Figure 5 represents the lightness differences, ΔL^* , between the washed and unwashed EMPA standard soiled fabrics 116 with 0, 5, 10 & 15% of NaPB and 0, 2.5 and 5% of TAED added to the washing powder agent at 40 °C, 60 °C & 90 °C.

For soil 116 (blood/milk/ink), the washing results are better at lower temperatures and without TAED. The addition of NaPB improves the lightness markedly at 40 °C and to some extent at 60 °C, while the addition of TAED decreases it. At 90 °C the addition of bleaching agents deteriorates the results of washing. This can be explained by the fact that blood cells incorporate iron, which catalyses the rapid decomposition of hydrogen peroxide, causes the formation of radicals and starts several uncontrolled reactions between the compounds in the washing bath and fibres. Another research confirmed this result, namely that the deterioration of washing occurs for soil 116 when oxidants are added, although the authors ascribed the bad effect to the coagulation of blood at high temperatures [23].

Figure 6 represents the lightness differences, ΔL^* , between the washed and unwashed EMPA standard soiled fabrics 160 with 0, 5, 10 & 15% of NaPB and 0, 2.5 and 5% of TAED added to the washing powder agent at 40 °C, 60 °C & 90 °C.

For soil 160 (chocolate), the washing results are generally bad. Very low improvement in lightness is achieved at all conditions, less than 10 units of ΔL^* . Some improvement is achieved when raising the temperature, but not with the addition of oxidants. This can be explained by the fact that chocolate consists of fats and is therefore too hydrophobic for the oxidants to attack it.

Figure 7 shows photographs of the unwashed EMPA standard soiled fabrics and samples washed with a washing powder agent and different concentrations of bleach activators at 40 °C, 60 °C & 90 °C.

Conclusions

The influence of two bleach activators: Sodium Perborate Tetrahydrate and

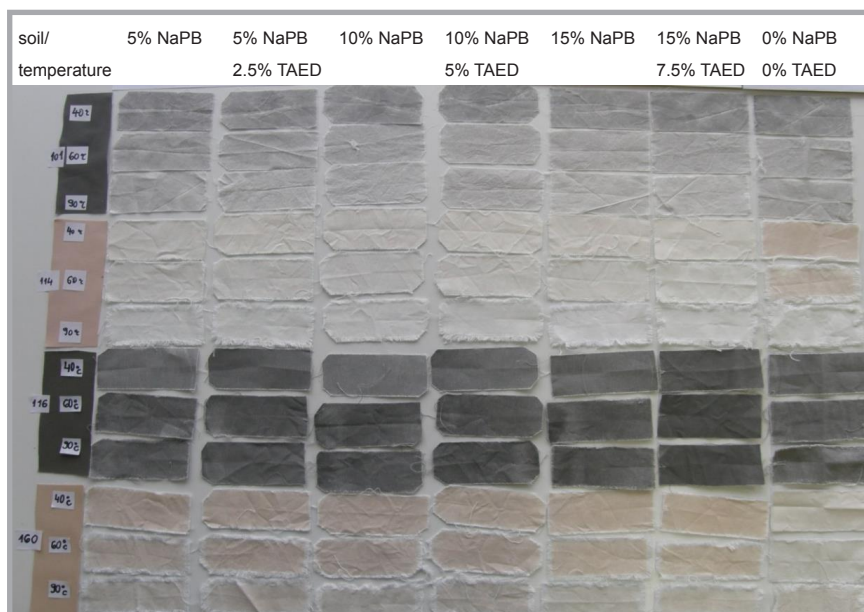


Figure 7. Unwashed standard soiled samples (first column) and samples washed with a washing powder agent and 5, 10 or 15 % of NaPB and 0, 2.5 and 5% of TAED at 40, 60 and 90 °C. (The samples washed without bleaching agents are in the last column).

tetraacetylenediamine, on the efficiency of removing soils from cotton fabric during washing was evaluated in the study. The improvement of the washing effect was evaluated by determining the lightness difference, ΔL^* , between the unwashed and washed fabric samples. The results obtained were ambiguous and different for every soil used in the study.

In general, better washing results were obtained at higher temperatures, irrespective of the addition of bleach activators, except for soil 116, with blood/milk/ink on the fabric.

The addition of NaPB generally improves the washing effects at higher temperatures, because it releases hydrogen peroxide, which is active at temperatures above 60 °C. The addition of TAED generally improves the washing effects at low temperatures, because it generates peracetic acid, which is active at 40 and 60 °C. This was confirmed for two soils: soil 101 (carbon black/olive oil) and soil 114 (red wine), but not for soil 116 (blood/milk/ink) and soil 160 (chocolate). For soil 116 (blood/milk/ink) the addition of NaPB improves the lightness only at 40 °C. At 60 °C the addition of NaPB has no effect, while at 90 °C its addition deteriorates the results of washing. TAED deteriorates the washing results at all conditions for this soil. This is most likely the result of the catalytic decomposition of hydrogen peroxide caused by iron in blood. For soil 160 (chocolate) the

addition of bleaching agents almost has no effects on washing results because of the hydrophobic nature of the soil.

We can conclude that the addition of Sodium Perborate Tetrahydrate and Tetraacetylenediamine bleach activators to the washing agents generally improves the results of washing, but not for all soils and at all conditions. More experiments are needed before we can confirm their benefits as additives in washing powder agents.

References

1. Technical Documentation of Belinka Perkemija, Ljubljana, Slovenia.
2. Hofmann J, Just G, Pritzkow W, Schmidt H. Bleaching Activators and the Mechanism of Bleaching Activation. *J. prakt. Chem.* 1992; 334: 293-297.
3. Carson PA, Fairclough CS, Mauduit C, Colsell M. Peroxy bleaches Part 1. Background and Techniques for Hazard Evaluation. *Journal of Hazardous Materials* 2006, A136: 438-445.
4. Zahran MK, Ahmed HB. A Greener Approach for Full Flax Bleaching. *The Journal of The Textile Institute* 2010; 101(7): 674-678.
5. Tran L et al. Depletion Rate of Hydrogen Peroxide from Sodium Perborate Bleaching Agent. *JOE* 2017; 43 (3): 472-476.
6. Hickman WS. Peracetic Acid and Its Use in Fibre Bleaching. *Review of Progress in Coloration and Related Topics* 2002; 32: 13-27.

7. Laitala K, Mallan Jensen H. Cleaning Effect of Household Laundry Detergents at Low Temperatures, *Tenside Surfactants Detergents*. 2010; 47(6): 413-420.
8. Honisch M, Brands B, Weide M et al. Antimicrobial Efficacy of Laundry Detergents with Regard to Time and Temperature in Domestic Washing Machines. *Tenside, Surfactants, Detergents* 2016; 53(6): 547-552.
9. Lambert E, Bichler S, Stamminger R. Hygiene in Domestic Laundering - Consumer Behavior in Germany. *Tenside, Surfactants, Detergents* 2015; 52(6): 441-446.
10. Ferri A, Osset M, Abeliotis K, et al. Laundry Performance: Effect of Detergent and Additives on Consumer Satisfaction. *Tenside, Surfactants, Detergents* 2016; 53(4): 375-386.
11. Yun C, Patwary S, LeHew M. et al. Sustainable Care of Textile Products and Its Environmental Impact: Tumble-drying and Ironing Processes. *Fibers and Polymers* 2017; 18(3): 590-596.
12. Brands B, Brinkmann A, Bloomfield S et al. Microbicidal Action of Heat, Detergents and Active Oxygen Bleach as Components of Laundry Hygiene, *Tenside, Surfactants, Detergents* 2016; 53(5): 495-501.
13. Špička N, Forte Tavčer P, Low-Temperature Bleaching of Knit Fabric from Regenerated Bamboo Fibers with Different Peracetic Acid Bleaching Processes. *TRJ* 2015; 85: 1497-1505.
14. Fijan S, Šostar-Turk S. Antimicrobial Activity of Selected Disinfectants Used in a Low Temperature Laundering Procedure for Textiles. *FIBRES & TEXTILES in Eastern Europe* 2010; 18, 1(78): 89-92.
15. Špička N, Zupin Ž, Kovač J, Forte Tavčer P. Enzymatic Scouring and Low-temperature Bleaching of Fabrics Constructed from Cotton, Regenerated Bamboo, Poly(lactic acid), and Soy Protein Fibers. *Fibers and Polymers* 2015; 16 8: 1723-1733.
16. Forte Tavčer P. Peracetic Acid Bleaching in Textile Processing. *Tekstilec* 2003; 46(1/2): 19-24.
17. Forte Tavčer P. Low-Temperature Bleaching of Cotton Induced by Glucose-Oxidase Enzymes and Hydrogen Peroxide Activators. *Biocatalysis and Biotransformation* 2012; 30(1): 20-26.
18. Lim SH, Gürsoy NC, Hauser P, Hinks D. Performance of a New Cationic Bleach Activator on a Hydrogen Peroxide Bleaching System. *Coloration Technology* 2004; 120: 114-118.
19. Shao JZ, Huang Y, Wang ZH, Liu JQ. Cold Pad-Batch Bleaching of Cotton Fabrics with a TAED/H₂O₂ Activating System. *Coloration Technology* 2010; 126: 103-108.
20. Lim SH, Lee JJ, Hinks D, Hauser P. Bleaching of Cotton with Activated Peroxide Systems. *Coloration Technology* 2005; 121: 89-95.
21. Xu C, Hinks D, Shamey R. Bleaching Cellulosic Fibers via Pre-Sorption of N-[4-(Triethylammoniummethyl)-Benzoyl]-Butyrolactam Chloride. *Cellulose* 2010; 17: 849-857.
22. Liu K, Zhang X, Yan KL. Low-Temperature Bleaching of Cotton Knitting Fabric With H₂O₂/PAG System. *Cellulose* 2017; 24 (3): 1555-1561.
23. Drol P, Kert M, Simončič B, Hladnik A. Evaluation of the Influence of Different Parameters in Removing Standard Soil from Cotton Fabric Using Multi-Functional Analysis of Variance. *Tekstilec* 2012; 55(3): 194-205.

□ Received 27.03.2018 Received 14.01.2020

ŁUKASIEWICZ RESEARCH NETWORK – INSTITUTE OF BIOPOLYMERS AND CHEMICAL FIBRES

RESEARCH NETWORK
ŁUKASIEWICZ



IBWCh

LABORATORY OF PAPER QUALITY



Since 02.07.1996 the **Laboratory has had the accreditation certificate of the Polish Centre for Accreditation No AB 065.**

The accreditation includes tests of more than 70 properties and factors carried out for:

- pulps, ■ tissue, paper & board, ■ cores, ■ transport packaging, ■ auxiliary agents, waste, wastewater and process water in the pulp and paper industry.

The Laboratory offers services within the scope of testing the following: raw -materials, intermediate and final paper products, as well as training activities.

Properties tested:

- general (dimensions, squareness, grammage, thickness, fibre furnish analysis, etc.),
- chemical (pH, ash content, formaldehyde, metals, kappa number, etc.),
- surface (smoothness, roughness, degree of dusting, sizing and picking of a surface),
- absorption, permeability (air permeability, grease permeability, water absorption, oil absorption) and deformation,
- optical (brightness ISO, whiteness CIE, opacity, colour),
- tensile, bursting, tearing, and bending strength, etc.,
- compression strength of corrugated containers, vertical impact testing by dropping, horizontal impact testing, vibration testing, testing corrugated containers for signs „B” and „UN”.

The equipment consists:

- micrometers (thickness), tensile testing machines (Alwetron), Mullens (bursting strength), Elmendorf (tearing resistance), Bekk, Bendtsen, PPS (smoothness/roughness), Gurley, Bendtsen, Schopper (air permeance), Cobb (water absorptiveness), etc.,
- crush tester (RCT, CMT, CCT, ECT, FCT), SCT, Taber and Lorentzen&Wettre (bending 2-point method) Lorentzen&Wettre (bending 4-point method and stiffness resonance method), Scott-Bond (internal bond strength), etc.,
- IGT (printing properties) and L&W Elrepho (optical properties), etc.,
- power-driven press, fall apparatus, incline plane tester, vibration table (specialized equipment for testing strength transport packages),
- atomic absorption spectrometer for the determination of trace element content, pH-meter, spectrophotometer UV-Vis.

Contact:

INSTITUTE OF BIOPOLYMERS AND CHEMICAL FIBRES
ul. M. Skłodowskiej-Curie 19/27, 90-570 Łódź, Poland
Anita Świętonowska, M. Sc., tel. (+48 42) 638 03 31, e-mail: a.swietonowska@ibwch.lodz.pl