Introduction

Sodium perborate tetrahydrate (NaPB), with the chemical formula Na\textsubscript{2}B\textsubscript{4}O\textsubscript{7} \cdot 4H\textsubscript{2}O, 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 peroxyborate 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.

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 cellulose 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 tetraacetyl ethylenediamine (TAED),
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 nonanoyloxybenzene 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 HO$_2$– in a nucleophilic manner to generate one molecule of diacetylenthylenediamine (DAED) with the release of two molecules of PAA. Peracid formation depends on pH, temperature and concentrations of peroxide 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 tetraacetylthielenediamine (TAED) was purchased from Sigma Aldrich.

#### Treatment process

The washing of fabrics was conducted in accordance with the SISTENISO105-C06 standard at 40 °C, 60 °C and 90 °C for 30 min in one washing cycle. Laundometer apparatus was used for washing. The dimensions of the test specimen were 100 mm x 40 mm. No adjacent fabrics 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%, carboxymethyl-cellulose – 1%, anionic surfactants – 1%, and a non-ionic active substance + moisture – 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.

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

<table>
<thead>
<tr>
<th>Soil No.</th>
<th>Soil</th>
<th>L*</th>
</tr>
</thead>
<tbody>
<tr>
<td>101</td>
<td>carbon black/olive oil</td>
<td>45.41</td>
</tr>
<tr>
<td>114</td>
<td>red wine</td>
<td>75.53</td>
</tr>
<tr>
<td>116</td>
<td>blood/milk/ink</td>
<td>43.25</td>
</tr>
<tr>
<td>160</td>
<td>chocolate</td>
<td>76.21</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>NaPB, %</th>
<th>TAED, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>2.5</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>15</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>15</td>
<td>7.5</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
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.

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.

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.
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 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).

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 Tetraacetylatedylenediamine 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.

### Conclusions

The influence of two bleach activators: Sodium Perborate Tetrahydrate and tetraacetylatedylenediamine, 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 improvement of the 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].

### References

1. Technical Documentation of Belinka Perkemija, Ljubljana, Slovenia.
the scope of testing the following: raw materials, intermediate and final paper products, as well as training.

Cellulose 2015; 52(6): 78-84
Laitala K, Mallan Jensen H. Cleaning activities. The Laboratory offers services within the scope of testing the following: raw -materials, intermediate and final paper products, as well as training.

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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 (bending 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 rezonanse 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.

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