Performances of a Builder System with Low Content of Sodium Tripolyphosphate

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The effect of a builder system with low content of sodium tripolyphosphate (STPP), consisting of sesquicarbonate (SQ), 10% sodium disilicate (SD) and 10% STPP, SQ/SD system, less aggressive for the environment than the usual amount of 30% STPP as builder, on removal of some physically adsorbed (carbon black/olive oil) and chemically bound soils (immedial black, cocoa/milk and red wine) out from cotton test fabrics in detergent compositions formulated with 13% anionic and nonionic surfactants and its influence on sodium perborate (SPB) and sodium perborate/tetraacetylethlenediamine (TAED) bleaching system at low and medium temperatures was investigated. The results were compared with those obtained by the corresponding formulations containing 30% STPP. Replacing 2/3 of STPP by the SQ/SD builder system in the detergent compositions is a good choice, the washing performances being pretty similar for all the types of soil studied. Addition of SPB improves the washing power irrespective of the builder system and temperature for all the tested soil, excepting cocoa/milk, for which the presence of SPB does not influence the washing performance. The highest increase was recorded for red wine i.e., the washing power increased about 2.0 times at 40°C and 1.8 times at 60°C. TAED improves detergency performances at 40°C for all the types of soils, with a maximum at 10% TAED concentration, especially for red wine. At 60°C the performances increase with the raise in TAED concentration for red wine, but no change was obtained for cocoa. In the case of immedial black and carbon black/olive oil the performances increase when TAED concentration rises from 5% to 10% and remain the same with 15% TAED for both types of detergents.

Keywords: detergent builders, sodium tripolyphosphates, sodium sesquicarbonate, sodium disilicate, sodium perborate, tetraacetylethlenediamine, washing performances

Phosphates accomplish a vital function in detergents [1], being the most widely used inorganic builder until the restriction imposed in USA starting with 1960s and later in Europe, due to their contribution to the phosphorus load of rivers, lakes and inshore water. So, the use of STPP in detergents has to be under control [2-4].

Because the STPP is performing very useful functions, it is impossible to be replaced by a single chemical product but some combinations of compounds can act similarly.

Soil attached on textile substrate by physical adsorption or by electrostatic forces is removed by a simple washing, while when it is attached by covalent bonds can generally be removed only by chemical means (use of oxidizing agents or enzymes) [5].

The effects of a builder system consisting of 10% sodium disilicate, 10% STPP and sodium sesquicarbonate necessary to fill the compositions on removal of some physically adsorbed and chemically bound soils in detergent compositions, as well as of those containing the above builder system and sodium perborate or sodium perborate/tetraacetylethlenediamine bleaching system at low and medium temperatures were presented into the paper. The washing results have been compared with those obtained using the formulations containing the usual amount of 30% STPP in detergents.

Experimental part

Materials used were: alkylbenzenesulfonic acid sodium salt (LAS) prepared in laboratory from alkylbenzenesulfonic acid, 96.6%, average molecular weight 320 g/mol (NANSA SSA, Albright&Wilson) and sodium hydroxide reagent grade; alcohol (C12-C15) etoxylate 7EO (AE) (EMPLILAN KCL 7, Albright&Wilson); amorphous sodium disilicate (SD), laboratory product obtained from NaOH and SiO2, both technical grade; sodium perborate tetrahydrate (SPB), 9.43% active oxygen; tetraacetylethlenediamine (TAED), 93.56% active content (Hoe S 3870, Hoechst AG); builder salt technical grade: sodium sesquicarbonate Na2CO3·NaHCO3·2 H2O (SQ), 48.70% Na2CO3 and 39.50% NaHCO3 (Soda Product Works Govora, Romania), sodium carbonate (SC), sodium sulfate (SS) and sodium tripolyphosphate (STPP).

Cotton standard soiled test fabrics used in detergency tests were: EMPA 101 (carbon black/olive oil) R=18.5 %; EMPA 115 (immedial black) R=31.5 %; EMPA 112 (cocoa/milk) R=28.6 %; EMPA 114 (red wine) R=45.8 %.

Methods: detergency performances were assessed by measuring the reflectance of the standard soiled cotton fabrics using a Data Color 2000 Spectrophotometer, after washing and drying in air at room temperature. Detergency tests had been carried out under specific conditions: equipment: Linitest plus; temperature: 40°C and 60°C; cycle length - 40 min; water hardness: 10°dH; washing solution concentration: 7.5 g/L and liquor ratio - 1/150.

Washing performances was calculated using the modified Kubelka-Munk relation [18]:

\[ W_p = 100 \cdot \left( R_w - R_s \right) / \left( R_0 - R_s \right) \]

where:
- \( W_p \) is the washing performances,
- \( R_w \) - reflectance of standard soiled test fabric after washing,
- \( R_s \) - reflectance of standard soiled test fabric before washing,
- \( R_0 \) - reflectance of unsoiled test fabric.

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REV. CHIM. (București) ● 60 ● Nr. 5 ● 2009 http://www.revistadechimie.ro 439
Results and discussion

It is well known that the builder systems influence the removal both of physically adsorbed and covalently bound soils, so that the efficiency of each detergent composition must be evaluated.

STPP, the best builder so far identified, acts both in primary and secondary washing processes performing the following functions [6]: sequestering of hardness salts, removal and prevention of encrustation on fibers, enhancement of the washing process, carrier for other detergent ingredients.

SQ (Na₂CO₃·NaHCO₃·2H₂O) is known to have a good effect in detergency, combining the properties of sodium carbonate and bicarbonate: source of alkalinity, maintaining of pH value higher than 9 even after of divalent ions precipitation and water hardness felt of, reducing of excess alkalinity due to other detergent components [7, 8]. On the other hand, SD accomplishes complex functions in detergents [9-12]: water softening and buffer effects, dispersing abilities, prevention of soil re-deposition and high Ca²⁺ and Mg²⁺ removing capacity, being able even to replace STPP with pretty satisfactory results. Thus, the combination SQ/SD performs almost all the STPP functions and could be used as STPP substitute.

Real soil are mixtures of physically adsorbed and chemically bound compounds and their removal requires detergents containing bleaching systems, which exhibit oxidative features and are usually based on either hydrogen peroxide or hypochlorite.

SPB tetrahydrate (10.2% active oxygen content [13]), has been the predominant source of hydrogen peroxide in laundry formulations [1, 14, 15], but hydrogen peroxide has as main disadvantage the reduced efficacy at low temperature. Bleach activators, by acting as acylating the perhydroxyl ion to generate peracids and peracyl anions, must be used to decrease its decomposition temperature, the peracid being a more active bleaching species, providing effective bleaching in the temperature ranges 10 – 60°C [16, 17].

Taking account of the above mentioned facts, the compositions presented in table 1 were formulated.

Cotton standard soiled test fabrics used in the detergency tests contained both physically adsorbed [EMPA 101 (carbon black/olive oil)] and chemically bond soils [EMPA 115 (immedial black), EMPA 112 (cocoa/milk) and EMPA 114 (red wine)].

The washing performances vs. type of standard soil test fabrics at 40 and 60°C for compositions containing or not SPB are presented in figure 1a, b.

Washing results show that, in the absence of SPB, detergency performances of the composition STPP are about 9% higher than SQ/SD for physically adsorbed soil (EMPA 101, fig. 1a) at 40°C. SPB increases performances with about 30% in the case of SQ/SD and with only 20% in that of STPP at the same temperature. Increasing of temperature produces an increase of washing power of both compositions (fig. 1b) in the absence and presence of SPB, the highest increase – about 30% – being obtained for STPP, so that both types of detergents containing SPB have the same washing performances.

Immedial black is removed in the same measure by STPP and SQ/SD compositions at both temperatures (fig. 1a, b). Addition of SPB produces an increase of performances, higher for composition containing SQ/SD at 40°C, while at 60°C the washing performances increase with about 50% for both compositions.

Cocoa/milk soil (EMPA 112) is removed better by SQ/SD irrespective of the presence of SPB at 40°C, while at 60°C there is no difference between the efficiency of the two types of compositions. Thus it can be concluded that SPB does not modify the washing performances of both builder systems at 40°C and increases them roughly with the same values at 60°C (fig. 1a, b).

Table 1

<table>
<thead>
<tr>
<th>Component*</th>
<th>STPP</th>
<th>STPP/SPB</th>
<th>STPP/SPB/TAED</th>
<th>SQ/SD</th>
<th>SQ/SD/SPB</th>
<th>SQ/SD/SPB/TAED</th>
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<tr>
<td>Sodium tripolyphosphate, STPP</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
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<td>30</td>
</tr>
<tr>
<td>Sodium disilicate, SQ</td>
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<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Sodium sesquicarbonate, SQ</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sodium perborate tetrahydrate, SPB</td>
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<td>15</td>
<td>15</td>
<td>15</td>
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</tr>
<tr>
<td>Tetracetylthiendiamine, TAED</td>
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<td>10</td>
<td>15</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sodium sulfate, SS</td>
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<td>26</td>
<td>21</td>
<td>16</td>
<td>11</td>
<td>-</td>
</tr>
</tbody>
</table>

*13% surfactants (anionic and nonionic), 5% sodium carbonate, until 100% water

Fig. 1a. Washing performances as a function of builder system containing or not SPB for the specified standard soiled test fabrics at 40°C
Red wine, a chemically bound soil, is removed a little better by the SQ/SD builder system at both temperatures. The performances are doubled by SPB in the case of STPP composition and increase about 1.8 times for SQ/SD one at 40°C. This important increase is due to the active oxygen delivered by SPB, which destroys the chemical bonds between soil and substrate by an oxidative process. At 60°C the red wine is removed with better results by the compositions containing SPB, the washing performance increasing more than 3 times and becoming similar for both systems.

Detergency performances as a function of builder system for formulations containing or not 5, 10 and 15% TAED at 40 and 60°C for EMPA 101 are shown in figure 2. Adding TAED, the washing power for carbon black/olive oil increases at 40°C, especially when concentration of TAED is 10% for both builder systems, whilst for 5 and 15% are roughly the same, the increase being a little higher for composition containing STPP. Increasing of temperature produces a small improvement of efficiency, irrespective of the composition of the builder system.

The same compositions were tested for removal of the standard soiled test fabrics: EMPA 115 (fig. 3), EMPA 112 (fig. 4) and EMPA 114 (fig. 5). Immedial black and cocoa/milk are much better removed in the presence of TAED by the both compositions (fig. 3 and 4) at 40°C, with a maximum for 10% TAED, but the increase is a little higher for STPP as builder. Washing efficiency for removal of immedial black increases for both builder systems with increasing TAED concentration. In the case of cocoa/milk this increase is lower for the two builder systems.

Fig. 1b. Washing performances as a function of builder system containing or not SPB for the specified standard soiled test fabrics at 60°C

Fig. 2. Detergency performances as a function of builder system and TAED concentration for EMPA 101 at specified temperatures

Fig. 3. Detergency performances as a function of builder system and TAED concentration for EMPA 115 at 40°C and 60°C
Fig. 4. Detergency performances as a function of builder system and TAED concentration for EMPA 112 at specified temperatures

Fig. 5. Detergency performances as a function of builder system and TAED concentration for EMPA 114 at 40°C and 60°C

Removal of red wine from cotton textile substrate (fig. 5) is increased by the presence of the bleaching system SPB/TAED, with similar values for 10 and 15% TAED at both temperatures, and has the same values – much higher for 60°C – irrespective of the builder system.

The total washing performances values at 40°C and 60°C for the four types of standard soiled test fabrics are presented, in figure 6a, b.

Considering the dependence of performances on TAED concentration for all the test fabrics and compositions, its increase from 10 to 15% is not justified.

A detergent is performing when it removes a large amount of soil at small concentration in the washing liquor. Totalizing the values of the washing performances for all the types of standard soiled test fabrics used, the total washing values in figure 6a, b were obtained.

Fig. 6a. Total washing performances as a function of builder system for all the standard soiled test fabrics tested at 40°C
The figure shows that the addition of TAED into the detergent compositions produces an increasing of the total detergency for both types of detergents at the two temperatures, the values of washing performances being higher and very similar for the two builder systems and the TAED concentrations 10 and 15%.

Conclusions

Replacing of 2/3 of STPP with SQ/SD builder system in the detergent compositions is a good choice, the washing performances of the two types of compositions being the same in the limits of experimental errors.

Addition of SPB improves the washing performances of all the tested soil irrespective of the builder system and temperature, excepting cocoa/milk soil, for which its presence does not modify the washing performance. The highest increase was obtained for red wine, the washing performances increasing about 2.0 times at 40°C and 1.8 times at 60°C.

Compositions containing TAED have improved detergency performances for all the types of soils, with a maximum at 10% TAED, especially for red wine, which needs bleaching components to be removed. Increasing of TAED concentration does not increase the washing power of soil tested at 40°C. At 60°C the performances increase with increasing TAED concentration for red wine, but no change was obtained for cocoa/milk. In the case of immedial black and carbon black/olive oil the performances increase when TAED concentration rises from 5% to 10% and no change is obtained with 15% TAED for both types of detergents.

Adding together the washing performances of all the types of standard soiled test fabrics, a remarkable similarity of the corresponding pairs of detergent compositions containing 30% STPP and the SQ/SD builder system was obtained, with an increase of performances when the bleaching system SPB/10% TAED was used at low and medium temperatures. But differences in the performance of the studied systems at 40 and 60°C are almost negligible, so the increase of temperature is not justified if the energy consumption is considered.

Given the similar performances of the detergents containing 30% STPP and SQ/SD/10% STPP as building systems it can be concluded that the last builder system (less aggressive for the environment) can successfully replace STPP.

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Manuscript received: 17.07.2008