

Volume 03, Issue 02, Article no. 24, pp. 213-219
<http://www.journalbinet.com/jstei-volume-03.html>
Original Research Paper

Cabrejos, W. (2016)

Current topics on builders in laundry products

Wilson Cabrejos Caracciolo

Colloidal Solutions, Independent Research Group, Lima, Peru.

Article info.

ABSTRACT

Key Words:

Builder, Phosphonates,
Tripolyphosphate, Bleaching,
Co-surfactant



Received: 29.04.2016
Published: 14.06.2016

Corresponding author*:
cabrejos.w@pucp.edu.pe

The present study aims to contribute with new insights on three main current topics on builders used in laundry products: a) the search for a replacement to sodium tripolyphosphate, b) an efficient system that works under oxidative conditions and c) the effect of a co-surfactant. For regular laundry formulations, we found a non-expected synergistic system which can perfectly replace sodium tripolyphosphate at the same formulation cost. For bleaching formulations, we found one alternative builder for phosphonates replacement, and some natural materials which are worth to be further studied. We also found an unexpected protection effect of the main anionic surfactant when combined with the appropriate co-surfactant without the need of a builder.

Citation (APA): Cabrejos, W. (2016). Current topics on builders in laundry products. *Journal of Science, Technology and Environment Informatics*, 03(02), 213-219.

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I. Introduction

Builders have a widespread use in household cleaning products, personal care products, institutional cleaners and industrial cleaning processes, and as water treatment additives in various applications. They are mainly employed to remove metal ions that might impair product's performance or stability. Other benefits which vary with the chemical character of each molecule are maintenance of alkalinity of the wash solution, entire deposition and soil dispersing properties and corrosion inhibition (Kuo-Yann, 2005). These compounds reduce metal ions availability by forming either soluble or insoluble compounds by sequestration, precipitation or ion exchange. While precipitation often results in the formation of insoluble deposits on clothes and washing machine components, and ion exchange has limited efficacy and needs to be reinforced usually by the use of an anionic polymer (e.g.

polycarboxylates), sequestration (or chelation) is the most preferred method due to the formation of soluble complexes and the high binding capacity of chelants. The best known sequestering agent is sodium tripolyphosphate (STPP), although phosphates use has been restricted during recent years for their association with eutrophication phenomena. Carboxylates are not as effective as phosphates and find limited use to formulations where high efficiency is not required, like in enzymatic products. Amino carboxylates and phosphonates have been increasingly used as phosphates replacement since they are able to form very stable and soluble complexes with metal ions, which on the contrary make them poorly biodegradable.

The first part of the study corresponds to the development of an adequate STPP replacement. Although STPP is classified as generally recognized as safe (GRAS) by the FDA (CFR182) and that it's approved to be used as food additive by the European Union (Directive 95), its use has been gradually reduced due to the association of phosphates with lakes and rivers' eutrophication phenomena. On the other hand, the INIA study of 2007 concluded that the use of phosphates in European laundry products increased the risk of eutrophication in only 0.5-3.0% (De Madariaga et al., 2007), being the largest contribution to eutrophication animal and human wastes, followed by fertilizers (Morse et al., 1993). Since then, several systems were proposed as replacements for STPP, but none has been able to match all its benefits in laundry products (Ho Tan Tai, 2000; Köhler, 2006) such as:

- Alkalinity, forming soluble complexes with Ca^{2+} and Mg^{2+} from water, dirt and textiles preventing the formation of crystals deposits, and also raising the pH of wash liquor, increasing charge of ions from dirt and fabrics
- Buffer, maintaining the pH over a wide range despite the addition of base or acid, which preserves performance
- Deflocculation, breaking up large particles like mud or clay
- Antiredeposition, by keeping deflocculated particles in suspension, by electrostatic repulsion of charged ions, and by emulsifying oily materials
- Rapid biodegradation, and
- Low formulation cost

Zeolites are the most common replacement for STPP, although they have some major disadvantages like treating only ions present in water through ion exchange, but not being able to remove ions deposited on clothes, soils or certain machinery parts, and also having limited solubility; that's why they have to be combined with carbonates and silicates (limited to small amounts to avoid precipitation), and also with dispersants such as synthetic polymers (poorly biodegradable) (Köhler, 2006).

The second part of the study evaluates builders' resistance under harsh working conditions, specifically in the presence of oxidants (e.g. hydrogen peroxide), under which the vast majority of builders decompose due to oxidative damage, being diphosphonates the safest choice for these products. But due to a recent published draft of the *Revision of European Ecolabel Criteria for laundry detergents, dishwasher detergents, industrial and institutional automatic dishwasher detergents, industrial and institutional laundry detergents, hand dishwashing detergents and all-purpose cleaners and sanitary cleaners* (Kaps et al., 2014), it is expected that phosphonates that are not aerobically-biodegradable will be banned, as proposed in that document. Thus, the total content of phosphonates/phosphonic acids must not exceed the limits specified herein according to the ecolabel criteria adopted by the European Union. Under this scope, several synthetic and natural molecules were tested in the presence of hydrogen peroxide for their capacity to prevent its decomposition when iron (II) sulfate was added.

The last part of the study considers the addition of a co-surfactant and its effect on solution properties of a linear alkylbenzene sulfonate (LABS) and soap, which are known to be very sensitive to water hardness. Selecting the right molecule would reduce water hardness sensitivity of LABS even in the presence of high levels of divalent ions, without the need of a builder.

II. Materials and Methods

All samples were commercial materials commonly used in the manufacture of laundry products, except for the ones of food origin which were acquired in a regular store.

The search for a replacement to STPP

For this study we evaluated the effect of several builders incorporated in an 11.52% (by weight) aqueous solution of LABS prepared from the neutralization of a 12.0 % (by weight) sulfonic acid solution with excess sodium hydroxide. A 0.05 g sample of this solution was added to a 5.0 g of hard water, prepared from dissolving CaCO_3 in deionized water, for a final water hardness of 400 ppm. Builders were tested separately as well as in mixtures, to find if there's a synergistic effect. The appearance of turbidity indicates that calcium ions are reacting with LABS, forming an insoluble salt that precipitates from the solution.

Evaluation of builder's efficacy under oxidative conditions

We tested several types of molecules (Table 01), some widely recognized as builders while others commonly used for other purposes, but whose molecular structure made them good candidates for the study. We designed the evaluation to test the effectiveness of a builder to prevent iron (II) ions to come into contact with dissolved hydrogen peroxide. For this purpose, 0.25 g of hydrogen peroxide were dissolved in 5.0 g of deionized water, followed by the addition of 0.1 g (as 100% active matter, except for honey, coffee, red wine and black tea which were all solutions) of the tested material. Finally, increasing amounts of 0.02 g of iron (II) sulfate were added to the solution. The appearance of a dark precipitate accompanied by the rising of bubbles and a mild heating of the vessel indicates that the material failed to protect the hydrogen peroxide from catalytic decomposition.

The effect of a co-surfactant

Two co-surfactants namely sodium lauryl ether-2 sulfate (LESS) and laureth-9 were added separately to an 11.52% (by weight) aqueous solution of LABS prepared from the neutralization of a 12.0 % (by weight) sulfonic acid solution with excess sodium hydroxide, without the presence of a builder. The same was made for soap but only using LESS as co-surfactant, in which four mixtures of soap/LESS were tested: 1.2:1, 3.3:1, 4:1 and 6:1. Of each of these probe solutions, 0.05 g was added to 5.0 g of hard water prepared from dissolving CaCO_3 in deionized water, for a final water hardness of 1500 ppm. The appearance of turbidity indicates that calcium ions are reacting with the main surfactant, forming an insoluble salt that precipitates from the solution.

III. Results and Discussion

The search for a replacement to STPP

As previously mentioned, several systems were proposed as replacements for STPP, but hardly one could match all its benefits. Boric acid and specially Citric acid are molecules that have structures and acidity constants that somehow resemble those of Phosphoric acid, so we decided to evaluate their salt forms for their efficacy, to later find if there's any synergy when combined with another complexing agent such as Methylglycine diacetic acid (MGDA). Table 01 summarizes our findings.

We started testing STPP as a standard builder to prevent Ca^{2+} impact on a solution of LABS at 400 ppm of water hardness, finding a protection effect at a level of 10.0%. Borax and Sodium citrate were tested at the same concentration, showing a lower performance compared to STPP. Zeolite A was also included to see how it performs. MGDA was not evaluated at this stage due to cost restrictions, but was chosen as a secondary builder. Then, Zeolite A and Sodium citrate were then mixed with MGDA at different rates, finding an unexpected synergistic effect in the case of the mixture Sodium citrate/MGDA.

Table 01. Evaluation of candidates for STPP replacement

System	STPP (%)	Borax (%)	Na citrate (%)	MGDA (%)	Zeolite A (%)	Comments
System 1	10.00					slightly hazy, no precipitate
System 2		10.00				very hazy, no precipitate
System 3			10.00			hazy, no precipitate
System 4					10.00	fine particles at the bottom
System 5				0.75	9.25	turbidity as well as fine particles
System 6			3.00		7.00	turbidity as well as fine particles
System 7			3.00	1.00		slightly hazy, no precipitate
System 8			5.00	0.50		clearer than previous, no precipitate

Evaluation of builder’s efficacy under oxidative conditions

Table 02 summarizes the results obtained from the evaluation. Interestingly, we found that some natural materials were in some cases surprisingly resistant and fairly effective.

Table 02. Evaluation of candidates for the prevention of hydrogen peroxide’s catalytic oxidation, the middle column indicates the amount of iron (II) sulfate that the system could tolerate before any sign of oxidation occurs

Materials	Fe ₂ SO ₄ (g)	Comments
Etidronic acid (HEDP)	1.80	clear solution up to 1.60 g, then turned slightly yellow
Phosphonoacetic acid (PAA)	0.54	clear solution up to 0.20 g, then turned slightly yellow
Tetrasodium EDTA	0.08	dark precipitate, bubbling, heating
Calcium disodium EDTA	< 0.02	dark precipitate, bubbling, heating
Pentetic acid (DTPA)	0.04	dark precipitate, bubbling, heating
Methylglycinediacetic acid	0.04	dark precipitate, bubbling, heating
Tetrasodium glutamate	< 0.02	dark precipitate, bubbling, heating
Monosodium glutamate	< 0.02	dark precipitate, bubbling, heating
Sodium citrate	0.16	dark precipitate, bubbling, heating
Zeolite A	0.08	dark precipitate, bubbling, heating
Sodium stannate	< 0.02	dark precipitate, bubbling, heating
Zinc pyrithione	0.04	dark precipitate, bubbling, heating
Salicylic acid	0.04	dark precipitate, bubbling, heating
Guar hydroxypropyltrimonium	< 0.02	dark precipitate, bubbling, heating
Carboxymethylcellulose	< 0.02	dark precipitate, bubbling, heating
Honey	0.18	dark precipitate, bubbling, heating
Coffee (Nescafe instant coffee)	0.12	dark precipitate, bubbling, heating
Red wine (Casillero del diablo)	0.16	dark precipitate, bubbling, heating
Black tea	< 0.02	dark precipitate, bubbling, heating
Cocoa poder	< 0.02	dark precipitate, bubbling, heating
Fructose	0.22	dark precipitate, bubbling, heating
Sucrose	0.24	dark precipitate, bubbling, heating
Tannic acid	< 0.02	dark precipitate, bubbling, heating
Galic acid	< 0.02	dark precipitate, bubbling, heating

It is well known that heavy metal ions (eg., Fe²⁺, Cu²⁺ and Mn²⁺) can catalyze the homolitic decomposition of hydrogen peroxide, resulting in the formation of hydroxyl radicals (HO•) which leads to oxidative damage of the cellulosic fibre and lower whiteness. This is why bleaching formulations based on hydrogen peroxide incorporate a builder, usually a diphosphonate like Etidronic acid (HEDP) since the majority of builders decompose under such oxidative conditions. Precisely, HEDP showed the best performance of all the builders we evaluated, followed by a not so commercial Phosphonoacetic acid (PAA), although its solution turned milky long before HEDP did, which make us believe that its binding capacity compared to HEDP might be lower (there is not much information about PAA), and therefore, more PAA should be employed. In the case of aminocarboxylates, they all failed almost immediately, being Tetrasodium EDTA the “best” among them. Zeolite A also failed, and was surpassed by an often underestimated Sodium citrate. Sodium stannate is a compound used to stabilize commercial hydrogen peroxide by virtue of the stannic acid colloid formed on hydrolysis, where polyvalent ions are adsorbed and deactivated ([Patent US3383174 A](#); [Patent US 3387939 A](#); [Lewis and Walters, 1960](#)), but in our test, it showed no protective effect. We also evaluated some natural materials and initially found that red wine, coffee and sugar showed some activity. In the case of red wine and coffee, it has been mentioned that polyphenols could act as complexing agents in the presence of divalent ions ([Amitha Rani, 2012](#)). We decided to evaluate Tannic and Galic acid, since they were both identified as responsible for the complexing activity previously mentioned ([Matamala et al., 2000](#)) although both of them failed in our tests. Further studies are recommended to elucidate the underlying mechanism of protection showed by red wine and coffee. On the other hand, honey’s protective effect was easier to assess. A later evaluation of saccharides fructose and sucrose showed that both were, not only surprisingly resistant to oxidation, but also fairly good at preventing catalytic decomposition of hydrogen peroxide. Its mechanism has been proposed to be based on the adsorption of a thin film over the metal surface, acting as a physical barrier ([Vrsalović et al., 2012](#)) but in our case, we found the same inhibitory effect in solution. The possibility of an interaction between functional groups on the saccharide structure and metal ions should be confirmed.

The effect of a co-surfactant

As an extension of the previous studies, we wanted to know how a co-surfactant impacts the water hardness sensitivity of LABS and soap, so we mixed them with two different surfactants (Sodium laureth-2 sulfate and Laureth-9) in a solution of 1500 ppm. In the case of soap, we only mixed it with LESS. Tables 03 and 04 summarize the findings of that evaluation.

Table 03. Evaluation of the effect of a co-surfactant with LABS

	Sodium laureth-2 sulfate (%)	Laureth-9 (%)	Comments
LABS	4.2	-	clear solution, no precipitate
LABS	-	4.2	turbid solution with precipitates

Table 04. Evaluation of the effect of a co-surfactant with soap

	Soap (weight ratio)	Sodium laureth-2 sulfate (weight ratio)	Comments
System 1	1.2	1.0	clear solution, no precipitate
System 2	3.3	1.0	clear solution, no precipitate
System 3	4.0	1.0	clear solution, no precipitate
System 4	6.0	1.0	slightly haziness, no precipitate

While the mixture LABS/Laureth-9 was not effective to prevent the formation of precipitates (a salt formed by the reaction of Ca²⁺ with LABS), the mixture LABS/LESS gave a clear solution. The result was the same even when we increased the concentration of Ca²⁺ to get a final water hardness of 2000 ppm.



The same was found when mixing soap and LESS at all evaluated ratios (at 6:1 ratio, a slight haziness appeared but without any precipitate). Mixing two surfactants of different hydrophilic-lipophilic balance (HLB) and strong affinity might account for this effect (LABS and soap are more hydrophobic and Sodium laureth-2 sulfate is more hydrophilic).

IV. Conclusion

In search for a replacement to STPP, an unexpected mixture of Sodium citrate and MGDA was found to be as efficient, being both readily biodegradable. As for hydrogen peroxide-based formulations, we found that phosphonoacetic acid could be a good replacement to phosphonates, being readily biodegradable but with a lower binding capacity that should be corrected through dosage. Saccharides like Fructose and Sucrose are worth to be considered. Red wine and Coffee showed interesting properties, but the origin of their benefits should be elucidated. Finally, we also found an unexpected change in sensitivity towards Ca^{2+} of LABS and soap when combined with another surfactant of different HLB and strong affinity, even at high levels of water hardness.

Acknowledgements

Materials and equipments used for the manufacture of prototypes were supplied by Alicorp's laboratory of New Products Development, Lima, Peru.

V. References

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How to cite this article?

APA (American Psychological Association)

Cabrejos, W. (2016). Current topics on builders in laundry products. *Journal of Science, Technology and Environment Informatics*, 03(02), 213-219.

MLA (Modern Language Association)

Cabrejos, W. "Current topics on builders in laundry products." *Journal of Science, Technology and Environment Informatics*, 03.02 (2016): 213-219.

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Cabrejos, W. Current topics on builders in laundry products. *Journal of Science, Technology and Environment Informatics*, 03, no. 02 (2016): 213-219.

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