

ALTERNATIVE SURFACTANTS FOR LAS IN ENVIRONMENTALLY FRIENDLY DETERGENT COMPOSITIONS

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Due to performances, the linear alkylbenzenesulphonates (LAS) is the most used anionic surfactant in detergent compositions. Being petroleum derived, its cost is continually increasing. In addition the environment legislation recommends its replacing with biodegradable surfactants obtained from renewable resources as alkylsulphates, alkylethersulphates, alcohol ethoxylates and soap.

The effect of three types of anionic surfactants (alkylethersulphate, AES, secondary alkanesulphate, SAS and sulphatated fatty alcohol, AGS) in the absence and presence of a new protease (Liquanase, Lq) on removal of different types of soils at low temperature (40°C) was studied and the washing results were compared with those obtained with LAS. Physically adsorbed soils are removed in the same measure by all the surfactant solutions both in the absence and presence of enzyme, while the chemically bound and combined soils are much better removed by AGS solution. Addition of enzyme increases the removal of specific stains (2 times) from cotton substrate, excepting LAS solution for which the increasing is only about 1.5.

INTRODUCTION

The reducing of detergent impact on environment can be done either by the utilization of biodegradable surfactants and builders or/and by improving their performances.

The increase of performances has as effect the reducing of the amount of detergent required by a washing cycle which, in its turn, allows the decreasing both of the amount of detergent eliminated into the environment at the end of the washing and the consumption of raw materials.

In the washing process, a complex mixture of soils must be removed, consisting of compounds physically adsorbed and/or covalently bound on textile substrate.¹

The surfactants are able to clean the physically adsorbed soils. Their removing depends on surfactant nature and correlates with their adsorption on textile substrate, the anionic surfactants being the most used. The oily soil is also better removed from the cotton substrates by anionic surfactants, which adsorb with their negative charges towards the bath, as far as possible from substrate. In this way the hydrophilic character of the substrate

increases when surfactant concentration is high and the substrate/bath interface tension is thus decreased, favouring detergency. Particulate soil is cleaned better by the anionic surfactants irrespective of the nature of substrate, due to the increase of the electric potential between the soil and substrate.²

The anionic surfactants, and especially sodium alkylbenzenesulphonate (LAS), are the most used in the detergent compositions.³ But LAS is obtained from petrochemical raw materials and the prices of such products are continually increasing. Moreover, the environment protection legislation recommends its replacing by biodegradable surfactants obtained from renewable natural sources like alkylsulphates, alkylethersulphates, polyethoxylated alcohols and soap.⁴⁻¹⁰

Besides surfactants, some other components that increase the performances are present into the detergent compositions. The enzymes, compounds with protein structure, easily and entirely biodegradable, nontoxic, obtained from renewable natural sources, efficient in small amounts facilitate especially the removal of chemically bound soils.^{11,12} Depending on their composition, they are able to increase the hydrolysis of washing

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resisting soils of different natures. The new generations of enzymes are multifunctional components that interpose in each stage of the detergency process: cleaning, whitening, removal of stains, protection of fabrics and colours.¹³ Their use has also as effect the decreasing of surfactants' content in detergent, reducing the amount of detergent required by the washing process¹⁴ and washing temperature,¹⁵ and thus of the amount of detergent delivered in the environment.

The detergent performances, expressed as reflectance of the test soil fabrics after washing with 20% surfactant solutions of LAS and of three anionic surfactants obtained from renewable natural sources belonging to alkylethersulphate (AES), secondary alkanesulphate (SAS) and sulphatated fatty alcohol (AGS) classes for physically absorbed (EMPA 101), chemically bound (EMPA 111 and EMPA 112) and combined (EMPA 116) soils at 40°C in the absence and the

presence of a new protease (Liquanase, Lq) were studied in the present paper.

RESULTS

The type of used surfactant and the content of Liquanase in their 20% solutions are given in Table 1.

The reflectance obtained using for washing the 20% solutions of surfactants given in Table 1 in the absence of enzyme at 40°C for the four test fabrics specified are presented in Fig. 1.

The results of washing tests for the compositions from Table 1 containing enzymes at the same temperature are given in Fig. 2.

The sum of reflectance of all the standard soiled test fabrics obtained after washing using the 20% solutions of the specified surfactants is represented in Fig. 3a, b.

Table 1

The type of used surfactant and content of Liquanase in their 20% solutions

Surfactant	Liquanase, %
Linear alkylbenzensulphonates	0 %
	0.5 %
Alkylethersulphate	0 %
	0.5 %
Secondary alkanesulphate	0 %
	0.5 %
Sulphatated fatty alcohol	0 %
	0.5 %

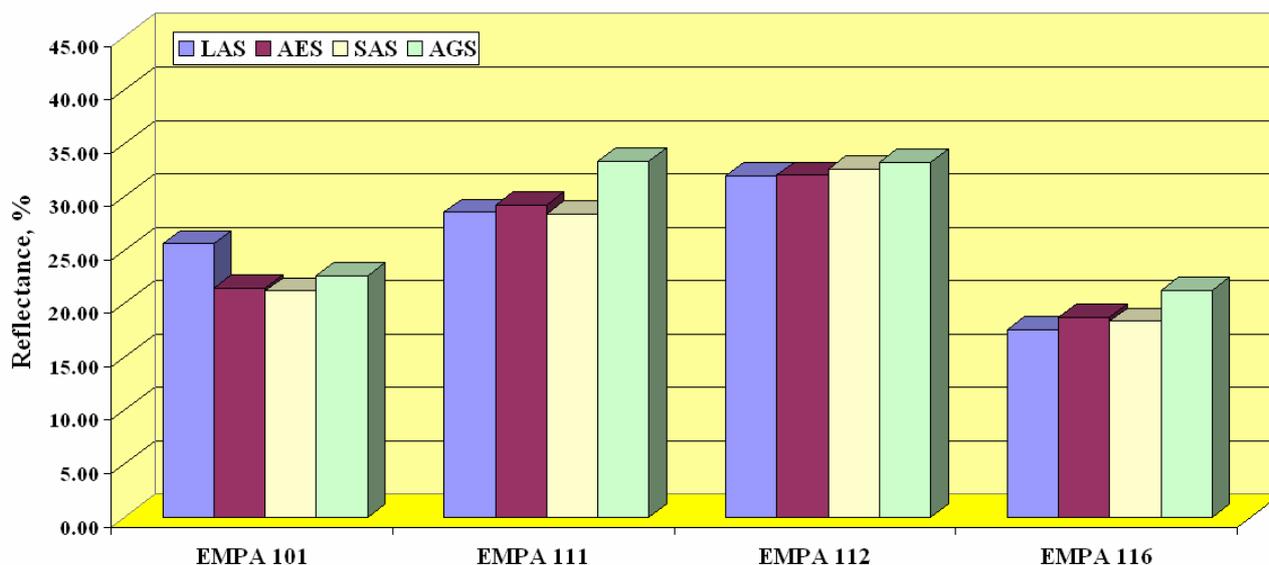


Fig. 1 – The reflectance after washing as a function of type of surfactant for the specified standard soiled test fabrics washed with 20% surfactant solutions at 40°C.

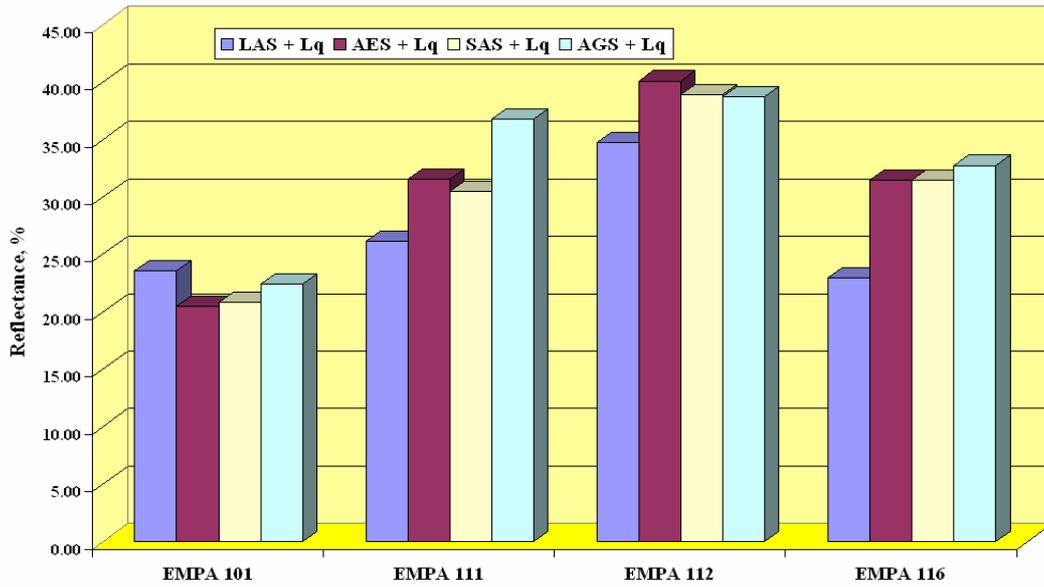


Fig. 2 – The reflectance after washing as a function of type of surfactant for the four standard soiled fabrics tested using surfactant solutions containing 0.5% enzyme at 40°C.

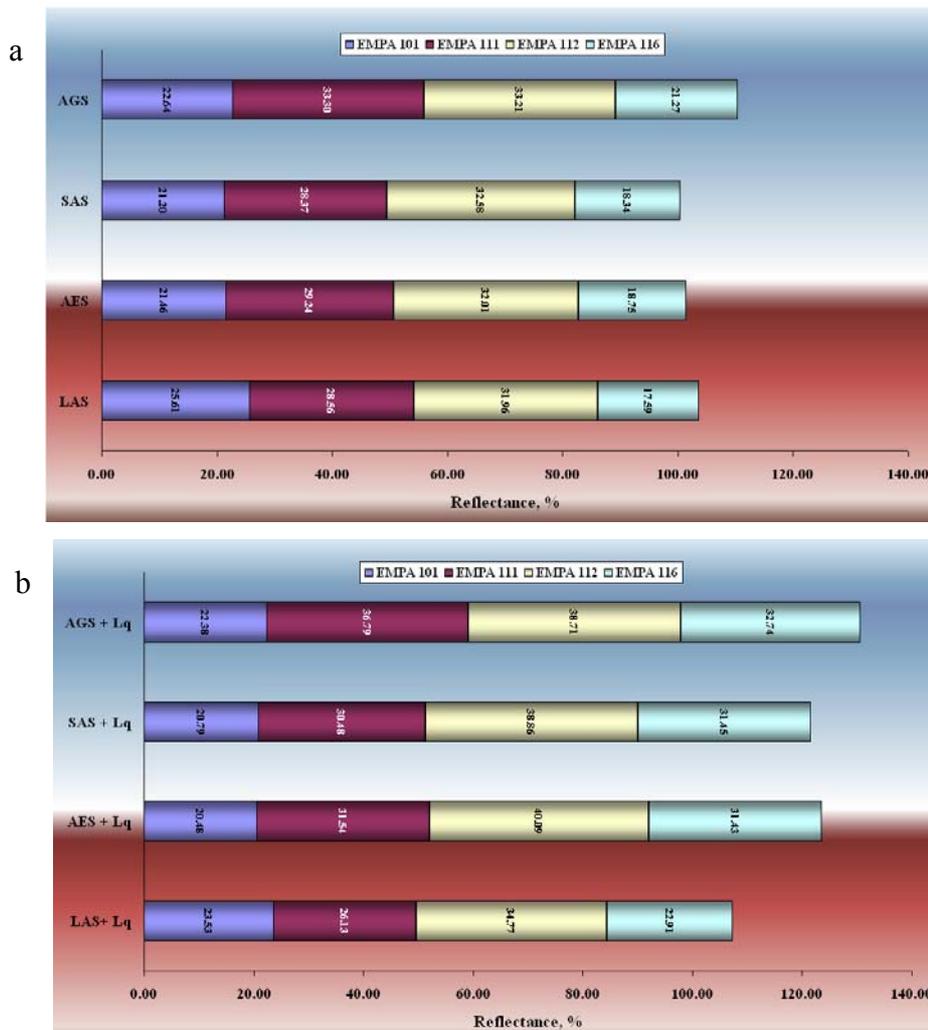


Fig. 3 – Sum of reflectance of all the standard soiled fabrics tested at 40°C as a function of type of surfactant in solutions: a – not containing; b – containing enzyme.

DISSCUSION

The most important components of a detergent composition are the surfactants. Due to the different types of soil and substrates implied in the detergency process, the correlation of detergency with the chemical structure of surfactants is a very complicated action.

The performances of three types of anionic surfactants obtained from renewable natural sources were studied using washing tests at 40°C performed on different types of cotton standard soiled test fabrics. They were compared with those of sodium linear alkylbenzenesulphonate, having in view its replacing from detergent composition but with preserving or even increasing of performances. The influence of an enzyme, Liquefanase, on the performances of the four surfactants was also established, as can be seen from the compositions of the washing solutions given in Table 1.

The values of reflectance of test fabrics after washing with 20% surfactant solutions from Fig. 1 show that soils physically adsorbed on cotton substrate (EMPA 101) are better removed by LAS solution followed by AGS, while AES and SAS solutions have the same efficiency in the limits of experimental errors.

Considering the values obtained for the removing of blood from the same figure – test fabric (EMPA 111) – it can be concluded that LAS, AES and SAS solutions have practically the same efficiency, while AGS one is about 1.2 times more efficient.

The mixed chemically bound cocoa/milk soil (EMPA 112) is removed in the same measure by the four surfactant solutions.

The performances of surfactant solutions for the more complex blood/milk/China Ink (EMPA 116) mixed soil are pretty low compared with that for the other types of soils, but if the first three surfactant solutions behave similar, AGS one is roughly 1.2 times more efficient.

The results obtained for the washing of the four test fabrics with surfactant solutions containing 0.5% Liquefanase presented in Fig. 2, show that the enzyme has no effect on removal of physically adsorbed soils, that is it does not influence the general detergency.

The values of reflectance obtained for blood stain show that Liquefanase reduces a little bit the efficiency of LAS solution, whilst those of the solutions of the other three surfactants are increased between 7 and 10%, the greatest increase being obtained for AGS.

Thus, the efficiency of AGS solution becomes 40% higher than that of the LAS one.

If the increasing of performances of LAS solution in the presence of enzyme can be neglected for chemically bound cocoa/milk soils, the differences between reflectance values being in the limits of experimental errors, in the case of the other three surfactant solutions the performance is – on average – 23% higher.

Liquefanase has the greatest effect on the removal of mixed soil blood/milk/China Ink (EMPA 116), as can be seen comparing the corresponding data in Figs. 1 and 2. The reflectance increases for each surfactant solution: 1.34 times in the case of LAS solution, 1.70 times for AES, 1.75 times for SAS and 1.60 times for AGS. At the same time, the efficiency of the solutions of the last three surfactants is, on average, 50% higher than that of LAS solution if Liquefanase is present.

A detergent is considered performing if it is able to remove as many types of soils as possible. Totalizing the values of reflectance for all the four types of standard soiled fabrics tested, the values from Fig. 3a, b are obtained.

Comparing the efficiencies of the washing performances of surfactant solutions as such, Figure 3a, it can be seen that AGS solution has the greatest washing efficiency followed by LAS, while SAS and AES give practically the same values. The AGS solution is 7% more performing than the LAS one.

If the enzyme is present, Fig. 3b, the order of efficiencies of surfactant solutions are: AGS > AES > SAS > LAS. The AGS solution is again the most performing, its efficiency being 1.22 higher than that of the LAS one.

Considering the sum of reflectance of all the standard soiled test fabrics, it can be concluded that Liquefanase increases the performances of all the 20% solutions with 18 to 22%, excepting that of LAS that is practically unaffected and that the AGS solution is the most performing both in the absence and the presence of enzyme. This means that AGS is not only a substitute for LAS, but it is expected that AGS containing detergents be more efficient than those formulated with LAS if no special interactions between AGS and builders manifests.

EXPERIMENTAL

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 de reagent grade, primary alcohols (C₁₂-C₁₅) ethoxy (2.5) sulphate 70 % aqueous solution (Dobanol 25-2S/70, Shell Chemie GmbH), secondary alkanesulphate, 60 % active matter (Hostapur, Clariant GmbH), sulphatated fatty alcohol, 30 % active matter (Emal 30 E, Kao Chemical), Liquanase 2.5L (Novozymes).

Cotton standard soiled test fabrics used in detergency tests were: EMPA 101 (carbon black/olive oil) R = 18.5 %; EMPA 111 (blood) R = 17.8 %; EMPA 112 (cocoa/milk) R = 28.6 %; EMPA 116 (blood/milk/China Ink) R = 13.5 %.

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; cycle length – 40 minutes; water hardness – 10⁰dH; washing solution concentration – 20% by weight and liquor ratio – 1/150.

CONCLUSIONS

Soil physically adsorbed on cotton substrate (carbon black/olive oil) is removed in the same measure by all the surfactant solutions, both in the absence and the presence of enzyme, which means that enzyme does not interpose in the general detergency.

For removing blood from the cotton substrate in the absence of enzyme the best performance was obtained with AGS solution, the other three surfactant solutions having lower and very similar efficiency.

Enzyme increases the efficiency of AES, SAS and AGS solutions for blood with 7-10%, while that of LAS solution is a little bit decreased; AGS solution is about 40% more efficient than the LAS one.

All the surfactant solutions have the same performance for removing chemically bound cocoa/milk soil, but enzyme increases their performances with about 23%, excepting that of LAS which increases only with 10%.

The greatest effect of enzyme was obtained in the case of the mixed soil blood/milk/China Ink, the increase being on average 70% in the case of AES, SAS and AGS and only 34% for LAS; the efficiency of the first three surfactants becomes

about 50% higher than that of LAS in the presence of enzyme.

The sum of reflectance for all the standard soiled test fabrics used shows that the AGS solution is the most performing irrespective of the presence or absence of enzyme and thus it is able to replace more than successfully LAS in detergent formulations.

REFERENCES

1. S. Florescu and M. Leca, "Detergents and Detergency", Editura Academiei Române, Bucharest, 2003, p. 104-106.
2. M.J. Rosen, "Surfactants and Interfacial Phenomena", John Wiley and Sons, New York, 1987, p. 379-384.
3. P. Goon, R.G. Bhirud and V.V. Kumar, *J. Surf. Deterg.*, **1999**, 2, 489-493.
4. P. McWilliams and G. Payne, "Bioaccumulation potential of surfactants: A Review", in "Chemistry in the Oil Industry VII: Performance in a Challenging Environment", T. Balson, H.A. Craddock, J. Dunlop, H. Frampton, G. Payne, P. Reid eds., Royal Society of Chemistry, Cambridge, 2002, p. 44-55.
5. L.N. Britton, *J. Surf. Deterg.*, 1998, 1, 109-117.
6. T. Cserhati, E. Forgacs and G. Oros, *Environ. Int.*, **2002**, 28, 337-348.
7. M.J. Scott and M.N. Jones, *Biochim. Biophys. Acta*, **2000**, 1508, 235-251.
8. C. Verge, A. Moreno, J. Bravo and J. Berna, *Chemosphere*, **2001**, 44, 1749-1757.
9. D. Prats, C. Lopez, D. Vallejo, P. Varo and V.M. Leon, *J. Surf. Deterg.*, **2006**, 9, 69-75.
10. H. Azica and A. Tazerouti, *J. Surf. Deterg.*, **2007**, 10, 185-190.
11. H.S. Olsen and P. Falholt, *J. Surf. Deterg.*, **1998**, 1, 555-567.
12. K.H. Maurer, *Curr. Opin. Biotechnol.*, **2004**, 14, 330-334.
13. P. Falholt, "Biotechnology in Detergents", 6th World Conference on Detergents. Defining and Designing Our Future, Montreux, 2006.
14. S. Florescu, M. Leca, A. Golgojan and G. Stoica, "Enzymes – Performing Builders for Detergent Compositions", 5th World Surfactants Congress, Berlin, 2004, P-04-05.
15. S. Florescu, M. Leca, A. Golgojan and G. Stoica, "Enzymes – a Way to Increase the Efficiency of the Detergents and Protect the Environment", 5th World Conference on Detergents. Reinventing the Industry: Opportunities and Challenges, AOCS Press, Champaign, Illinois, 2003, p. 154-158.

