Redepositon of Impurities on Wool Fabric during Washing with Ecological Surfactants and Solvent Microemulsion

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ABSTRACT
The aim of this paper was to study addition of a non-toxic solvent microemulsion to conventional wash formulations with the aim of improving the performance of the conventional washing. In this work, the redeposition performance during washing was studied after washing a wool fabric with addition of a solid impurity The non-toxic solvent used was dimethyl sulfoxide micro-dispersed with an amphoteric surfactant as emulsifier. The fabric was washed with SDBS and biodegradable non-ionic surfactants such as an alcohol ethoxylate (AE) with 7 m. EO and an alkyl polyglucoside with 1.4 glucoside groups (APG). The fabric used was EMPA 217 wool fabric. The anionic and non-ionic surfactants and mixtures of the non-ionic surfactants were used separately and in mixture in varying proportions for the washes. Carbon black was used as the solid impurity in the washing. Sodium carbonate and sodium chloride were used as builders. The fabric was washed at low temperature (30º C) with water of different hardness. In all the cases, the performance in terms of redeposition of the solid impurity (carbon black) was enhanced (decreased) for all the mixtures tested when using the microemulsion of DMS in the washing formulation.

Keywords: surfactants, washing, redeposition, wool and microemulsion.

INTRODUCTION
The process of cleaning a textile substrate in a liquid solution comprises three elements, a) the substrate (the surface to be cleaned), b) the impurities (undesirable substances to be removed from the substrate in the cleaning process) and c) the solution or washing "bath" (aqueous solution of the detergent applied to the substrate to facilitate the elimination of impurities). The washing process essentially has two stages. The first stage is the removal of the impurities from the substrate, and the second stage is the suspension of the impurities in the washing bath and prevention of their redeposition on the substrate during the washing [1,2].

Wool, being proteinaceous, is attacked by strong alkali.This attack causes softening and swelling with reduction in strength of the wool fibers. Therefore, wool may only be cleaned in weakly alkaline environments [3, 4].

The conventional washing of wool employs anionic and non-ionic surfactants along with inorganic salts used as builders. Common surfactants (wetting agents) are soap, sodium dodecylbenzene sulfonate (SDBS), alkylphenol ethoxylates, and fatty acid ethoxylates [1]. At all times, the washing pH is less than 10 for washing wool [5]. Since detergents for wool are primarily intended for use in washing machines, low temperatures, short washing times, high bath ratios, and limited agitation are used to prevent damage to the wool fibers [6].

In this work, the redeposition of a solid impurity on a standard wool fabric (EMPA 217) was studied for conventional wash formulations containing a non-toxic solvent microemulsion. The non-ionic solvent was dimethyl sulfoxide; suitably dispersed using an amphoteric surfactant as an emulsifier.

The detergency of wool fabric with this proposed washing formulation has been discussed previously in other papers [7,8]. The non-toxic solvent used was dimethyl sulfoxide, suitably dispersed using an amphoteric surfactant as emulsifier [9]. The biodegradable non-ionic surfactants used in the wash were an alcohol ethoxylate (AE) with 7 m. EO and an anionic surfactant and an alkyl polyglucoside with 1.4 glucoside groups (APG). A standard fabric EMPA 217 was used for the redeposition testing. The non-ionic and anionic surfactants were used separately and in mixture in varying proportions for the washes. Sodium carbonate and sodium chloride

were used as builders. Washing was carried out at low temperature and with different water hardness.

EXPERIMENTAL

Fabric

EMPA 217, standard fabric, unsoiled wool fabric, 109g/m^2 muslin, supplied by Testmaterialien AG (Switzerland).

Chemical Products

Surfactants

Three surfactants were used for the detergent formulations. The first was the anionic surfactant sodium dodecylbenzene sulfonate, (SDBS) reagent for analysis, supplied by Sigma (purity of 80%), with average molecular weight of 348.48 g mol^{-1}. The second was a non-ionic surfactant, alkyl polyglucoside (APG) with 1.4 glucoside groups and an alkyl chain length of C_{12}–C_{14}, supplied by Cognis-Iberia S.L. under the trade name Glucopon 600 CS UP. The amount of active ingredient was 50–53% and the average molecular weight was 409.8 g mol^{-1}. The third was a fatty acid ethoxylate with 7 m.EO average (AE-7) called Synperonic A7, formerly supplied by Uniquema at Redcar (England), and now supplied by Croda (Spain), with an active ingredient purity of 100% and molecular weight of 516 g mol^{-1}.

The total concentration of surfactants was 5 x 10^{-3} M; this concentration ensured total deposition of all the carbon black on the fabric after removal of all aqueous solution by boiling. The surfactants, however, were used as mixtures. SDBS was mixed with AE-7 and APG was mixed with AE-7. For both surfactant mixtures, the molar proportions were 1:0, 0.8:0.2, 0.6:0.4, 0.4:0.6, 0.2:0.8, and 0:1.

A microemulsion was used in some formulations. The non-toxic solvent dimethyl sulfoxide (DMS) was obtained from Panreac (purity: 99%). Pure soy lecithin with a concentration of over 97%, supplied by Carlo Erba, was used as the emulsifier for the DMS. The DMS was microemulsified by mechanical energy with 2.4 g/L^{-1} soy lecithin, producing particle sizes between 50 and 200 nm. The DMS was 10% by volume in the microemulsion.

Sodium chloride (NaCl) supplied by Merck (highest purity product) and sodium carbonate (Na_2CO_3) supplied by Panreac (99.8% purity) were used as builders. The concentrations were held constant at 0.5 g/L-1 for sodium carbonate and 2 g/L^{-1} for sodium chloride.

Solid Impurity

The solid impurity was carbon black, manufactured by Columbian (Raven 1040), with a primary particle diameter of 29 nm and a surface area of 85 m^2 g^{-1}. It was dispersed in 2-propanol at a concentration of 4 mg/ml^{-1} using a vibroshaker for use as the solid impurity.

Equipment

Washing Equipment

A Launder-Ometer from Atlas Instruments (USA) was used for the washing tests.

Spectrophotometer

The reflectance of the fabric specimens was measured using a Color i7 spectrophotometer running Color iQC Standard software from X-Rite Incorporated (USA), located in Europe in Regensdorf (Switzerland). This instrument had a Xenon D65 lamp and a measurement range of 360 to 750 nm at intervals of 10 nm. The repeatability was 0.01 RMS ΔE CIELAB.

The unsoiled and soiled fabric samples were evaluated with the spectrophotometer, folding the fabric to eliminate the background effect, and each reflectance measurement was the average of four measurements with rotation of the sample through 90º after each measurement. A similar technique was used to measure the soiled samples.

Sub-micra particle size measurement

A Zetasizer Nano Z/S, ZEN 3600 from Malvern (UK) was used for sub-micra particle size measurement.

Procedures

Evaluation of Fabric Reflectance

The unsoiled fabric sample (10 x 4 cm) was evaluated with the spectrophotometer, folding the fabric to eliminate the background effect, and each reflectance measurement was the average of four measurements with rotation of the sample through 90º after each measurement.

Redeposition Test Method

Redeposition was carried out according to the specifications of ISO Standard 105-106 /DAD 1. The unsoiled EMPA 217 fabric was cut to 10 cm x 4 cm specimens. The amount of carbon black introduced in the washing was 10 mg, adequately dispersed in 2.5 ml 2-propanol. The fabric was washed in a standard Launder-O-meter apparatus (Atlas

Instruments, USA) with 500 ml containers and standard agitation. The water used for the washing solutions was commercial distilled water passed through a Milli-Q reverse osmosis apparatus to assure almost zero conductivity. The hardness of this water was adjusted to 20ºhf, 30ºhf, and 40ºhf by adding magnesium chloride ($MgCl_2.6\ H_2O$, 99% purity, Panreac) and calcium chloride ($CaCl_2$, 95% purity, Panreac) salts in molar proportions of 3:1 [11]. The bath volume was 150 ml, the wash temperature was 30ºC, and the wash time was 30 minutes. The wool samples were rinsed three times after washing and dried at room temperature (20º C).

Assessment of the Degree of Soiling After Redeposition Test

The degree of soiling was determined by the Florio and Merserau Eq. (l) [10].

$$\Delta C = \{(X_S - X_P)^2 + (Y_S - Y_P)^2 + (Z_S - X_P)^2\}^{1/2} \quad (1)$$

Where: X_p, Y_p and Z_p are the tristimulus values of the white sample before the washing and X_s, Y_s and Z_s the tristimulus values of the sample after the deposition or soiling test. The reported values are averages of four reflectance readings, the sample being rotated through 90º before each reading. The linear relationship between the degree of soiling (obtained using the Florio and Merserau equation applied to the reflectance of the fabrics) and the logarithms of the amounts of carbon black deposited (X) expressed as mg/cm^{-2} had previously been determined. (The surfactant concentration was adjusted to provide this linear relationship.) For measurement of the different amounts of carbon black deposited after redeposition test washings, the linear fits Y = 49.363 X and the correlation coefficient R2 = 0.9837 were used for quantification of the amount of carbon black in the redeposition results. Therefore, from the degree of soiling observed and with linearity obtained previously, the amount of carbon black deposited was determined.

RESULTS AND DISCUSSION

Redeposition of carbon black on wool fabric, after one washing with and without the solvent microemulsion DMS for SDBS and AE with 7 m. EO alone and their mixtures.

The results for redeposition behavior of the solid impurity (carbon black) on wool fabric obtained through one washing with the surfactants and their mixtures and builders as stated with conventional washing and the same formulations with addition of the DMS microemulsion to all the formulations tested (with soft water and with water hardness) are shown in *Figure 1* for SDBS and AE with 7 m. EO alone and with different molar proportions, and *Figure 4* for APG and AE with 7 m. EO, alone and with different molar proportions.

Figure 1 shows that the use of the DMS microemulsion mixed with the anionic (SDBS) and non-ionic (AE with 7 m. EO) surfactants and builders as indicated above, in all the proportions tested, decreased the redeposition behavior near to zero values observed in comparison with the redeposition obtained with these surfactants and the builders (conventional wash) without the DMS microemulsion, using for both mixtures soft water and water hardness of 20º hf and 40º hf for both mixtures.

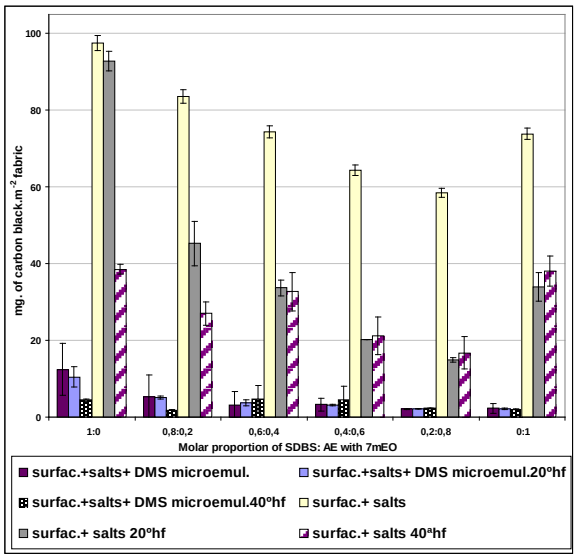

FIGURE 1. Redeposition of solid impurities (carbon black) after one washing of EMPA 217 wool fabric with ecological surfactants SDBS and AE alone and with different molar proportions, at total concentration of 5 x 10^{-5} M and builders (0.5 g/L^{-1} Na_2CO_3 + 2 g/L^{-1}NaCl) and the same ingredients plus 10% DMS in 2.4 g/L^{-1} of lecithin (average of two different test samples) with 20º hf and 40º hf water at 30º C.

Likewise, the results shown in *Figure 1* indicate, in general, that after one wash the greatest redeposition behavior was obtained with the anionic surfactant SDBS (1:0) and the lowest with the mixture of SDBS with AE with 7 m.EO (0.2:08) for mixtures of surfactants in soft water, with and without the DMS microemulsion. As for the mixtures of surfactants tested, redeposition decreased with the increase in the proportion of the surfactant AE with 7 m.EO in the mixture, giving values falling between those obtained with the surfactants SDBS and AE with 7 m.EO in the molar proportion 0.2:08 in the case of soft water and 20º hf water hardness. The redeposition results

for 20º hf and 40º hf, in general, were similar, except that SDBS alone with water of 20º hf, in general, was higher than with water of 40º hf.

Particle size of carbon black and DMS microemulsion in the washing formulations of SDBS and AE with 7 m EO

Figure 2 shows the particle size of carbon black in the different washing formulations tested in presence of SDBS and AE with 7 m.EO plus builders and DMS microemulsion. The results were similar to the variation between 351nm to 472 nm on average, with the lower value for the formulation with AE with 7 m. EO (molar proportions 1:0) and the mixture SDBS: AE with 7 m EO (0.2:0.8).

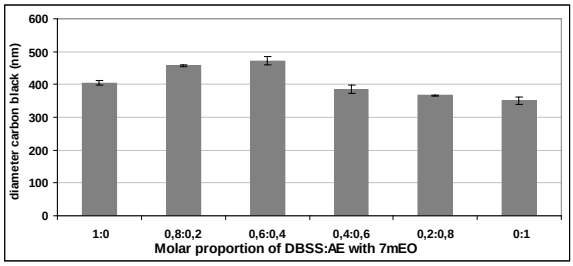

FIGURE 2. Particle size of carbon particles in the presence of SDBS and AE with 7 m. EO in the washing formulations with DMS microemulsion plus builders (inorganic salts) under the conditions indicated in *Figure 1* (soft water).

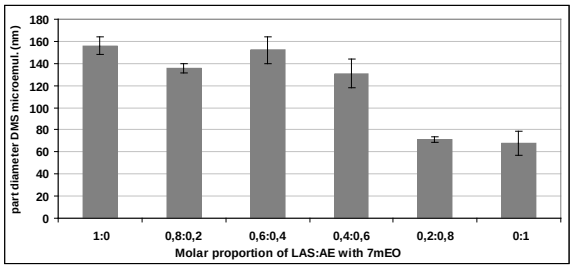

FIGURE 3. Particle size of DMS microemulsion in washing formulations of SDBS and AE with 7 m. EO and builders (no carbon black).

As shown in *Figure 3*, the particle size of DMS microemulsion in the washing formulations, with builders (inorganic salts) but without carbon black, was similar, between 135 nm and 155 nm, for the SDBS alone and the mixtures with AE with 7 m.EO (molar proportions: 1:0; 0.8:0.2; 0.6:0.4 and 0.4:0.6) and between 67 nm and 71 nm for the mixture SDBS:AE with 7 m. EO 0.2:0.8 and the AE 7 m. EO. These results for microdispersed DMS in the washing solutions were lower than for the same solutions with carbon black impurity.

Redeposition of carbon black on wool fabric, after washing with and without the solvent microemulsion DMS for APG and AE with 7 m . EO, alone and with their mixtures.

Figure 4 shows that the use of the DMS microemulsion mixed with APG and non-ionic (AE with 7 m. EO) surfactants and builders, in all the proportions tested, decreased the redeposition behavior near to zero, observed in comparison with the redeposition obtained with these surfactants and the builders (conventional wash) using soft water and water hardness of 20º hf and 30º hf.

Likewise, the results shown in *Figure 4* indicate, in general, that after one wash, in soft water and without the DMS mcroemulsion, the greatest redeposition behavior was obtained with the AE with 7 m. EO surfactant (1:0) and the lowest with the mixture of APG with AE with 7 m. EO (0.8:0.2). With regard to the mixtures of surfactants tested, redeposition increased with the increase in the proportion of the surfactant AE with 7 m.EO in the mixture, giving values falling between those obtained with the surfactants APG and AE with 7 m.EO in the molar proportion 0.8:02 and 20º hf and 30ºhf water hardness. The redeposition behavior values for the results at 20º hf and 30º hf are similar without significant difference and slightly lower than the results with soft water.

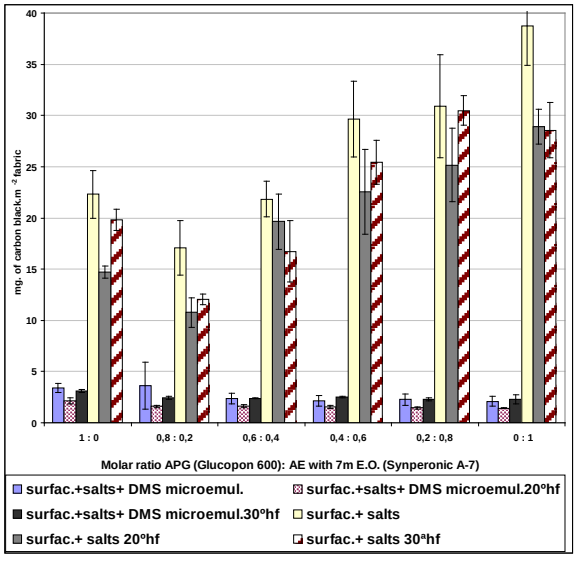

FIGURE 4. Redeposition of solid impurities (carbon black) after one washing for EMPA 217 wool fabric washed with ecological surfactants APG and AE with 7 m. EO alone and in different molar proportions, at total concentration of 5 x 10^{-5} M and builders (0.5 g/L^{-1} Na_2CO_3 + 2 g/L^{-1} NaCl) and the same ingredients plus 10% DMS in 2.4 g/L^{-1} of lecithin (average of two different test samples) with 20º hf and 30º hf water at 30ºC.

CONCLUSION

Based upon the results for the deposition of solid impurity after one washing, using the surfactants SDBS and AE with 7 m. EO and APG alone and their mixtures with the specified builders (conventional wash with salts) and the same formulation with addition of the DMS microemulsion (proposed for improvement), both with soft water and with different water hardnesses, after one washing, the following conclusions were reached:

4.1) The microemulsion of DMS mixed with the surfactants used (mixtures of SDBS with 7 m. EO and APG with AE with 7 m. EO) and builders, in all the cases, dramatically reduced (near to zero) the performance of the solid redeposition of carbon black impurity obtained for all the mixtures tested and the surfactants used.

4.2) The amount of carbon black deposited in the presence of SDBS was greater than with AE 7 m. EO (in soft water and without the DMS microemulsion), and in general, redeposition decreased with the increase in the proportion of AE 7 m. EO in the mixture for soft water and with different water hardness. In general redeposition decreased with increasing water hardness, except that for SDBS alone with water of 20º hf, it was higher than with water of 40º hf.

4.3) The particle size of microemulsified DMS in the presence of SDBS and AE with 7 m. EO with builders (without water hardness) was within the range of 135 nm to 155 nm and with carbon black in presence the same formulation with builders (salts) the average was between 351 and 472 nm.

4.4) The quantity of carbon black deposited by AE with 7m. EO was greater than with APG (in soft water and without the DMS microemulsion), and in general, the redeposition decreased with the decrease in the proportion of the AE 7 m. EO in the mixture for soft water and with different water hardnesses. With increased water hardness the redeposition values are similar without significant differences.

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