Linear Alkylbenzene Sulfonates in the Prevention of Vagrant Dye Pick-up on Polyester Textile Fabric during Laundering

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ABSTRACT

The unwanted pick-up of low levels of vagrant dyes during washing of textile fabrics can be a significant contributor to long-term polyester appearance degradation. Fabric appearance loss from pick-up of small quantities of a standard yellow dye are measured on both optically brightened and unbrightened polyester. Linear alkylbenzene sulfonate (LAS) surfactant micelles act as effective dye scavengers, reducing the level of dye pick-up by the fabric substantially. The efficacy of LAS as a dye scavenger is quantified as a function of alkyl chain length and use concentration. Dye scavenging ability per unit weight of LAS increases with increasing molecular weight and decreasing critical micelle concentration (cmc). Dye scavenging of up to 80% of the transferable dye is achieved at high LAS concentrations. Results with C_9, C_{11}, C_{13} and C_{15} single homolog alkyl chain lengths, and with several mixed chain length blends are presented.

INTRODUCTION

In laundering of the textile materials used in apparel and linens, the household wash load is normally separated to divide whites and light-colored materials from darker-colored materials. This is done for the important reason of preventing the staining of the whites or lighter colors by dyes' bleeding or transferring from the more intensely colored fabrics (1). The pick-up of even very small quantities of vagrant dyes can have a substantial detrimental effect on the visual appearance of a white fabric over time, even if the degradation during one wash cycle is visually imperceptible. This pick-up of vagrant dyes during the washing process can lead to a gradual graying and/or yellowing of the fabric, particularly when the sorting process is imperfect.

Polyester, the most common of the synthetic textile fibers, is susceptible to this type of vagrant dye pick-up, particularly when the dyes present are nonionic disperse types. Disperse dyes, by design, have very low solubilities in water but are very soluble in the organic matrix of the polyester fiber (2). The organic core of surfactant micelles can also solubilize dyes of this type, so there is a competition between fabric and micelles for the available dye (3). By solubilizing the vagrant disperse-type dye molecules inside linear alkylbenzene sulfonate (LAS) micelles, the apparent dye concentration available to the fabric is lowered and the resulting discoloration is reduced. As the micelle is acting as a dye trap, the more of the surfactant present in micellar form, and the higher the micelle concentration, the more effective its action should be. The concentration at which a surfactant begins to form micelles, i.e., the critical micelle concentration (cmc) is lowered as the hydrophobe chain length is lengthened. Formation of micelles at lower concentrations means that less surfactant is required to provide dye solubilization, or conversely, for a given weight of surfactant, more of the longer chain material will be in micellar form than a similar shorter chain length variety. Another factor involved is that longer chain lengths have more hydrophobe for solubilizing the dye per unit weight of surfactant than the shorter chain length material.

In this study, polyester swatches are washed in a typical synthetic detergent solution to which a very small concentration of a special test blend of four different selected yellow disperse dyes have been added. The degradation of appearance of the polyester is examined as a function of the concentration of LAS in the wash liquor and of the alkyl chain length of the LAS. Single homolog materials, C_9, C_{11}, C_{13} and C_{15}, as well as blended materials of average chain lengths, $\bar{C}_{11.2}$ and $\bar{C}_{13.1}$ are examined. Appearance degradation by dye pick-up is measured by determining the decrease in appearance numbers of the swatches on a colorimeter.

BACKGROUND THEORY

Dyeing of polyester fabrics is a reversible process in which high dye concentration and strong dye affinity for a fabric is used to "push" dye into the interior of the fiber (2). The reverse process occurs to a slight extent in subsequent washings, resulting in vagrant dyes in the wash solution. These dyes can attach themselves to whites or light colors causing an effect most often observed as gradual graying or yellowing after a number of washes. Because the eye is very sensitive to yellow wavelengths, only minute amounts of yellow dye result in quite easily detectable appearance degradation. In order to balance or compensate for the yellowing of fabrics, materials called fluorescent whitening agents (FWA) or brighteners have been frequently used as detergent components. These materials are actually fluorescent dyes which absorb light in the ultraviolet regions and reemit light in the visible blue region. This compensates for the blue wavelengths being absorbed by the yellowed fabric (4).

In addition to decreasing the amount of visible light reflected by a fabric by absorbing incident visible light, vagrant dyes may also absorb in the ultraviolet region. This ultraviolet light absorbed by unwanted dyes is no longer available to fluorescent whitening agents and results in less blue light being emitted. Thus, the effect is 2-fold. Unwanted dyes reduce the amount of light reflected from the fabric as well as the amount emitted by the FWA.

The effect of a dye on the appearance of a white fabric is dependent on the color of the dye. Whiteness of a fabric is subjective and appearance numbers have been devised

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to quantify whiteness as perceived by an observer. One such appearance number is given by the formula:

$$AN = R_d + 3a - 3b,$$

where R_d, a, and b are measured by a tristimulus colorimeter (5,6). The R_d value is a measure of the diffuse reflectivity of a sample whereas a and b are related to color. The appearance of a fabric can be viewed in a 3-dimensional coordinate system in which the axes are black to white, red to green, and blue to yellow. The R_d value relates to the black-white axis where 0 would correspond to a totally absorbing or black surface whereas 100 would correspond to perfectly diffuse reflecting or white surface. The a value relates to the redness or greeness of the surface with red having a positive effect and green having a negative effect on appearance. Likewise, b is a measure of the amount of the blue or yellow in the surface. Blue has a positive effect on appearance whereas yellow has a negative effect.

Trace amounts of blue or red dyes can actually have a positive effect on appearance whereas yellow or green have a negative effect. Mixed dyes eventually result in gray, which is also negative. Thus, low level pick-up of various color dyes eventually will result in a graying. It is this appearance loss due to vagrant dye pick-up with which this work is concerned.

Micelle Formation

When the concentration of a surfactant in solution reaches a certain critical level, the molecules begin to orient themselves into dynamic assemblies called micelles. The concentration at which this begins to occur is the cmc. The interior of the micelle is liquid-like and generally composed of the hydrophobic organic tails of the surfactants whereas the hydrophilic head groups are oriented to the exterior, i.e., toward the aqueous phase. This hydrophobic micelle interior can readily solubilize the nonionic disperse-type dyes generally used for synthetic textiles such as polyester. In fact, solubilization of dyes of this type has been used in the laboratory to study the formation of micelles (3). In the wash solution, the hydrophobic micelle interior is in competition with the hydrophobic fiber for the dye. Available surface areas and rates of transport across the interfaces influence the process.

Adsorption by solids is an alternative to micellar adsorption of dye if sufficient surface area is available. Activated carbon, e.g., is very effective in adsorbing dyes from the wash bath in the absence of textile fabrics. But, use of carbon black obviously poses a problem as a detergent ingredient because it is also a very effective soiling agent.

EXPERIMENTAL DETAILS

Linear Alkylbenzene Sulfonates (LAS)

The single homolog C_9, C_{11}, C_{13} and C_{15} samples were laboratory samples. Alkylbenzenes were first prepared by the Friedel-Crafts reaction of linear monoolefins with benzene in the presence of HF catalyst and then sulfonated. Monoolefins of 9, 11, 13 and 15 carbons were used to prepare their respective LAS samples. Samples with average carbon numbers of $\overline{C}_{11.2}$ and $\overline{C}_{13.1}$ were prepared by sulfonating commercial alkylbenzenes having mixed length alkyl sides chains with average chain lengths of 11.2 and 13.1 carbons.

Fabric

The polyester test fabrics were swatches of Style 760, 100% Spun Dacron 54W obtained precut to 4 in. × 6 in. from Test Fabrics, Inc. The swatches were prewashed twice with a commercial detergent formulation in a standard automatic washing machine and then dried in a standard commercial dryer. The average appearance number of the prewashed swatches was 101.4 ± 0.32.

Test Dyes

Commercial samples of several disperse yellow dyes were screened for their effects on polyester. Dyes showing the greatest effect were chosen so that 4 different chemical classes were represented. The pure dyes were obtained by extraction from the commercial dyes and purified by recrystallization. The Color Index number, chemical type, and structure (where available) of the selected dyes are given in Table I (7).

Only yellow dyes were chosen for 2 reasons. Appearance number is very sensitive to yellow and thus measurable differences may be seen in one test cycle. The dose level of dye used in each test was chosen to result in a total loss of ca. 10 appearance numbers in a single test cycle when a typical surfactant level of about 300 ppm is used. The use of only yellow dyes minimizes offsetting or competing effects if several different colors were used.

The stock dye solution was prepared by dissolving equal weights of the 4 dyes in acetone to give a solution containing 6.25×10^{-4} g, total dye/mL. The addition of 50 μL of this stock dye solution to the 1-L wash bath results in an overall dye concentration of 31.25 ppb.

Equipment

The "washings" were done in a United States Testing Company, Inc., (Hoboken, NJ) Terg-O-Tometer. The appearance numbers of the swatches were calculated from R_d, a and b values read on a Gardner XL-23 Tristimulus Colorimeter, Gardner Laboratory, Inc., Bethesda, Maryland.

Wash Solutions

The wash solutions were prepared by combining aliquots of stock solutions of the various ingredients and then adjusting the volume to 1 L. In addition to the added detergent ingredients, the water hardness was adjusted to give a total water hardness of 150 ppm $CaCo_3$ or equivalent. The Ca-to-Mg ratio was 3:2.

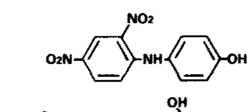
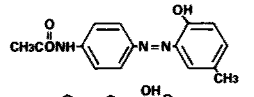
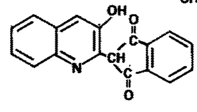
The resulting wash bath contained 360 ppm sodium tripolyphosphate, 90 ppm RU silicate, 150 ppm sodium carbonate, 622.5 ppm sodium sulfate, 7.5 ppm carboxymethylcellulose and from 0 to 3,000 ppm LAS. At a typical use level of 270 ppm LAS, the overall simulated standard detergent concentration was 0.15%.

Procedure

The 1 L of the detergent stock solution containing 100-

TABLE I

Dyes Used in Test Solution

COLOR INDEX NUMBER	CHEMICAL TYPE	CONSTITUTION NUMBER	STRUCTURE
C.I. Disperse Yellow 1	Nitro	10345	
C.I. Disperse Yellow 3	Azo	11855	
C.I. Disperse Yellow 54	Quinoline	47020	
C.I. Disperse Yellow 56	Diazo	—	X - N = N - Y - N = N - Z

3,000 ppm LAS is added to the Terg-O-Tometer bucket at room temperature. The water bath in the Terg-O-Tometer is maintained at 50 C and the temperature of the wash liquor is 45-47 C at the end of the cycle. After the wash liquor is added, the agitator (100 rpm) is started and 50 μL of concentrated dye solution is injected to simulate a 31-ppb level of vagrant dye. After 15 sec, 4 100% PE swatches are added and "washed" for 15 min. The swatches are rinsed in tap water and finally dried in a commercial dryer. The R_d, a and b are read on the Gardner with the UV filter out, and the appearance number is calculated.

RESULTS

The appearance numbers of the polyester swatches washed in liquors containing added disperse yellow dyes and various levels of alkylbenzene sulfonate are given in Table II. The original appearance numbers of the prewashed swatches averaged 101.4. This number drops to 86.5 after only one washing in a wash bath containing 31.25 ppb of disperse yellow dyes when alkylbenzene sulfonate was omitted from the detergent formulation. The results from the various LAS samples are summarized graphically in Figures 1 through 4, in which the appearance numbers of the swatches are plotted as a function of the LAS concentration or the alkyl chain length. For all samples, the efficacy in preventing dye pick-up increases with increasing molecular weight at any surfactant concentration. The blended chain length samples fall in positions near those expected for comparable homolog samples.

DISCUSSION

Disperse dyes have very low solubility in water but have very high affinity for and solubility in polyester. The penetration of the dye into the fiber is slow at typical wash temperatures but repeated exposure to washer and dryer cycles will allow the dye to migrate into the fiber. Once the dye penetrates the fiber, it is virtually impossible to remove during washing. It is, therefore, important that the dye be prevented from reaching the fiber surface in the first place. One way to do this is by providing a competing region of high dye affinity. Because we are initially concerned about surface affinity of the dye for the polyester, it would be desirable for the competing material to be of high surface area. (Activated carbon works well as a competing surface, but has obvious problems as a detergent ingredient.) As surfactant micelles have a very high surface-to-volume (and weight) ratio and the hydrophobic interior has a high affinity for the dyes, the effectiveness of surfactant micelles in this task seemed worth studying. In our test conditions (100-3,000 ppm LAS and about 30 ppb dye in the wash liquor) the ratio of micelles to dye molecules is of the order of 30-1,000, assuming ca. 100 surfactant molecules/micelle.

A plot of the appearance numbers of test swatches after washing in various levels of single homolog LAS is shown in Figure 1. The general shape of these curves is typical of properties related to the formation of micelles (8) but perhaps less sharp than properties measured more directly. It can be seen most clearly with the C_{11} data that little change or effect is observed upon increasing the concentration from 0 to ca. 300 ppm, but above this concentration, the effect from increasing surfactant concentration begins to climb rapidly before once again flattening as the upper limit of performance is approached. The lower portion of the type of performance curve is best exemplified by the C_9 curve whereas the C_{13} and C_{15} curves demonstrate the mid-to-upper regions of such curves.

This family of curves illustrates 2 main points. The first is that, for a given concentration of LAS, the higher molecular weight homolog will out-perform a lower molecular weight homolog in preventing pick-up of disperse dyes by polyester. The second point is that high levels of dye pick-up prevention can be achieved at sufficiently high LAS levels, regardless of molecular weight. In Figure 2, the data for the $\overline{C}_{11.2}$ and $\overline{C}_{13.1}$ LAS are added to show how the mixed chain length LAS performs relative to the single chain length. The mixed chain length LAS samples show a slight performance advantage over single homolog LAS. A more in-depth study of the effects of single homolog blending, isomer distribution in single homologs and in mixed isomers is of interest, but beyond the intended scope of this study.

Figure 3 presents the data differently. In this figure, the appearance numbers of the swatches were plotted vs the alkyl carbon number for different LAS concentration. This

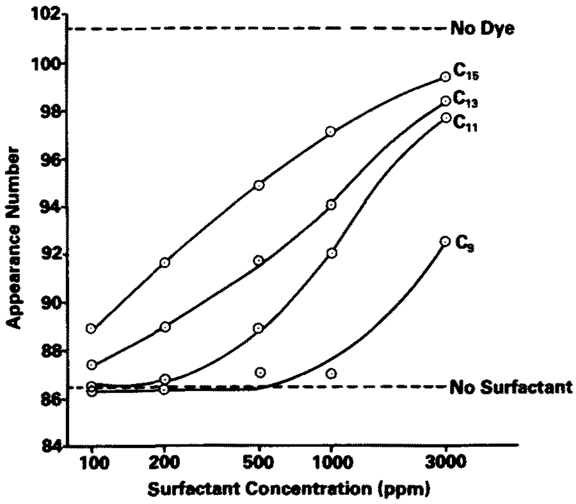


FIG. 1. Appearance protection by increasing levels of pure LAS homologs.

TABLE II

Appearance Numbers of Swatches after Dye Pick-up

Alkyl chain length	LAS in solution (ppm)					
	0	100	200	500	1000	3000
C_{15}	86.5	88.9	91.6	94.8	97.1	99.4
C_{13}	86.5	87.4	89.0	91.8	94.1	98.4
C_{11}	86.5	86.5	86.8	88.9	92.1	97.7
C_9	86.5	86.4	86.4	87.1	87.0	92.5
$\overline{C}_{11.2}$	86.5	86.8	86.8	90.0	93.4	98.1
$\overline{C}_{13.1}$	86.5	88.4	90.1	92.4	94.7	98.5

Initial AN of swatches before washing in the presence of yellow dyes averaged 101.4 ± 0.32.

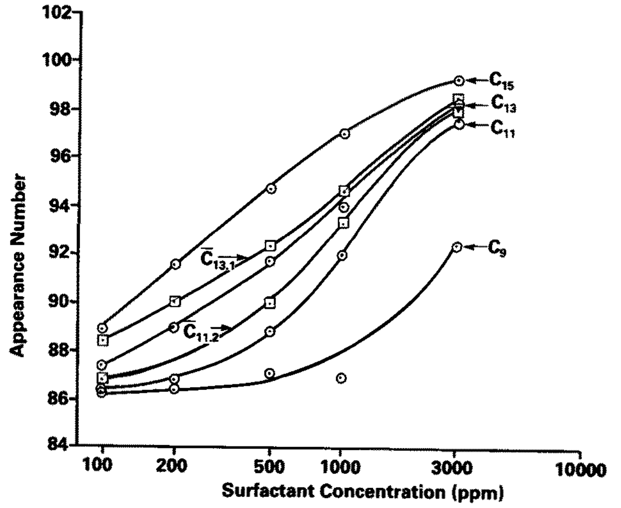


FIG. 2. Appearance protection by increasing levels of pure and mixed LAS homologs.

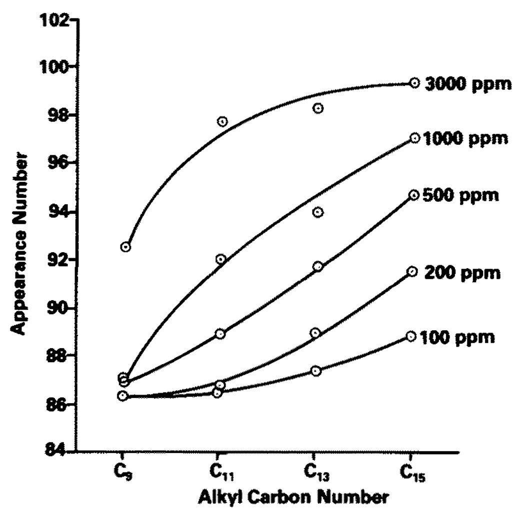


FIG. 3. Appearance protection as a function of average alkyl carbon number.

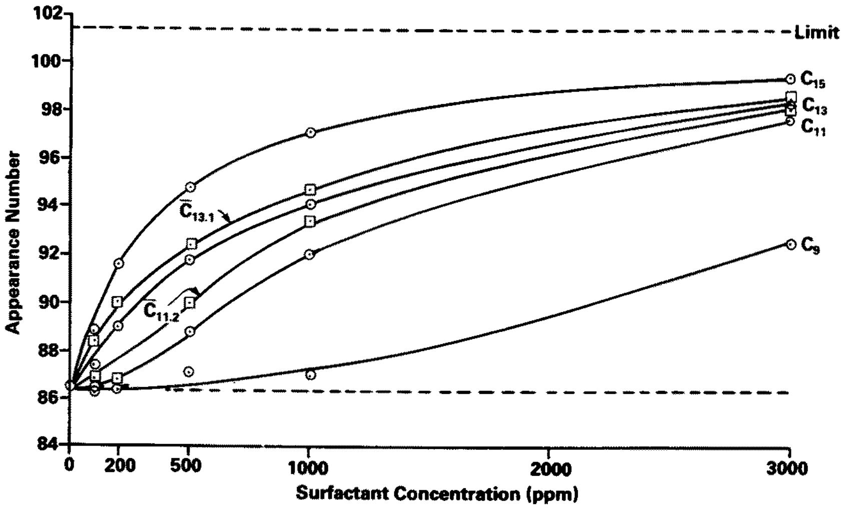


FIG. 4. Appearance protection as a linear function of surfactant concentration.

format emphasizes the increased performance observed as the alkylcarbon number or molecular weight increases.

For more practical considerations, the performance or appearance number is plotted vs concentration on a linear scale in Figure 4. Presenting the data in this manner emphasizes the steep slope of the performance curves of some of the higher molecular weight materials in the reasonable use level range of 200-500 ppm. Because appearance number changes of about ±2 are visible to the eye, there can be a decidedly detrimental effect from surfactant and/or detergent underuse in situations where pick-up of trace dyes is possible. It also illustrates more clearly the diminishing returns for use of surfactant concentrations beyond 1,000 ppm.

In summary, the efficiency of the LAS on a weight basis is favored by the higher molecular weights. This is particularly evident in the curves of the single homolog materials (Fig. 1), where at 1,000 ppm, C_9 LAS has shown little effect whereas C_{15} LAS has prevented almost 75% of the possible appearance loss. Viewed another way, C_{15} LAS at ca. 200 ppm is as effective as C_9 LAS at 3,000 ppm at keeping the dyes from the fabric. Of course, this is an oversimplified test and many other factors must be balanced in the choice of LAS molecular weight and use level, but the potential for substantial improvement in the vagrant dye problems has been shown. Alternative approaches to the dye problem, including the use of added bleaching agents, are also possible.

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