

## SURFACTANTS IN TEXTILE CONSERVATION

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**ABSTRACT** - In order to select surfactants that are suitable for conservation, it is first necessary to understand how these agents interact with soils and with textile materials under the conditions of treatment. The possibility that some surfactants may irreversibly adsorb onto fibers must be considered. Several types of surfactants should be available in the conservation laboratory to permit the removal of a variety of soils occurring on different substrates. Multiple washes with a succession of different formulations may result in more efficient cleaning and rinsing.

### 1. EVALUATING SURFACTANTS

Since our purpose is preservation, we aim to minimize damage to textiles during treatments. With this in mind, conservation practice seeks to identify certain parameters to govern the conditions for wet cleaning. These parameters are derived from the physical and chemical properties of textile materials. For example, wool and silk are washed in the presence of weak acids at pH values within their isoelectric range, approximately 4.5-5.5. Cotton is washed in the presence of weak bases at pH values between 7 and 8.5. Temperatures of bath and rinse vary from ambient to about 40° C. Mechanical action is kept to a minimum. It is also imperative that cleaning agents should not react irreversibly with the substrates being cleaned. Operating within limits, which often narrow considerably depending upon the condition of the textile, the conservator strives to optimize the efficiency and effectiveness of soil removal. The suitability of surfactants for conservation wet cleaning, then, is judged by their performance within these prescribed limits. Furthermore, since conditions vary from textile to textile (or from one part of a textile to another), a variety

of surfactants are required so that the most appropriate formulation can be utilized for each unique situation.

In spite of a wealth of data on surfactants and detergency available since the 1930's, very few studies have addressed directly the issues that are vital to conservation. For those that have done so, it is difficult or impossible to extract useful information by comparing results and conclusions, since experimental conditions vary widely from study to study.

For the past twenty-five years or so, detergency and other interfacial studies have utilized radioactive tracers to directly measure adsorption and desorption phenomena. Previous studies used spectrophotometric techniques that measured differences in light remission between soiled and cleaned textiles, in order to evaluate the effectiveness of detergency. However, the results of many of those past experiments are now questioned, since it has been found that the delta of remission often does not correlate with the degree of soil removal. One must therefore be cautious when considering the results of such studies (Kissa 1987b).

The properties and performance of surfactants are only valid for the experimental conditions under which they are studied. Changes in concentration, pH, temperature, mechanical action and length of treatment change the adsorption/desorption characteristics of surfactants and, as a consequence, affect their value as cleaning agents. For each surfactant there is set of factors which maximizes its performance and defines its usefulness. As these factors or combination of factors change,

the behavior of the surfactant in solution and at the interface also changes (Rosen 1995). For this reason each surfactant is limited in the type and mode of its application. Since production of sodium lauryl sulfate began in 1930, thousands of surfactants have been created, tailored to meet the wetting, detergency and emulsification requirements for specific conditions and substrates.

The comparative study of surfactants is further complicated because surfactant characteristics differ from one manufacturer to another. For instance Neodol 25-9 and Tergitol 25-L-9 are both linear primary alcohol ethoxylates with C<sub>12</sub>-C<sub>15</sub> hydrophobes and 9 moles of ethylene oxide. They are chemically identical. However, the Neodol has an Hydrophile-Lipophile Balance (HLB) of 13.3 and a cloud point<sup>1</sup> of 74° C., while the Tergitol has a lower HLB of 12.8 and a lower cloud point of 60° C. (Shell 1982). This is because surfactants are mixtures of a series of related species identified by their mean value, while the actual distribution of hydrophobic and hydrophilic chain lengths varies from product to product (Larson 1995). Similar products from different companies must be studied independently, since they are not equivalent.

## 2. CONSERVATION ISSUES

A primary concern to conservators is that textiles may undergo irreversible modification during wet treatments. Some kinds of modifications may be promoted or enhanced by the presence of surfactants. Many dyes form complexes with surfactant monomers and micelles in solution, and it is possible for weakly bound dyes and pigments to be solubilized directly from the fiber surface. Surfactants remove waxes from cotton fibers

and form complexes with the nonkeratinous gelatins of wool, facilitating their extraction (Leeder and Marshall 1982). The physical spreading forces of surfactants which loosen, lift and suspend particulates may also accelerate the separation of damaged cuticle cells from wool or a damaged primary cell wall from cotton.

Another point of concern is that the adsorption of surfactants onto textiles is not completely reversible. Since the late 1940's, several studies have demonstrated that anionic surfactants (such as Orvus) irreversibly chemisorb<sup>2</sup> onto wool and silk (Aickin 1944, Weatherburn and Bayley 1952, Holt and Onorato 1989). Alkyl sulfate and alkyl sulfonate ions react through ion exchange with positively charged amino and imino end groups. The actual number of sites available for sorption is pH-dependent, increasing with decreasing pH, but some sites are available even at high pH (Schott 1995). Arginine, lysine and histidine are particularly rich in positive groups. The isoelectric point of arginine, for example, is 12; that is, it has a net positive charge up to a pH of 12. Surfactants chemisorb less onto silk than onto wool, since fibroin, whose main constituents are glycine, alanine and serine, is not as rich in amino groups as keratin. Chemisorption of alkyl sulfates onto cotton is proportional to its protein content, most of which is located within the lumen (Mauersberger 1947). With longer washing times and higher concentrations, surfactants penetrate into the cells of wool cortex, and into the lumen and the amorphous regions of cotton fibers. Most of the surfactant, whether anionic or nonionic, which has absorbed<sup>3</sup> into the internal volume of the fiber is not removed under practical washing conditions (Freeland et al. 1985).

It is difficult to estimate the relative contributions of chemisorption and physical adsorption to the total adsorption of surfactants onto wool, except theoretically. It has been observed that sodium lauryl sulfate (Orvus) can sorb onto wool at a pH below the isoelectric point to the extent of twenty-five to thirty percent of the dry weight of the fiber. At pH 7 and 25° C., this adsorption is five to seven percent on the weight of the fiber at equilibrium, however it takes a couple of weeks at this temperature for equilibrium to be achieved (Griffith and Alexander 1967; Zahn et al. 1967). The effectiveness of rinsing depends both upon the conditions under which the surfactant is adsorbed and the conditions of the rinse. Very few studies have been conducted on the desorption of surfactants. Physically adsorbed (hydrophobically bonded) surfactant can be eventually completely rinsed, given enough time and fresh water. However, little or none of the chemisorbed surfactant will be rinsed, even at high pH and at the boil (De Boos 1995).

Hardness ions also contribute to surfactant residues on textiles. This is an important consideration even if deionized or softened water is used, since soil is a significant source of these ions. (The first cleaning of many ethnographic textiles, for instance, may result in initial hardness levels in excess of 500 ppm.) Calcium ions, which are present in most soils, utilize their double valences to form bridges which bind anionic surfactants to negatively charged substrates. Calcium forms salts with anionic surfactants. These salts (calcium alkyl sulfates and sulfonates) have Kraft points<sup>4</sup> that are generally higher than the temperatures normally employed in conservation wet cleaning. This results in the precipitation of surfactant onto textiles. The calcium salt of sodium lauryl sulfate for instance, is insoluble below 50° C (Falbe 1987).

Are surfactant residues on textiles harmful? The answer is yes. Sulfated and sulfonated surfactants ultimately biodegrade to CO<sub>2</sub>, water and sulfuric acid (Wentz 1983). Sulfuric acid depolymerizes keratin, fibroin and cellulose by scission of the main chains at the peptide and glucosidic linkages.

### **3. SOME CHARACTERISTICS AFFECTING SURFACTANT SELECTION**

Generally speaking, surfactant affinity for the textile surface increases as the size of the hydrophobe increases and the length of the hydrophilic head group decreases. The presence of a benzene ring, as in alkyl benzene sulfonates and alkyl phenyl ethoxylates (Triton X-100, Synperonic N, Igepal 630) increases the strength of hydrophobic bonding, making rinsing more difficult (Yang 1995). Higher temperatures increase the rate of adsorption for both nonionic and anionic surfactants; however, equilibrium adsorption is greatest at lower temperature for both types. The adsorption of nonionic surfactants is not affected significantly by pH and electrolyte; however, anionic surfactants adsorb more with decreasing pH. Electrolytes depress the electric double layer at the liquid/solid interface, thereby increasing the adsorption of anionic surfactants. Anionic surfactants adsorb rapidly, but desorb slowly. Nonionic surfactants adsorb slowly, but desorb rapidly (Jakobi 1987; Rosen 1989).

### **4. SOME PRACTICAL CONSIDERATIONS**

Ideally, protein fibers should be washed with nonionic surfactants in the isoelectric region.

Cellulosic fibers can be washed with both anionic and nonionic surfactants, but anionics should be used only for brief wash times.

For an anionic surfactant, the best choice, in my opinion, is an ethoxylated alkyl sulfate having an alkyl chain length of  $C_{12}$ - $C_{15}$  and 2-3 mols of ethylene oxide. Sodium ethoxy sulfate is insensitive to a wide range of pH. It is highly soluble and, therefore, easily rinsed. Its detergency at decreasing concentrations and increasing water hardness is greater than linear alkyl benzene sulfonate and sodium lauryl sulfate (SLS) (Linfield 1976; Stupel 1977). The calcium salt is soluble below 0° C. (Falbe 1987). Its critical micelle concentration (CMC) is one third that of sodium lauryl sulfate (Mukherjee 1971). Since adsorption of anionic surfactants onto cotton begins above 90% of the CMC, detergency can be achieved with smaller concentrations compared to SLS.

Other anionic surfactants which merit study are ethoxylated alkyl carboxylates and ethoxylated alkyl phosphates.

For the time being, most suitable nonionic surfactants appear to be linear primary alcohol ethoxylates and linear secondary alcohol ethoxylates. The alkyl chain length again is  $C_{12}$ - $C_{15}$ . However, two or three surfactants having the same hydrophobe, but with degrees of ethoxylation from 3 mols to 14 mols, are chosen and blended to create mixed systems with varying HLB values for different cleaning situations. A lower HLB mixture (ten to twelve) would be used for oily soil, while a higher HLB mixture (thirteen to fifteen) would be used for particulate soil. A two or three- step wash, starting with a lower HLB and ending with a higher HLB, is often a practical way to achieve the most complete cleaning and rinsing (Kravetz 1995).

Alkyl phenol ethoxylates are not considered good choices for nonionic surfactants since they

have questionable health consequences, are slow to biodegrade (Schick 1987) and are relatively more difficult to rinse (Yang 1995).

A second wash with a nonionic surfactant having an HLB of around 14 will assist in solubilizing residual surfactant, both anionic and nonionic, from the fiber surface. The addition of a chelate, such as citric acid or sodium citrate, will aid in the rinsing of insoluble calcium salts of anionic surfactants (Simion et al. 1989).

Anionic surfactants are rinsed better at higher temperatures. Nonionic surfactants rinse better at ambient temperatures (Rosen 1989).

Desorption is an equilibrium process; that is, the amount of soil or surfactant in solution will always strive to be in equilibrium with the amount on the textile (Ramey 1995) and is achieved best in a continuous flow of fresh water. If this is impractical, a high bath-to-fabric ratio is desirable with some mixing to reduce the diffusion gradient near the surface of the textile, since the time of both washing and rinsing are lengthened dramatically when the bath is stagnant (Kissa 1987a).

## 5. CONCLUSION

There are four points that I would like to emphasize:

5.1 The conditions of washing and rinsing (pH, temperature, method of handling, degree of mechanical action, length of treatment) are always determined by the preservation needs of the textile. These needs should not be subordinated to conditions that may be required for the optimum functioning of any cleaning formula.



5.2 Surfactants will be appropriate in a specific cleaning situation if a) they do not interact adversely or irreversibly with fibers, dyes and other textile components, b) their performance characteristics are not impaired by the conditions determined for the treatment, and c) they are effective for the type of soil present.

5.3 Utilizing three or four surfactants in a variety of combinations, the conservator should be able to create formulations specifically suited to most wet cleaning situations.

5.4 I believe that it is of tantamount importance that wet cleaning studies are coordinated so that experiments can be designed with uniform conditions. This will enable an organized body of knowledge relevant to conservation to be progressively assembled.

#### NOTES

1. The cloud point is the temperature at which the surfactant undergoes a change of phase, separating into surfactant-rich and surfactant-lean phases (thus turning the solution cloudy). Non-ionic surfactants exhibit a temperature dependence that is the inverse of most substances: as the temperature of a solution increases, the solubility of most non-ionic surfactants decreases. Detergency of organic soils is generally greater at temperatures in the vicinity of the cloud point.

2. Adsorption of surfactant onto a substrate is a complex process and usually involves several mechanisms operating at the same time. Chemisorption occurs when the charged head group of the surfactant molecule interacts with a group of opposite charge in the substrate (as in ion exchange, ion pairing, acid-base interactions and hydrogen bonding). Physical adsorption occurs when the hydrocarbon tail group of a surfactant monomer adsorbs onto a substrate due to the action of London-Van der Waals dispersion forces and hydrophobic bonding.

3. Though sounding alike, absorption and adsorption refer to two different phenomena. Absorption occurs when the absorbent passes through a surface boundary or membrane into the internal volume of a substrate. During adsorption, molecules of the adsorbent are brought into close contact with a surface or interface.

4. The Kraft point is the temperature below which an anionic surfactant exists as a crystalline solid in equilibrium with free monomers. Micelles cannot form below the Kraft point. Above this temperature solubility increases dramatically. For example, the Kraft point of SDS is about 10 degrees C. At 12 degrees C solubility is .02%. This increases to .2% at 16 degrees C and to .3% at 17 degrees C.

#### REFERENCES

Aickin, R.G. 1944. The Adsorption of Sodium Alkyl Sulphates by Wool and Other Fibers. *Journal of the Society of Dyers and Colourists*, 60:60-65.

De Boos, Allan. July 1995. CSIRO, Melbourne, Personal communication, Internet.

Falbe, J., ed. 1987. *Surfactants in Consumer Products*. Springer-Verlag, New York. 134-137.

Freeland, G.N., Guise, G.B., and Russell, I.M. 1985. Sorption and Analysis of Some Nonylphenol Ethoxylate Surfactants on Wool. *Textile Research Journal*. 55(6):360-362.

Griffith, June, and Alexander, A.E. 1967. Equilibrium Adsorption Isotherms for Wool/Detergent Systems, Part I. The Adsorption of Sodium Dodecyl Sulfate by Wool. *Journal of Colloid and Interface Science*. 25:311-316.

Holt, L.A., and Onorator, J. 1989. Substantivity of Various Anionic Surfactants Applied to Wool. *Textile Research Journal*. 653-657.

Jakobi, Gunter, and Lohr, Albrecht. 1987. *Detergents and Textile Washing*. New York: VCH. 49-59.

- Kissa, Erik. 1987a. Kinetics and Mechanisms of Soiling and Detergency. *Detergency - Theory and Technology*, Cutler, W. Gale, and Kissa, Erik, eds. Surfactant Science Series. New York: Dekker. 20:225-260.
- 1987b. Evaluation of Detergency. *Detergency - Theory and Technology*, Cutler, W. Gale, and Kissa, Erik, eds. Surfactant Science Series, New York: Dekker. 20:58-78.
- Kravetz, Lou. April 1995. Shell Development Company. Personal communication.
- Larsen, Eric. July 1995. Internet. Personal communication.
- Leeder, John D., and Marshall, Robert C. 1982. Readily-Extracted Proteins from Merino Wool. *Textile Research Journal*. 52(4):245-248.
- Linfield, Warner. 1976. *Anionic Surfactants - Part I*. Surfactant Science Series. New York: Dekker. 7:135-217.
- Mauersberger, Herbert, ed. 1947. *Matthews' Textile Fibers*. New York: Wiley and Sons. 269.
- Mukerjee, Pasupati, and Mysels, Karol. 1971. *Critical Micelle Concentration of Aqueous Surfactant Systems*. National Bureau of Standards National Standard Reference Data Series, NSRDS-NBS 36. Washington, D.C.:U.S. Govt. Printing Office. 110.
- Ramey, Kirk. May 1995. Shell Development Company. Personal communication.
- Rosen, Milton. 1989. *Surfactants and Interfacial Phenomena*. New York: Wiley and Sons. 363-389.
- Rosen, Milton. May 1995. Surfactant Research Institute. Personal communication.
- Schick, Martin. 1987. *Nonionic Surfactants - Physical Chemistry*. New York: Dekker. 800.
- Schott, Hans. April 1995. Temple University School of Pharmacy. Personal communication.
- Shell Chemical Company. 1982. *Properties Guide - NEODOL Ethoxylates and Competitive Nonionics*. Houston. 10.
- Simion, Frederick et al. 1989. Fabric Rinse Composition to Remove Surfactant Residues. U. S. Patent. No. 4,828,750. May 9, 1989.
- Stupel, H. 1977. The Application of Primary Alcohol Ethoxylates in Laundry Detergents. *Technical Bulletin sc:173-77*. Houston: Shell Chemical Company.
- Weatherburn, A.S., and Bayley, C.H. 1952. The Sorption of Synthetic Surface-Active Compounds by Textile Fibers. *Textile Research Journal*. 797-804.
- Wentz, Manfred. 1983. University of Wisconsin. Personal communication.
- Yang, Prof. May 1995. Institute of Textile Technology, Charlottesville. Personal communication.
- Zahn, H., Stein, W., and Blankenburg, G. 1967. Influence of Tensides on the Mechanical and Absorption Properties of Wool Fibers. *Textile Research Journal*. 37(8):702.
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# CONTACT CLEANING OF TEXTILES

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**ABSTRACT** - This paper describes the development and use of contact cleaning at the Textile Conservation Workshop. The techniques of water application and removal and materials used are detailed. Also covered are the types of textiles treated in this manner. Descriptions of modifications illustrate the versatility of the method. Some explanation of the mechanisms at work is provided, along with some cautionary notes.

## 1. INTRODUCTION

Contact cleaning was developed at the Textile Conservation Workshop (TCW) over a period of several years beginning in 1992. We wanted to treat some textiles with water, but needed more control of both wetting and drying than is possible with traditional immersion and drying methods. Although the suction table/disk is an alternative, the extent of soiling, dimensions, or other physical features frequently reduce the viability of these methods.

At the TCW, we have treated a wide range of soiled textiles using contact cleaning methods. It has proved successful on water-stained crewel-work, bleeding dyes, ink spots, and general discoloration and stains.

We define success in contact cleaning according to the same criteria as successful in wet cleaning. Soil is removed; fibers are re-hydrated; hand, smell and appearance of the object is improved.

## 2. EVOLUTION OF THE TECHNIQUE

Our method evolved from a belief that the blotting techniques used for simple testing and spot cleaning could be expanded. We noticed that during the testing prior to wet cleaning,

individual stains were removed more completely than during full scale wet cleaning. This was despite the fact that we test with the same solution percentages, and at roughly the same temperature as when we wet clean. This suggested that techniques of water application and drying were as important as detergent and temperature. We wondered whether repeated wetting during testing caused swelling and rehydration of fibers, and the solvated soils were then drawn out by the capillary action of the blotting process.

Added to this was Kathy Francis's paper on drying techniques. She suggested that control could be maximized through wicking and blotting. We started to think that textiles previously considered ineligible for treatment with traditional aqueous methods might be treated with careful control of water application and removal (Francis 1992).

We began to experiment by swabbing soiled areas with water and using cotton flannel as an underlayer. Acid-free blotters were used to extract soils from the top of the textile. As we found ourselves treating larger and larger areas, applying water with a swab became impractical and we began careful use of a plant mister or sprayer. Similarly, blotters gave way to using flannel both above and below the stained area.

## 3. METHOD

### 3.1 EQUIPMENT

Contact cleaning requires simple, easily accessible equipment. We use undyed cotton flannel sheeting, acid-free blotters, swabs, plant misters, a fan, a hair dryer, mylar, and softened