THE CHEMICAL INTERACTION OF SURFACTANTS WITH FIBERS, ESPECIALLY SILK

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ABSTRACT - Without a visually apparent alteration of the silk, anionic surfactants like Orvus Paste or Orvus Liquid are adsorbed onto the fiber of silk. Fabric composition is affected. Comparisons of adsorption for different fibers will be reviewed, especially with nonionic and anionic surfactant solutions. The importance of this data in developing treatment programs for silk and mixed fiber textiles (embroideries, tapestries) is discussed. The purpose of this presentation is to provide the practicing textile conservator with data from research and from experimental confirmation. Keywords: anionic, nonionic, wet cleaning, surfactant, silk, adsorption.

1. INTRODUCTION

In the past textile conservators and conservation scientists have focused on a variety of issues associated with the use of soaps and detergents for cleaning antique textiles. Among those issues are the type of cleaning agent, the use of auxiliary agents, the effect of water hardness, the type of soiling, the degree of cleanliness achieved, and the most appropriate formulation (Rice; Hofenk de Graaff, 1968,1980,1982; Ewer and Randolph). In addition, there is another important factor to consider: the chemical interaction of the surfactant with textile fibers.

It is this last area of research, specifically the effect of sodium lauryl sulfate on silk, that is the focus of our current research project. This paper will provide some context for current experiments and will suggest some general concerns regarding textile wet-cleaning.

Conservators who have wet-cleaned tapestries or carpets may have observed the amount of soap or surfactant residue that appears when an antique textile is first submerged in water. Other conservators or conservation scientists may have noticed a difficulty in rinsing out the soap or surfactant from silk samples with deionized water. Some older conservators were trained to "sour" the final rinse with acetic acid to reduce the level of soap redeposition or precipitation. These phenomena are the results of the chemical interaction of the cleaning agent with the textile fibers during wet cleaning.

Because textile fibers are chemically so very different - cellulosic like cotton or flax, protein like silk or wool, hydrocarbon like polypropylene or polyethylene (Figure 1) - it is not surprising to us that the different fiber substrates adsorb different classes of dyes or that they react to acid and bases differently, just as they also have different mechanical properties. Nevertheless, the general characteristics of working properties and of soiling, of logistic considerations, have led textile conservators towards a certain uniformity in cleaning formulae for antique, natural fiber fabrics.
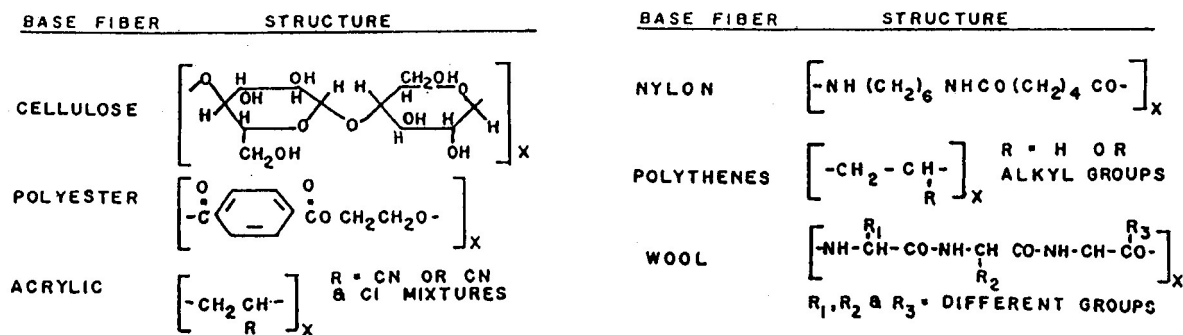

Figure 1. Chemical Structure of Major Fibers

2. HISTORY

Principal among surfactants used in North America today is sodium lauryl sulfate--Orvus WA Paste--recommended over a generation ago to an American textile conservator by a senior member of Procter and Gamble. Sodium lauryl sulfate or sodium dodecyl sulfate has twelve carbons. It belongs to the class of surfactants known as linear alkyl sulfates, made by reacting a fatty alcohol with sulfuric acid and the result with sodium hydroxide (caustic soda):

$$C_{11}H_{23}CH_2OH \xrightarrow{H_2SO_4} C_{11}H_{23}CH_2OSO_3H \xrightarrow{NaOH} C_{11}H_{23}CH_2OSO_3^- Na^+$$
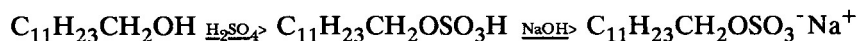
It has a molecular weight of 288, a critical micelle concentration of 0.01 mole/liter or 2.8 grams/liter. This is a foamy surfactant with good cleaning properties, even in hard water. It is the basis of many shampoos and detergents (Trotman; Moffatt; Morrison and Boyd; *Orvus*). This particular synthesis of linear alkyl sulfates was developed in the years leading up to World War II (Cahn and Lynn).

Later, Orvus was described in an early Procter and Gamble brochure as having distinct advantages: stable to acids, bases, salts, hard water; compatible with chlorine bleach, lime soaps (meaning calcium sensitive soaps), and--unlike natural soaps--unable to turn rancid. Its commercial use was a part of the post-World War II revolution in organic chemistry (Cahn and Lynn; *Orvus*).

3. REVIEW OF LITERATURE

This revolution did not go unnoticed by textile technologists, textile scientists. Studies on surfactants--on surface active agents--appeared in the 1950's and 1960's. An early article describes the adsorption of linear alkyl sulfates on wool appears in March, 1944. R.G. Aickin found that up to 2.5% owf (on weight of fabric) of sodium alkyl sulfate was retained by wool fibers under neutral pH conditions (Figure 2).
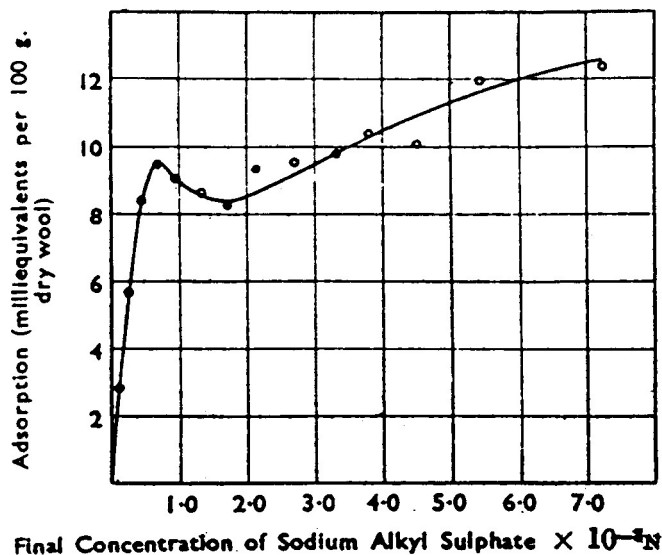

Figure 2.   Graph of Final Concentration of Sodium Alkyl Sulfate vs. Adsorption for wool. After Aickin, 1944a,b.

He likened the alkyl sulfate ion to a colorless dye. He differentiated this absorption with that typical of soaps, still used at that time for textile cleaning:

The sodium alkyl sulphates are adsorbed by wool from neutral solutions to a very

much greater extent than soap. In the latter case the amount of oleic acid adsorbed decreased with increasing concentration of sodium oleate...the adsorption of soap by wool appears to be mainly a removal of the alkali of the soap by reaction with the carboxyl groups of the wool, with consequent deposition of fatty acid upon the fibre. The adsorption of the anionic detergents of the sodium alkyl sulphate type is of a different nature, in that it increases with increasing concentration of the detergent until a critical concentration is reached. After this point there is a temporary decrease followed by a nearly constant adsorption (Aickin, 1944b).

After World War II, Weatherburn and Bayley found cotton, viscose rayon, nylon also sorbed surface active compounds from aqueous solution. Cationic compounds were adsorbed the most, nonionic, the least (Weatherburn and Bayley).

Perhaps most surprising is the range of adsorption among fiber types--how distinctly a particular fiber responds to a class of surfactants (Figure 3). This chart compares the length of the non- polar hydrocarbon chain on linear alkyl sulfate with adsorption by fiber type; the vertical axis shows the amount of adsorption. The C-12 sodium alkyl sulfate is adsorbed by wool in solution--at nine or ten times the level it is adsorbed by cotton.
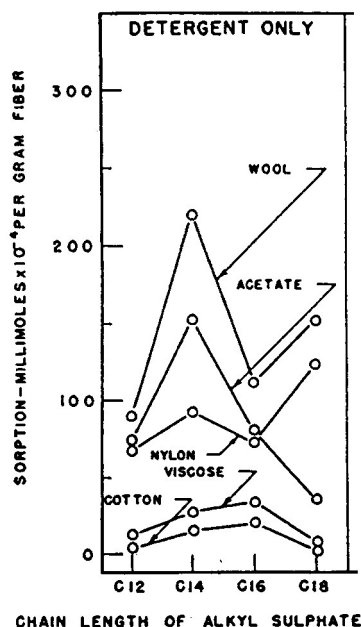

Figure 3.   Sorption of Sodium Alkyl Sulfate by various Fibers. Graph of Chain length vs. Sorption. After Weatherburn and Bayley.

This means that the surfactant is being taken up by the fiber itself--like an acid dye. As some CSIRO researchers concluded in a 1992 review of this adsorption phenomenon, anionic surfactants are bound to the wool fiber:

Under normal wool dyeing conditions, anionic surfactants show good substantivity to wool. The factors that influence this are liquor ratio, length of surfactant side-chain, and pH. Greater than 95% exhaustion or retention of surfactant can be obtained at pH 6 for most surfactants at low liquor levels. The longer chain length surfactants show greater substantivity. (Holt et al.)

However, altering the type of surfactant or the pH may produce other difficulties. For example, cationic surfactants (with a positive charge) are also adsorbed by wool fibers and can induce yellowing on cellulosic fabrics (Figure 4).

Nonionic surfactants produce an entirely different set of sorption characteristics (Figure 5). Nonionics are adsorbed by cotton more than an anionic like sodium lauryl sulfate, although wool has less adsorption with nonionics surfactants. A 1985 study found a 0.4% owf concentration even after thirty minutes and two rinses (Figures 6,7). Those authors were concerned that the levels and effects of nonionics on wools were not being evaluated, but could affect wet processing operations:

> Processed wool generally contains small amounts of nonionic surfactants as a consequence of their ready absorption onto wool from aqueous processing operations, e.g., as detergents in scouring; as surfactants in carbonizing, dyeing, milling, setting or other treatments; and as emulsifiers (often around 5% by weight) in carding, spinning and other processing oils. In spite of this ubiquity, nonionic detergents on wool are usually ignored or considered to be inert. (Freeland et al.)

As regards pH, the alteration of acidity or alkalinity is not a panacea for anionic surfactants according to the early study by Weatherburn and Bayley (Table I). It does not produce radically different results for wool (see the top third of the chart) and its use for cotton with a nonionic is questionable, since the nonionic surfactants adsorb into cotton categorically more than a comparable anionic.

Table I. Effect of pH on Sorption.
After Weatherburn and Bayley.

Compound	Fiber	Sorption ($mM \times 10^{-4}/g$.) Acid solution	Alkaline solution
Sodium lauryl sulfate	Cotton	11	8
	Viscose	8	1
(3.0 mM/l.; 50°C)	Acetate	83	56
	Nylon	125	68
	Wool	140	139
Sodium myristyl sulfate	Cotton	13	6
	Viscose	52	34
(3.1 mM/l.; 50°C)	Acetate	171	137
	Nyion	156	65
	Wool	300	232
Cetyl trimethyl am-monium bromide	Cotton	81	121
	Viscose	262	318
(0.08%; 50°C)	Acetate	102	122
	Nylon	29	54
	Wool	480	520
Di-isobutyl cresol-ethylene oxide Ratio 1:10 (0.1%; 30°C)	Cotton	54	25

4. CURRENT RESEARCH: SILK

In the preceding review there was no discussion of silk, no reference to silk among the charts and graphs. Although silk has an important role in the textile history, its position as a 20th century commercial fiber in the West has been limited due to geographic and political 20th century history. In the 1930's when linear alkyl sulfates were developed, silk was available in the West, in North
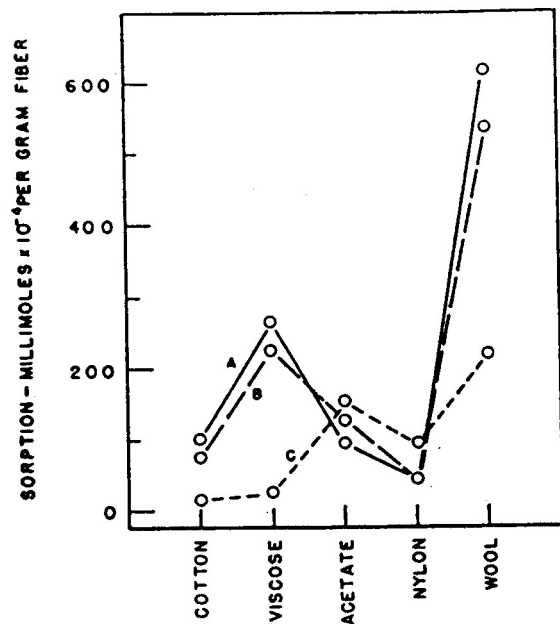
Figure 4. Sorption of Cationic Compounds by Fibers. A-Cetyl trimethyl ammonium bromide. B--Cetyl pyridinium bromide. C-Sodium myristyl sulfate. After Weatherburn and Bayley.
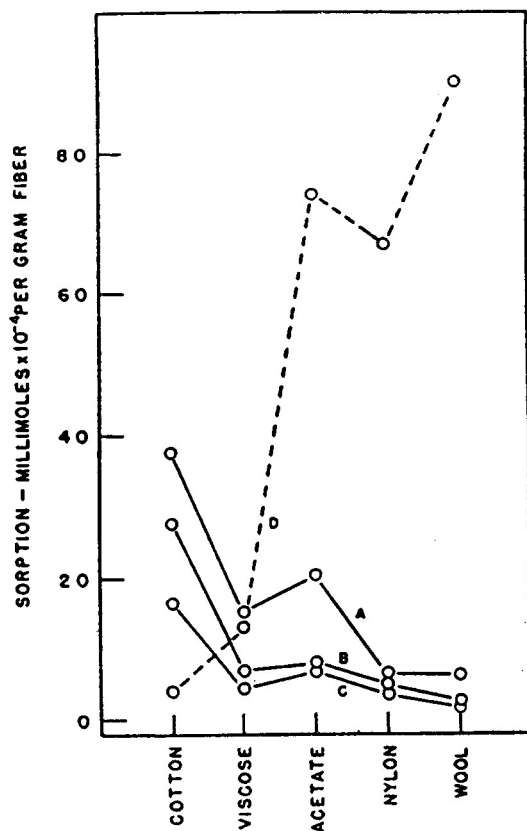

Figure 5. Sorption of Nonionic Compounds by fibers. The molar ratios of di-isobutyl cresol to ethylene oxide were as follows: A--1:10; B--1:15; C--1:20. Curve D--Sodium Lauryl Sulfate. After Weatherburn and Bayley.
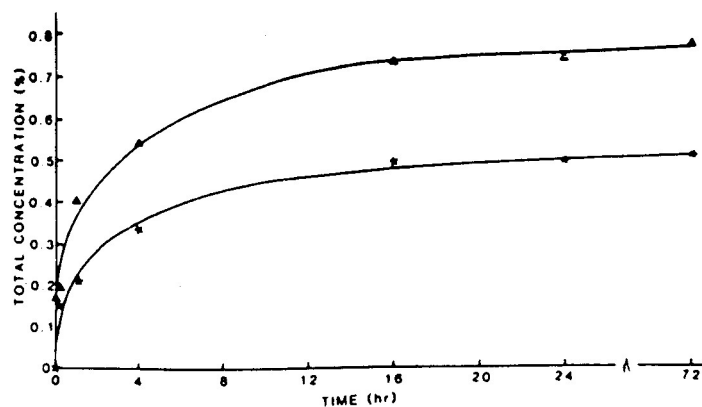

Figure 6. Sorption of Lissapol TN450 onto wool (fabric 2); change of total nonionic surfactant concentration (▲--60°C.*--40°C).
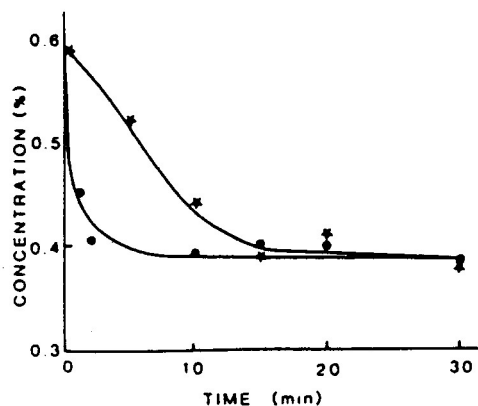After Freeland et al.

Figure 7. Desorption of Lissapol TN450 from fabric 7: change of concentration of nonionic surfactant inside fibers (--100°C, *--40°C).
After Freeland et al.

32

America. Yet, during World War II, silk apparel--like silk stockings--was severely curtailed. Trade with China, suspended in 1949, was not considered again until 1970. In the meantime, synthetic fibers, especially polyester and nylon, were substituted. The present popularity and pricing of silk apparel on the American market can be traced to trade agreements on tariffs and trade (GATT, as well as the multifiber trade act) and most recently to MFN (Most Favored Nation) agreements with China.

Our current research on silk seeks to redress the absence of surfactant silk data. To date we have found that qualitatively silk does adsorb sodium lauryl sulfate (Compare Figures 8 and 9). Using the colorimetric test method, we have found the adsorption as high as 2.73%±0.3% owf. The amount of sodium lauryl sulfate that is desorbed from the silk by rinses varies (Figure 10). On the first rinse 75-80% of the adsorbed surfactant is removed. If the rinsing time is increased, so is the desorption. If the temperature is increased, so is the desorption. The residual amount in the silk can be plotted as a percentage on weight of fiber or as a percentage of total initial adsorption (Figure 11).
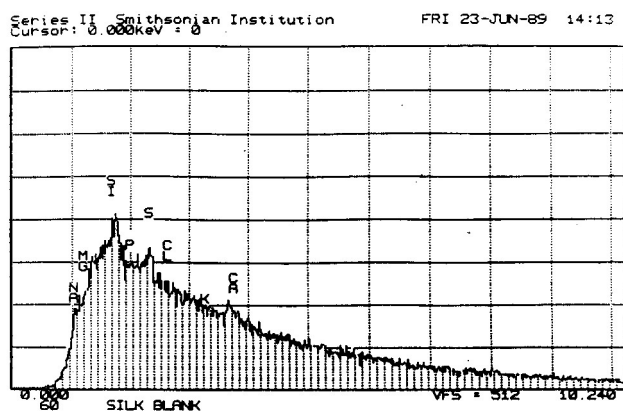

Figure 8. Scanning Electron Microscope Energy Dispersive Spectroscopy (SEM-EDS) of Modern Silk. After Rhee and Ballard, 1993.
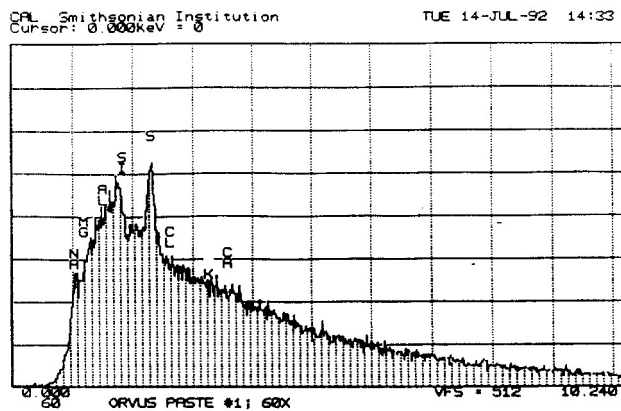

Figure 9. Scanning Electron Microscope Energy Dispersive Spectroscopy (SEM-EDS) of Silk Washed with Sodium Lauryl Sulfate. After Rhee and Ballard, 1993.
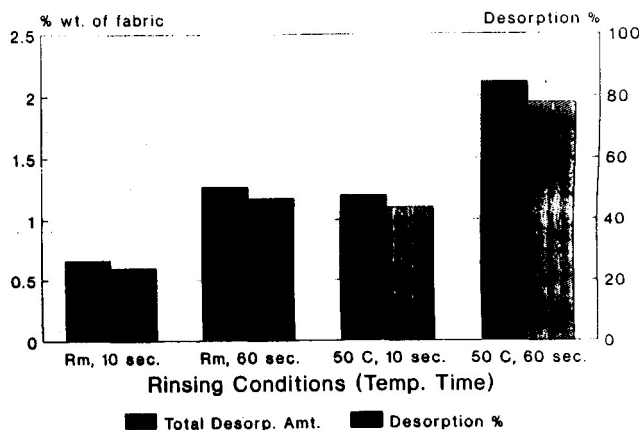

Figure 10. Rinsing conditions in terms of Time and Temperature for the Desorption of Sodium Lauryl Sulfate from Modern Silk. After Rhee and Ballard, 1993.
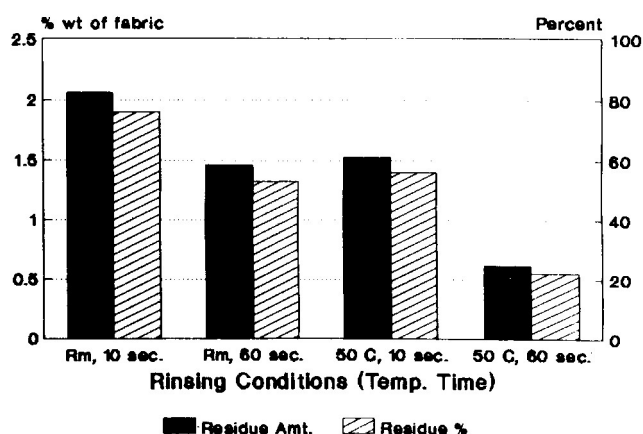

Figure 11. Residual Amount of Sodium Lauryl Sulfate After Three Rinses. Left, expressed as a Percentage OWF (on weight of fabric). Right, as a Percentage of Total Initial Adsorption. After Rhee and Ballard, 1993.

The effect of sodium lauryl sulfate upon the subsequent working properties of silk has also been explored. We found that wicking was not significantly affected if the sample was well rinsed (Table II). Left unrinsed, the hydrophobic character of silk significantly increased. Similarly well rinsed samples were not significantly affected in torn of tensile strength (Table III). Comparable color changes alter light ageing were also minimal (Table IV). At the present time, we are working on the effect of pH changes around the isoelectric range and on the effect of ethanol (found for example in Orvus liquid).

Table II. Results of Wicking Test
After Rhee and Ballard, 1993

SAMPLE	WICKING TIME (sec)[a]	RATE (cm/√sec)
Control	196.5 ± 33	0.373
Rinsed three times	208.4 ± 7	0.373
0.25% Treated	220.4 ± 25	0.350

[a] Time to reach 5 cm

Table III. Results of Tensile Testing
After Rhee and Ballard, 1993

SAMPLE	TENSILE STRENGTH (lb/force)
Control	35.0 ± 5.3
Sodium Lauryl Sulfate[a]	39.0 ± 4.0
Octylphenoxypolyethoxyethanol[b]	42.0 ± 0.5

[a] Trade Name: Orvus Paste
[b] Trade Name: Triton X-100

Table IV. Color Difference (ΔE) After Accelerated Light Ageing
Measured in CIE L*a*b*
After Rhee and Ballard, 1993.

SAMPLE	AGED TO L5	AGED TO L6	AGED TO L7
Perchloroethylene	2.31	3.76	5.12
Sodium Lauryl Sulfate[a]	2.48	3.92	5.79
Octylphenoxypolyethoxyethanol[b]	2.51	3.94	5.20

[a] Trade Name: Orvus Paste
[b] Trade Name: Triton X-100.

5. CONCLUSION

We can summarize our work as follows: surfactant residues are a function of fiber type (i.e., chemical structure of the fiber); they will decrease with longer rinsing at higher temperature; and

34

tensile strength and wicking (hydrophilicity) will not be significantly altered if the silk well rinsed.

While these results are helpful, it seems also worthwhile to remember that the working properties--logistical problems--associated with different fibers are very different: wool and silk in water along--with no surfactant--are significantly weaker than when dry--and that for wool at least, that weakness is magnified as the temperature of the water rises (Meredith).

Wet-cleaning protein fibers with anionic surfactants, and to a lesser extent, it seems, with nonionics, will leave a residue. These residues may be innocuous, or they may be beneficial or detrimental. Hair care products advertise "shampoo and conditioner" all in one. The issue, ultimately, is the desirability of this feel and its relationship to the "original" hand of the finished silk. We are all aware that fabrics and fabric finishes--like hair styles--go in and out of fashion. The larger question, then, is whether or not current wet-cleaning formulae are out-dated or inappropriate for antique textiles.

This issue is actually a very real one for practicing textile conservators and collection managers. Kathryn O. Scott, a retired textile conservator, always warned her students to plan a textile treatment for longevity: at least seventy-five years to one hundred years. Always, she said, do the best work possible, talk to the experts. Orvus WA Paste was the best available product for textile wet cleaning operations back in the 1950's/1960's but forty years later, in 1993, it is still current practice. Are we short-changing the textiles and ourselves? How many other methods and materials are we using based on protocols established several decades ago?

NOTE

For a detailed explanation of experimental procedures and conditions please refer to "Residues of Surfactant on Silk" by the authors in *Preprints, ICOM Committee on Conservation.* Marina del Rey, California: Getty Conservation Institute, 1993.

SOURCES OF MATERIALS

Habutae silk, style #604 was purchased from Testfabrics, P.O. Box 420,200 Blackford Avenue, Middlesex, New Jersey, 08846-0420.

Triton X-100, Orvus Liquid, and Orvus Paste were purchased from Conservation Materials Ltd. 1165 Marietta Way, P.O. Box 2884, Sparks, Nevada, 89431.

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