

The Application of Pluronic Surfactants to Textile Conservation

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ABSTRACT—Textile conservators at the H. F. duPont Winterthur Museum are searching for a surfactant that will be suitable for the washing of its oversized rugs, as well as for disposal directly into groundwater systems. Pluronic surfactants—nonionic block copolymers of propylene oxide and ethylene oxide—were considered as possible alternatives to commonly used surfactants such as Triton XL-80N and Orvus WA Paste. This paper examines both the methods that can be used to measure the real-time degradation of a surfactant, with Pluronic surfactants used as the case study, as well as the effectiveness of Pluronics in cleaning wool textiles.

INTRODUCTION

Wetcleaning with surfactants is an important part of textile conservation. Water's polarity, ready availability, low cost, and lack of toxicity all make it a good washing solvent. Surface-active agents, also known as surfactants, act as wetting agents in reducing the surface tension of the water, allowing easier penetration of the wash solution into the textile (Timar-Balazsy, 1998). Surfactants also aid in dislodging and removing dirt from the textile by forming micelles with the greasy, or hydrophobic, portions of the soil.

Many types of textiles are difficult to clean because of their large size. They cannot fit easily into a wash tank and so must be folded or rolled for cleaning. The H. F. DuPont Winterthur Museum, a museum of early American decorative arts, has a large number of these oversized textiles, primarily in the form of carpets. Currently the museum is undergoing a six-year project to improve the lighting in its period rooms, while adhering to conservation standards. Some objects whose condition was acceptable in the former dim lighting now require conservation treatment; the taking down of the rooms for the installation of the lighting system allows easy access to those rugs which are normally located under multiple heavy and/or fragile objects.

The Winterthur Textile Conservation Laboratory's 6-foot-by-12-foot wash tank is smaller than many of the rugs in the museum, whose length and width are too large even to allow rolling for washing in the tank. But the Winterthur estate, with more than 900 acres of land, offers many possibilities for outdoor washing. Rugs can be washed on pieces of plastic, providing

that the surfactant/water runoff is safe for direct disposal into local waterways.

While a major concern of art conservation is residues left on the object, the residues left in the environment are also of utmost importance. A commonly used group of nonionic surfactants are ethylene oxide adducts with alkylphenols, including Synperonic N and Triton X-100. These alkylphenolic compounds have been found to break down into estrogen-like projects, which have been linked with increased cancer rates and damage to reproductive systems in both humans and wildlife (Routledge, 1996; Stravroudis, 1995). Triton XL-80N breaks down into safe products but only does so when processed in waste-treatment facilities.

For washing wool rugs, nonionic surfactants are preferred over anionic surfactants such as Orvus WA Paste, for several reasons. Anionic surfactants have positively and negatively charged portions, while nonionics do not have charged portions; their structures are sufficiently polar to have an affinity to water. Their substantivity, or affinity for the fibers in the textile, is therefore less, and so they are easier to remove from the object. Another factor is the concentration of surfactant necessary; Orvus is used in a 1 percent volume to volume solution, while nonionic surfactants such as Pluronics and Triton XL-80N are used in solutions of about 0.05 weight percent to achieve optimum cleaning.

Pluronic surfactants are nonionic block copolymers of propylene oxide and ethylene oxide, and are available in a wide range of molecular weights and HLB numbers. Samples used in this research were obtained from BASF

Corporation. The investigation of the use of Pluronic surfactants was divided into two parts:

- 1) determining the rate of degradation of Pluronic in the natural environment (a local waterway)
- 2) determining whether Pluronic are as effective in cleaning as Triton XL-80N

CLEANING EXPERIMENTS

Expendable samples (about 6 inches by 9 inches) of wool pile carpets similar in structure, materials, and design to many of the oversized carpets in the Winterthur Museum's collection were chosen. To simulate several generation of walking, pollution, and other dirt, artificial soiling (lamp black and mineral oil in an acetone carrier) was applied (Cutler, 1987). The samples were placed in an Atlas Sunchex weatherometer for 144 hours, which is roughly equivalent to two generations of aging.

The samples were cut into 2-inch-by-2-inch sections. Color measurements of each section were performed with a Minolta Chroma Meter 100 using the L*a*b* system. Areas to be measured were marked on a Mylar template to ensure that readings would be taken in the same areas before and after washing. In order to gain an estimate of precision of the measurements, three or more measurements were taken in each marked area. Samples were chosen at random and washed in a solution of three to four times the critical micelle concentration (the minimum fully effective wash concentration) of one of four different surfactants: Triton XL-80N, Pluronic F-38, Pluronic F-127, and Pluronic L-44. Three different samples were washed in each of the surfactants. The samples were washed, rinsed, blotted, and dried under a drying cloth in the manner usually used in the Winterthur Textile Conservation Laboratory. Visual discrimination of areas cleaned with different surfactants was difficult.

Colorimetric measurements were repeated on each of the samples after

Table 1.

Colorimetry measurements and calculations

Minolta Chroma Meter 100 calibrated to read through mylar

L* value measures light to dark

a* value measures green to red

b* value measures yellow to blue

Sample	Surfactant	color	delta L	delta a	delta b
A	control (no soiling)		n/a	n/a	n/a
B2		red	+3.69	+2.00	+1.79
		blue	+0.25	-0.02	+0.46
		green	+3.97	-0.43	-0.70
D1	control (no washing)	red	+3.84	-0.92	-0.81
		blue	-0.72	-0.29	+0.48
		white	+4.57	-0.26	+0.43
E1	control (no washing)	red	+1.17	0.00	+0.21
		blue	+3.03	-0.40	+0.16
		brown	-0.19	-0.35	+0.40
G2	control (no washing)	red	-0.84	-0.96	+0.23
		blue	+2.31	-0.04	+0.44
		green	+0.44	+0.45	+0.34
I1	control (no washing)	red	-0.57	+0.45	+0.49
		blue	-0.06	+0.20	+0.22
		blue2	+1.31	-0.29	+0.13
control	average/standard deviation		+1.48/1.92	-0.06/0.70	+0.28/0.58
C2	Pluronic F38	red	+2.51	+0.54	-0.16
		blue	+1.89	+1.16	+0.52
		green	-0.44	+0.38	-0.45
F2	Pluronic F38	red	-0.26	+0.75	-0.53
		blue	+0.02	+0.06	+0.74
		green	-1.58	+0.11	-0.09
I2	Pluronic F38	red	+1.45	+0.58	-1.10
		blue	+1.70	+0.93	-0.69
		yellow	-0.25	+1.41	-1.41
F38	average/standard deviation		+0.56/1.36	+0.66/0.45	-0.35/0.70
C1	Pluronic F127	red	+1.48	+1.08	-0.08
		white	+4.90	+0.06	+1.70
		brown	+0.44	-0.48	-0.30
E2	Pluronic F127	red	+4.71	+0.80	+0.01
		blue	+3.03	-0.08	+0.27
		yellow	-2.03	+0.87	-0.32
		green	+1.54	+0.24	+0.61
G2	Pluronic F127	red	+1.02	+0.91	-0.45
		blue	+3.77	+0.76	+0.49
		brown	-0.98	+0.34	-0.56
B1	Pluronic L44	red	+1.88	+2.10	+0.14
		blue	+2.26	+1.12	-0.45
		green	+5.75	+0.89	-0.13
F1	Pluronic L44	red	-0.76	+0.69	+0.58
		blue	+3.65	+0.60	+0.31
		blue2	-0.75	+0.42	+0.31
H1	Pluronic L44	red	-1.55	+0.83	-1.20
		green	-1.71	+0.80	+0.37
		brown	-1.16	+0.40	+0.26
L44	average/standard deviation		+0.85/2.66	+0.87/0.51	+0.02/0.55
D2	Triton XL80N	red	+2.23	+0.61	+0.91
		blue	+5.09	+0.45	+0.73
		green	+4.25	+0.40	-0.13
H2	Triton XL80N	red	-1.13	+0.56	-0.67
		blue	+1.05	+1.00	+0.10
		green	+1.97	+1.03	-0.44
J2	Triton XL80N	red	-0.06	+0.14	-0.95
		green	-0.09	+0.21	-0.39
		brown	+5.37	+0.62	-0.22
XL80N	average/standard deviation		+2.08/2.38	+0.56/0.31	-0.12/0.61

washing and drying. The results, expressed in ΔE (total change in color), are listed in Table 1 with the equations used. Pluronic surfactants and Triton XL-80N lightened the carpet samples as expected. However, no significant difference was found in the degree of lightening of samples cleaned with Pluronics versus those cleaned with Triton. The conclusion drawn from these experiments is that cleaning with Pluronics gives similar results to cleaning with Triton XL-80N in all color categories; thus, Pluronics are acceptable substitutes in terms of cleaning ability.

DEGRADATION PRODUCTS

Fourier Transform Infrared Spectroscopy

Accepted practices of FTIR usage in analyzing surfactant concentration involve substantial preparation and purification of the sample before analysis can be run (Swisher, 1987; Karsa, 1995). Previous experiments (Miller, 1998) designed to measure the degradation rates of surfactant using FTIR indicated that characteristic Pluronic bands disappeared after 144 hours of artificial aging. Miller concluded that the surfactants had broken down into small, relatively volatile molecules. FTIR was used as a tool to measure surfactant degradation in the present study as well. Solutions of surfactants in water were analyzed using an Analect RFX-65 with spectrometer. The samples were placed by dropper on a KRS-5 thallium bromide iodide plate. The KRS-5 plate, though toxic, was chosen as the support because it would not react with the aqueous sample, which the usual alkali halide FTIR sample support would. The microscope attachment allowed the sample to be run in a horizontal orientation, which is important when dealing with liquids.

Initial runs with FTIR showed that the presence of Pluronics was obscured by water at concentrations of less than 10 percent (volume to volume). A range of solutions of Pluronics from 10 to 50 percent were then made in order to locate peaks whose presence was related to surfactant concentration. Runs were normalized for easier comparison. One peak, at 1115 cm^{-1} , maintained a constant height until the concentration of the surfactant fell into the 10 to 20 percent range, and then disappeared at about 10 percent Pluronic concentration. This experiment showed that surfactants at high concentrations (10 percent or greater) would probably

not behave in a manner similar to those at low concentrations, and so FTIR should not be used as a means of measurement.

Ultraviolet/visible spectrometry

Ultraviolet/visible spectrometry has been used by the Historic Royal Palaces Textile Conservation Studios at Hampton Court Palace to measure Synperonic N detergent residues left in rinse-bath solution (Cartwright, 1993). Unfortunately, Pluronics do not have chromophores that absorb in the UV/vis range, and so ultraviolet/visible spectrometry was not applicable to this particular experiment.

Foam testing

Foam testing was widely used in the wastewater industry in the 1950s and 1960s as the impact of commercial detergents on waterways was becoming evident (Swisher, 1987). Today, textile labs qualitatively judge the amount of surfactant in a rinse bath by shaking a vial of the bath water and observing foam formation. Foam testing is simple in that it requires only a timing device and will work for any foaming surfactant, regardless of chemical makeup, as it measures a physical property. The amount of foam is inversely proportional to the surface tension of the solution.

One easily performed method for estimating surfactant presence is to measure the amount of foaming at set time intervals on a scale from "nil" to "severe." The froth persistence is proportional to the susceptibility of the detergent to biological degradation (Bogan, 1956). A somewhat more quantitative version of this method involves diluting a known concentration of a surfactant by half until the foam disappears in a set amount of time. Solutions of unknown concentration can then be timed, and the times compared to those of the known solutions (Feng, 1962). Yet another testing method involves measuring maximum foam height and recording decaying foam volume at set time intervals to create decay curves (Bacon, 1966). For this experiment, the Pluronic solutions were manually shaken, and times were recorded from initial foam clearance to total foam clearance. Unfortunately, samples of local ground water produced significant foam before the addition of surfactant, making this method unsatisfactory for this experiment.

Surface tension

Surfactants work by lowering surface tension and allowing better wetting of the textile surface. As surfactant concentration increases, more of the surface become covered with surfactant molecules and the surface tension decreases (Figure 1). When the surface becomes saturated with the surfactant and critical micelle concentration (CMC) is reached, the surface tension remains constant even if more surfactant is added. For nonionic surfactants such as Pluronic, the critical micelle concentration is about 2 mmol per liter.

Surface tension, therefore, is a value related to micelle concentration. Below critical micelle concentration, surface tension and the log of the surfactant concentration have a linear relationship. Surface tension, like foaming, is an empirical measurement that examines physical properties, not chemical structure.

Conditions of Pluronic breakdown in groundwater were simulated. Washing solutions of 3 to 4 times critical micelle concentration were formulated in deionized water of pH 5, which was the water in which the solution would be made to wash the textile. These solutions were then placed in shallow trays on the roof of the Winterthur Research Building for periods of 24 hours and 48 hours. Ambient conditions were sunny, without cloud cover, with a temperature ranging from 65° Fahrenheit during the day going down to 40° Fahrenheit at night. Sam-

ples for surface tension measurements were taken from these trays.

These samples were taken to the Surface Properties Laboratory at the DuPont Specialty Chemicals facility in Deepwater, NJ. Under the direction of Dr. Richard Thomas and Mr. David Glaspey, three different methods of measuring surface tension were applied. The primary method was the du Nouy ring tensiometer. With the du Nouy ring tensiometer, a ring attached to a torqued wire is immersed in the solution being measured (Adamson, 1990). The solution is then lowered, resulting in increased torque on the wire. The reading on the scale when the film breaks is the apparent interfacial tension (Central Scientific Company). To account for any evaporation of liquid, the densities of our solutions were measured and incorporated into the final calculations.

A second surface tension measuring device is a surface tensiometer "bubble machine". Here two tubes of differing diameter are immersed in the solution in question and nitrogen is bubbled through them. The pressure difference between the tubes is measured and converted into the surface tension, with no correction factor for density needed. A third method of measuring surface tension involves freeze framing a suspended drop on a pendant drop tensiometer. The computer performs least-squares fitting of the outline of the drop and can then calculate the surface tension of the drop based on its outline profile.

Fig. 1.

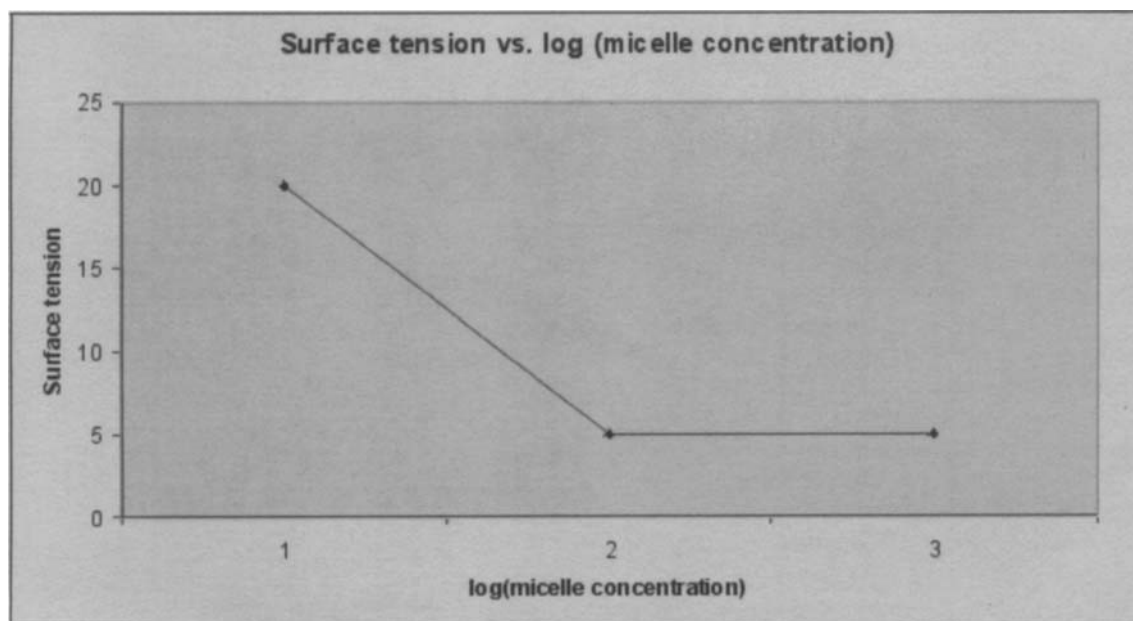


Table 2. Surface tension readings

Solution	P (ave)	d	f	(
Pluronic F38, 48 hours exposure	48.0	0.9984	0.908	43.6
Pluronic F38, 24 hours exposure	49.5	0.9984	0.910	45.0
Pluronic F38, newly mixed	48.9	0.9981	0.909	44.5
Pluronic F127, 48 hours exposure	42.0	0.9998	0.902	37.9
Pluronic F127, 24 hours exposure	42.7	0.9991	0.903	38.6
Pluronic F127, newly mixed	42.9	0.9997	0.903	38.8

P apparent interfacial tension of solution in dynes/cm
d density of solution in g/cm⁴
f correction factor found by correlating P/d to f on a chart specific for the instrument
(surface tension, dynes/cm
surface tension = P x f

All interfacial tension measurements were performed on the Cenco-du Nouy Interfacial Tensiometer, no. 70545.
R/r = 53.6
C = 5.992

The surface tension of all sample solutions was measured on the du Nouy ring tensiometer. The surface tension remained constant from one sample to another; the solutions had the same surface tension at 48 hours exposure as they did newly mixed (Table 2). Exposure to sunlight, in water, did not caused any of the Pluronics to break down from their 3 to 4 times CMC to below critical micelle concentration.

CONCLUSIONS

Although Pluronic surfactants were found to clean wool carpet samples as well as Triton XL-80N, they do not appear to break down quickly enough to be used in the outdoor washing of oversized textiles. This is a preliminary experiment, however, and additional work must be done before conclusive statements can be made.

Some conclusions about the best means of testing surfactant presence in solution may be drawn from this research. Fourier Transform Infrared Spectrometry analysis is good for pure or highly concentrated solutions, but not for dilute aqueous samples. A solvent other than water is needed to measure dilute concentration solutions. Ultraviolet/visible spectrometry is useful only if the surfactant has a chromophore that absorbs in the UV/vis range (200–780 nm). Foam testing is not a quantitative method but is useful for obtaining estimates. Surface-tension measurements proved most useful, and the equipment necessary, while not commonly found in a museum's analytical lab, are present at many universities and at other types of research facilities.

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