EFFECTIVENESS OF SOIL REMOVAL BY TWO NEW NONIONIC SURFACTANTS, ORVUS WA PASTE, AND SURFACTANT BLENDS

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ABSTRACT—Synperonic N, a widely-used nonionic surfactant, was phased out in Europe by 2000 because, as a nonylphenol ethoxylate, some of its breakdown products were toxic to fish. In searching for a replacement, two nonionics, Synperonic A7 and Triton XL-80N, were evaluated for their ability to remove soil from cotton, nylon and polyester fabrics. They were also tested in blends with the anionic surfactant Orvus WA Paste. Five replicate specimens of each fabric were washed in solutions with a detergent concentration equal to its critical micelle concentration (cmc). Pre-soiled fabrics were washed individually in canisters of a Launder-O-meter for 10 minutes at 35° C, with agitation provided by the movement of water in the cans as they rotated. Soil removal was determined from the total color change (ΔE) in the sample. Orvus WA Paste was most effective in removing soil from each fabric type, although blends of Orvus WA and a nonionic surfactant were also effective. Synperonic A7 and Triton XL-80N were not considered effective unless used at a concentration equal to four times the cmc. Further research on these and other nonionics is recommended before a replacement for Synperonic N is selected.

TITULO—EFECTIVIDAD DE LA REMOCIÓN DE TIERRA POR MEDIO DE DOS SURFACTANTES NO-IÓNICOS: PASTA ORVUS WA Y MEZCLAS SURFACTADAS. RESUMEN—Entre los “surfactantes” de Nolylphenol prohibidos en Europa durante el año 2000, se encuentra el Synperonic N, un conocido surfactante no-iónico. Dado que estos surfactantes han sido usados en los tratamientos húmedos de conservación, hoy deben buscarse nuevos productos que los reemplacen. El propósito de esta ponencia es comparar el rendimiento de dos nuevos surfactantes no-iónicos con la pasta Orvus WA, un surfactante aniónico manufacturado por Proctor & Gamble. El surfactante no-iónico Triton XL-80N (Union Carbide), el Synperionic A7 (Uniqema) y el aniónico Orvus, fueron probados en tres concentraciones: igual a su respectiva concentración "micelle" crítica (cmc), en 0.5 cmc y al doble del cmc. También se evaluaron mezclas de cada surfactante no-iónico y de Orvus. Se aplicaron test estándares de remoción de tierra en telas de algodón, nylon y poliester, lavándolas con los surfactantes en un “launderómetro” (Lavadora) por 10 minutos a 35º C. Se les dio a las telas una suave agitación por medio del movimiento de la misma solución y se comprimieron (o centrifugaron) en el tambor rotativo del Launderómetro. La remoción de la tierra quedó reflejada en un cambio total del color (ΔE_{CIELAB}) de las áreas sólidas de las telas testeadas después del lavado. Tres soluciones surfactantes removieron significativamente más tierra en el algodón, nylon y poliester, que otras soluciones: el Orvus (3g/L), Orvus (7.5 g/L) y una mezcla de Orvus WA con Synperionic A7. Estas soluciones de lavado produjeron los mayores cambios de color, esto es, removieron la mayoría de la tierra en el nylon (ΔE*23). Menos tierra fue removida del algodón y el poliester. El cambio de color en el algodón fue de ΔE*15 unidades

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CIELAB y en el poliester de ΔE*8 unidades CIELAB. La efectividad de estos dos surfactantes no-iónicos en la remoción de tierra en cada tipo de tela será también discutido.

1. INTRODUCTION

Textile conservators needed a surfactant to replace nonylphenol ethoxylate surfactants, including the widely-used Synperonic N, which were banned in Europe by 2000 (Hartog 1999). Although the surfactant biodegrades, some of the breakdown products such as nonylphenol are toxic to fish (Naylor 1995; Stavroudis 1995). Two new nonionic surfactants, Synperonic A7 (Uniqema, a subsidiary of ICI, New Castle, DE) and Triton XL-80N (Union Carbide, New Milford, CT) were evaluated as possible replacements. As part of the testing, the cleaning efficiency of these new nonionics was compared with the anionic surfactant Orvus WA Paste (Proctor and Gamble, Cincinnati, OH). Cotton as well as nylon and polyester fabrics were included in the study since many historic textile collections are now accumulating garments and household textiles made from synthetic fibers in addition to natural fibers.

Numerous researchers have studied the effectiveness of Orvus WA Paste and compared it with nonionics such as Synperonic N and Tergitol NPX (Union Carbide, New Milford, CT). The detergency variables used in these studies included the following: surfactant type and concentration (Boring and Ewer 1993; Eastaugh, 1987; Gentle and Müller 1995; Lewis 1996; Shashoua 1990; Shashoua 1996), temperature (Lewis 1996; Rhee and Ballard 1993), the addition of cmc (Eastaugh 1987; Lewis 1996), and rinsing method (Rhee and Ballard 1993; Shashoua 1990; Shashoua 1993). Lewis (1996) who was looking for a replacement for Synperonic N, evaluated Synperonic A5, blends of Synperonic A5 and sodium dodecyl sulfate, Berol 784 (Akzo Nobel, Arnhem, The Netherlands) which is a commercial anionic and nonionic mixture, and sodium dodecyl sulfate alone. It is difficult to summarize and compare the results of these researchers because the detergency variables were not the same, and both hand washing and mechanical agitation were used to remove soil in the cited experiments.

2. EXPERIMENTAL METHODS

2.1 FABRIC

Three pre-soiled test fabrics (Testfabrics, Inc. Pittstown, PA) of bleached cotton sheeting (STC TF405 and S/493), spun nylon 6,6 (STC TF361) and spun Dacron 54 polyester (STC TF777H) were used. The rolls of standard soiled test fabric are 23 cm wide with a 9 cm wide strip of synthetic soil printed onto the fabric slightly off center. The soil is a mixture of sodium alginate thickener, corn starch, water, mineral oil, oleic acid, morpholine, vegetable fat, butanol, Solvesso 150, ethyl cellulose, and carbon black (Testfabrics 1999). Because the soil is dark gray in color, it is possible to see many gradations of soil removal.

Table 1. Characteristics of three surfactants tested.

Surfactant	**Orvus**	**Synperonic A7**	**Triton XL-80N**
Manufacturer	Proctor & Gamble	Uniqema	Union Carbide
Class	anionic	nonionic	nonionic
Description	sodium dodecyl sulfate, water	fatty alcohol ethoxylate	alcohol oxylate
Purity	29% by weight	~100%	~100%
Solubility in water (by mass)	complete	>10 g/100 g	100% at 20°C
Cloud Point (°C)	unknown	45-50°C (1%w/v)	50°C
pH	7.0	5.66	6.3
Critical Micelle concentration	3.0 g/L	0.013 g/L	0.086 g/L
Specific gravity	1.04	0.958 at 50°C	0.985 at 20°C
Appearance	white paste or amber liquid	white viscous liquid	murky liquid

2.2 SURFACTANTS

Two nonionic surfactants were recommended by Uniqema and Union Carbide as possible replacements for Synperonic N in textile conservation, Synperonic A7, a polyethoxylated alcohol, and Triton XL-80N, a primary alcohol alkoxylate. The performance of the two nonionic surfactants was compared with Orvus WA Paste. Characteristics of these detergents are shown in Table 1.

The critical micelle concentration (cmc) of each surfactant was determined from a plot of surface tension (mN/m) versus concentration (g/L) using the ring method on a Krüss Tensiometer model K12 (Krüss GmbH, Hamburg, Germany). As surfactant is added to water, the surface tension of the water gradually decreases to a minimum and levels off. The surfactant concentration at the point where the minimum is first reached is the critical micelle concentration, the concentration at which micelle formation begins. The addition of more surfactant brings about no further decrease in surface tension. All measurements of cmc were taken at 35° C, which was the selected wash temperature. The surface tension versus concentration plots for Orvus WA Paste, Synperonic A7 and Triton XL-80N are shown in Figure 1.

2.3 WASHING PROCEDURE

Because of the difficulty in reproducing the hand-washing technique where a natural sponge is repeatedly pressed and released on a textile surface, a mechanical method of washing that would produce similar results was sought. A Launder-O-

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meter (Atlas, Chicago, IL) using 250 ml of wash solution in 500 ml canisters most closely matched the level of soil removal after hand washing. Agitation was provided by the motion of the wash solution as the canisters rotated through the water bath at 40 revolutions per minute. The washing parameters are shown in Table 2. A wash temperature of 35° C was used because it would facilitate dissolving the surfactants and softening the oily soils. It was important that the wash temperature not be above the cloud point of the nonionic surfactants because the surfactants would not be dissoved in the wash water above the cloud point. The solubility of nonionic surfactants decreases as the temperature rises and many nonionics have low temperature cloud points (Tímár-Balázsy & Eastop 1998, 202).

2.4 ASSESSMENT OF SOIL REMOVAL

Soil removal was determined by calculating the total color change (Δ E*) of the specimens from the L*, a*, and b* values of the soiled area on each specimen before and after washing. Five specimens per experiment were evaluated for color change. The total color change in CIELAB units was calculated from the relationship $\Delta E^* = [(\Delta L^*)2 + (\Delta a^*)2 + (\Delta b^*)2]^{1/2}$ where L* indicates light-darkness, a* indicates redness-greenness, and b* indicates yellowness-blueness. A Hunterlab Labscan XE instrument (Hunter, Reston, VA) was used to measure color change according to AATCC Evaluation Method 6 (AATCC Technical Manual 1998). The Labscan XE instrument geometry is 0°/45° with a D65 illuminant, a 10° observer and a 2.56 cm diameter port.

Table 2. Wash protocol

Detergent concentration	Orvus WA Paste: 1.5, 3.0 & 7.5 g/L Synperonic A7 0.0065, 0.013 & 0.026 g/L Triton XL-80N 0.086, 0.172 & 0.344 g/L Orvus/Syn A7 blend 3.6/0.0039 g/L Orvus/Triton blend 3.6/0.052 g/L
Fabric specimens	Prescilled cotton, nylon, polyester; 5 specimens per test. Each specimen 5 x 23 cm.
Water	Purified by reverse osmosis; used for wash and rinse.
Wash solutions	250 ml detergent solution for 1 specimen in 500ml canister.
Temperature	Wash and rinse solutions at 35 ± 2 °C.
Wash time	10 minutes, with agitation provided by rotation of canisters.
Rinsing	Five washed specimens rinsed together in 500ml beaker for 1 minute. Total of four rinses.
Drying	Specimens air-dried on glass, soil side up, wrinkles gently smoothed away.

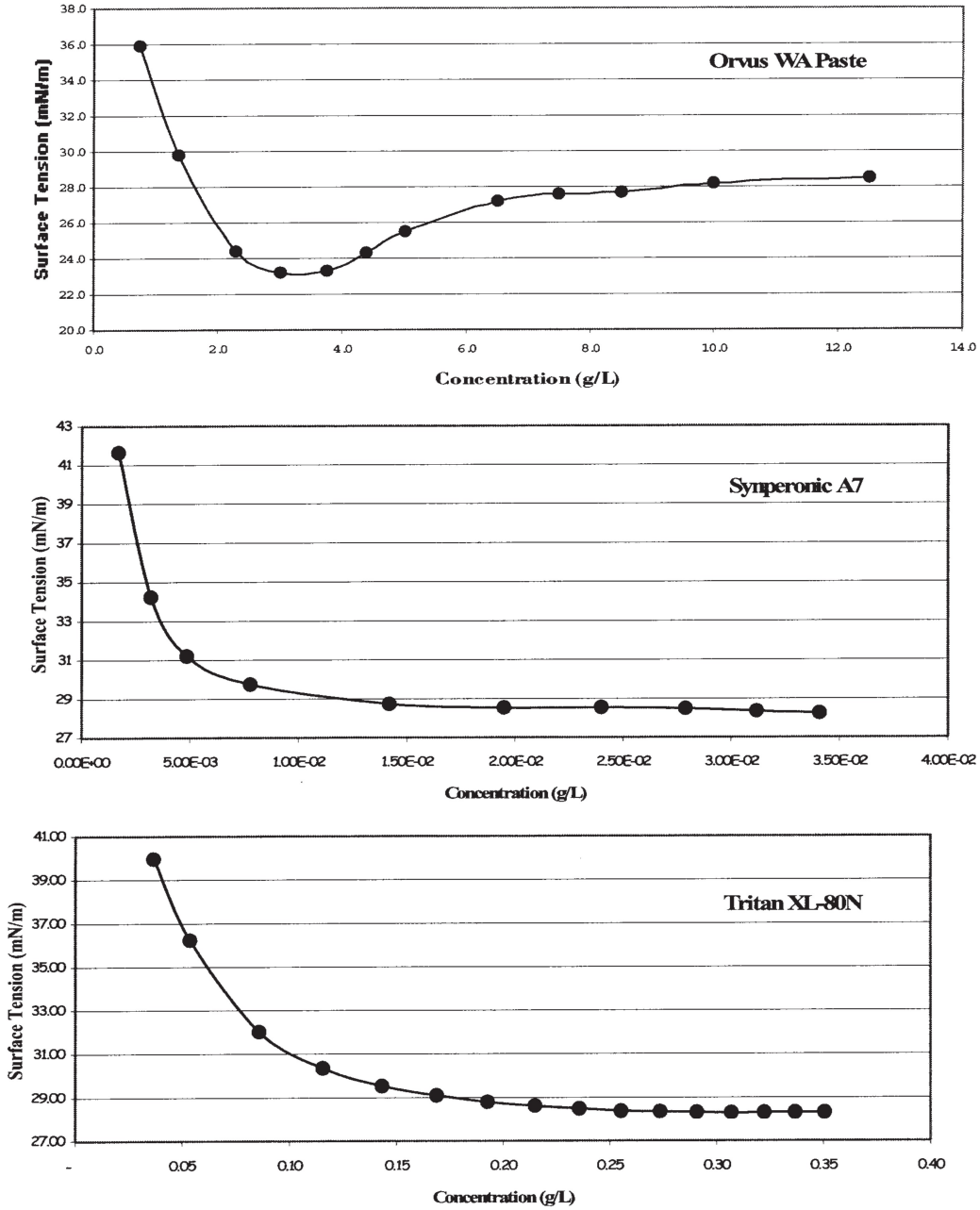

FIGURE 1. The cmc is determined from a graph of surface tension vs concentration.

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3. RESULTS AND DISCUSSION

The results of washing experiments in which three pre-soiled test fabrics (cotton, nylon and polyester) were washed for 10 minutes at 35° C in various surfactant solutions and surfactant blends are listed in Table 3. Four solutions produced the most effective soil removal from cotton (ΔE^*15_{CIELAB}): Orvus at 3g/L and 7.5g/L, Orvus/Synperonic A7, and Orvus/Triton XL-80N. The blend levels were comparable to that recommended by Delcroix and Bureau (1990-91), namely 120% cmc for the anionic surfactant and 30% cmc for the nonionic surfactant. When Triton XL-80N and Synperonic A7 were used alone to wash cotton, the results were poor even when the surfactants were used at twice their cmc concentrations or higher. For example, when the Synperonic A7 concentration was 0.39g/L (30 times the cmc), the ΔE* value was 7.4 CIELAB units. Lewis (1996), on the other hand, got very good soil removal (ΔE*15) when she used nonionics (Synperonic A5, Berol 784) and nonionic/sodium dodecyl sulfate blends. Her surfactant solutions had concentrations of 0.1 or 0.2%, that is, 1 or 2 grams per liter. Thus, her solutions were much more concentrated in the nonionic component than the above solutions. She worked with cool water (15-20° C) and warm water (30-34° C).

In these detergency experiments, soil was removed most effectively from the nylon soil test fabric. The smoothness of the nylon yarns may have facilitated soil removal. Delta E* values of 20 to 23 CIELAB units were obtained after washing with four detergent solutions: Orvus at 3g/L and 7.5g/L and the two Orvus/nonionic blends which contained 3.6 g/L Orvus. Delta E values of 12 to 13 CIELAB units resulted when the nonionics were used at their highest concentrations (4x cmc for Tritan XL-80N and 30x cmc for Synperonic A7).

Soil removal from polyester was poor and may reflect the tendency for polyester fibers to absorb and hold oily soils more strongly than do nylon or cotton. Delta E* values between 7 and 8 CIELAB units resulted when polyester was washed with Orvus at 3g/L and 7.5g/L, Orvus/Synperonic A7 blend, Synperonic A7 alone (30x cmc) and Triton XL-80N at 4x cmc. The Orvus/Triton blend was anticipated to perform as well as the plain Orvus solution because the blend contained 3.6g/L Orvus. This did not happen.

The researcher whose experiments most closely matched our study is Jane Lewis (1996) who completed her research at the Textile Conservation Centre, Hampton Court Palace, Surrey, England. She was seeking a replacement for the nonionic surfactant Synperonic N, and was particularly interested in blends of nonionic and anionic surfactant. Table 4 is a summary of her research findings and ours and shows the surfactant solutions that were most effective at removing soil from cotton, wool, nylon and polyester. Lewis used sodium dodecyl sulfate (SDS) instead of Orvus which is 29% SDS. Thus, Orvus, used at a concentration of 3g/L, is approximately equal to SDS used at 1g/L. Lewis obtained excellent

Table 3. Soil removal (ΔE_{CIELAB}) from cotton, nylon and polyester after washing for 10 minutes at 35°C in various surfactants and surfactant blends

Fabric	Surfactant	n	Concentration		Soil Removal	
			g/L	Fraction of cmc	ΔE_{CIELAB}	S.D.
Cotton	Water	5	0	-	4.9	0.50
	Orvus	10	1.5	0.5x	10.2	1.10
	Orvus	25	3.0	1.0x	14.9	1.26
	Orvus	10	7.5	2.5x	14.7	1.46
	Synperonic A7	5	0.0065	0.5x	5.2	0.53
	Synperonic A7	5	0.013	1x	5.1	0.47
	Synperonic A7	5	0.026	2x	5.3	0.65
	Synperonic A7	5	0.39	30x	7.4	0.50
	Triton XL-80N	5	0.086	1x	7.6	0.23
	Triton XL-80N	5	0.172	2x	8.7	0.37
	Triton XL-80N	5	0.344	4x	8.6	0.39
	Orvus/Syn A7	5	3.6/0.0039	1.2/0.3	16.1	1.45
	Orvus/Triton	5	3.6/0.052	1.2/0.6	14.6	0.61
Nylon	Water	5	0	-	0.4	0.16
	Orvus	10	1.5	0.5x	9.4	1.44
	Orvus	25	3.0	1x	22.0	0.73
	Orvus	10	7.5	2.5x	22.5	1.45
	Synperonic A7	5	0.0065	0.5x	0.4	0.24
	Synperonic A7	5	0.013	1x	0.8	0.39
	Synperonic A7	5	0.026	2x	2.8	0.47
	Synperonic A7	5	0.39	30x	12.7	1.14
	Triton XL-80N	5	0.086	1x	0.8	0.32
	Triton XL-80N	5	0.172	2x	0.4	0.05
	Triton XL-80N	5	0.344	4x	11.9	1.15
	Orvus/Syn A7	5	3.6/0.0039	3.6/1.2	22.3	0.40
	Orvus/Triton	5	3.6/0.052	1.2/0.6	20.4	1.27
Polyester	Water	5	0	-	0.2	0.04
	Orvus	10	1.5	0.5x	1.6	0.98
	Orvus	25	3.0	3.0x	7.8	0.86
	Orvus	10	7.5	7.5x	7.3	0.53
	Synperonic A7	5	0.0065	0.5x	0.4	0.27
	Synperonic A7	5	0.013	1x	0.7	0.41
	Synperonic A7	5	0.026	2x	1.9	0.38
	Synperonic A7	5	0.39	30x	7.1	0.49
	Triton XL-80N	5	0.086	1x	0.6	0.63
	Triton XL-80N	5	0.172	2x	0.5	0.30
	Triton XL-80N	5	0.344	4x	7.1	0.34
	Orvus/Syn A7	5	3.6/0.0039	1.2/0.3	7.7	0.89
	Orvus/Triton	5	3.6/0.052	1.2/0.6	4.6	0.38

Table 4. Surfactants and concentrations most effective in removing soil from cotton, wool, nylon and polyester pre-soiled fabric.

	Lewis (1996)			Tinkam/Kerr		
Fabric	Surfactant[2]	Conc.(g/L)	AE	Surfactant	Conc. (g/L)	AE
Cotton	Synperonic N	1	16	Orvus/Syn A7	3.6/0.0039	16
	Syn A5/SDS[1]	1/0.1	16	Orvus	3	15
	Syn A5/SDS[1]	2/0.2	16	Orvus/Triton XL-80N	3.6/0.032	15
	SDS	1	16			
Wool	Syn A5/SDS	2/0.2	28			
	Syn A5/SDS	1/0.1	26			
	Synperonic A5	2	23			
Nylon				Orvus	3	23
				Orvus/Syn A7	3.6/0.0039	22
Polyester				Orvus	3	8
				Orvus/Syn A7	3.6/0.0039	8
				Triton XL-80N	0.34	7

[1]Blend of Synperonic A5 with sodium dodecyl sulfate.
[2]Sodium carboxy methyl cellulose (0.05 g/L) used in all experiments.

cleaning results with Synperonic A5 when it was used at a concentration of 2g/L. If Synperonic A7 had been used at 2g/L, that concentration would be 154 times its cmc. These results suggest, however, that nonionic surfactants must be used at a concentration well above their cmc or blended with SDS if they are to be effective in wet cleaning.

4. DISCUSSION

The purpose of this research was to evaluate the cleaning ability of two nonionic surfactants (Synperonic A7 and Triton XL-80N) that might replace Synperonic N in textile wet cleaning and to determine whether these nonionics and Orvus WA Paste are equally effective in removing soil from nylon, polyester and cotton fabrics. The results of a number of washing experiments indicate that Synperonic A7 and Triton XL-80N are much less effective than Orvus WA Paste in removing soil from cotton, nylon or polyester fabrics. If they are to be used, a concentration at least 4 times the cmc is recommended. Among the three types of fabrics that were cleaned, the nylon fabric showed the greatest soil removal (ΔE^*23) and the polyester fabric was the most difficult to clean (ΔE^*8). Given the adherence of oily soils to polyester, it is not surprising that the mild washing procedure did not remove more soil. Further research with higher concentrations of Synperonic A7 and Triton XL-80N should be conducted before a decision is made to use them in textile conservation cleanings.

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SOURCES OF MATERIALS

Orvus WA Paste:
Available from local veterinary suppliers.
Distributed by Proctor & Gamble
Commercial Products Group, CPG TN6
2 Proctor & Gamble Plaza
Cincinnati OH 45202
www.pg.com/main.jhtml

Synperonic A7:
Uniqema
P.O. Box 54
Wilton Middlesbrough
Cleveland TS90 8JA
UK
www.uniqema.com

Triton XL-80N:
Union Carbide Corp.
200 Pickett District Road
New Milford, CT 06776.

Pre-soiled test fabrics:
Testfabrics, Inc.
P.O. Box 26, 415 Delaware Ave.
West Pittson, PA 18643.
www.testfabrics.com

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