Cold Water Detergency Studies Using Radiolabeled Soils[1]

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Abstract

The effects of single and multiple washing and of resoiling-rewashing of cotton and synthetic fabrics have been studied in Tergotometer tests at various levels of temperature, detergent concentration and water hardness. The soiling mixture consisted of a seven component sebum tagged with tritium and carbon-14; in some tests gamma-ray emitting Kaolinite clay was also used. Linear primary alcohol ethoxylate (LAEO) and linear alkylbenzene sulfonate (LAS) were used for surfactant type comparisons. In single wash tests in both hot and cold water, LAEO was generally more effective than LAS in removing sebum. This was particularly noticeable at low product concentration where insufficient sodium tripolyphosphate was present to sequester the water hardness. A 1/1 blend of the two surfactants approached LAEO in performance. The nonpolar sebum fraction was more readily removed from Dacron or nylon in cold water; otherwise, detergency was generally better at high temperatures. In rewash tests, using labeled lube oil, cholesterol and clay, a progressive increase in soil removal was found during five wash cycles. The nonpolar lube oil component was the most difficult to remove from permanent press Dacron-cotton (PP), but was more readily removed from cotton. The more polar cholesterol and especially the clay were more easily removed from PP. LAEO gave better detergency both hot and cold than LAS, especially in hard water. On cotton swatches resoiled with sebum after each wash the residual sebum content was still increasing after five cycles. With PP in soft water, a steady state was reached after three to five cycles. Soil buildup was greater as hardness increased and as wash temperature and active matter concentration decreased, and was generally greater on cotton than on PP. LAEO allowed appreciably less soil buildup than did LAS especially at low concentration in hard water, indicating a reduced requirement for sodium tripolyphosphate.

Introduction

The detergent industry has a continuing interest in improving its products and formulations. Two current needs are to improve detergency in cold water and to reduce the soil buildup on synthetic fabrics. Several workers have reported on the latter problem (1–3) and Hunter (4) has noted that stain removal is especially troublesome in the presence of inadequate amounts of anionic surfactants. Hoffman (5) found that polyester fabrics retain 50% more vegetable oil than does cotton. Gordon et al. (6,7) and also Fort et al. (8) observed considerable selectivity in the removal of sebum or oily soils from polyester, the more polar components being more readily removed. Detergency is usually poorer at low washing temperatures, but Spangler et al. (9) reported better cleaning of polyester at 60 F than at 120 F, and Gordon et al. (6,7) found a similar effect resulting primarily from the behavior of the nonpolar sebum fractions. Diffusion of fatty soils into the polyester at high temperatures may be a factor in the poor detergency (8). Schott (10) is concerned that oily soil removal in laboratory tests is usually greater from synthetic fabrics than from cotton, in spite of the fact that displacement should be energetically more favorable from cotton. He suggests that the problem may arise from the use of organic solvents in the application of the soil, allowing the sebum to penetrate into the lumen or fissures of the cotton, where it then is trapped when the cotton swells when contacted with water during the washing process. Spangler et al. (9), who pad from a sebum emulsion, find that cotton is more readily cleaned than polyester at low detergent concentrations, but not at high concentrations.

In the course of our work, we have developed several pieces of data which pertain to the ease of removal of sebum and also clay soils from various fabrics using anionic and nonionic surfactants in hot and cold water. Multiple soiling and rewashing tests as well as more customary single washing tests have been carried out.

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TABLE I
Composition of Radiolabeled Sebum

Component	Fraction, %	Label
Hydrocarbon (medium viscosity lube oil)	25	^{3}H
Tristearin	10	^{3}H
Arachis oil (peanut oil)	20	Unlabeled
Stearic acid	15	^{14}C
Oleic acid	15	^{14}C
Octadecanol	8	^{14}C
Cholesterol	7	^{14}C

TABLE II
Detergent Compositions

Component, wt, %	Single wash	Multiple wash
Surfactant	15	10–20
Sodium tripolyphosphate	35	40
Sodium silicate[a]	5	5
Sodium CMC	....	1
Sodium sulfate	35	34
Water	10	10–0

[a] 2.4/1 SiO_2/Na_2O ratio.

TABLE III
Effect of Temperature on Removal of Sebum Soil from Various Fabrics

Surfactant	Product[a] Conc. g/l	Fabric	Single Wash, 150 ppm — Soil Removed, % — ^{3}H 120 F	^{3}H 60 F	^{14}C 120 F	^{14}C 60 F
LAEO	1.0	Cotton	59	46	59	45
	1.5		63	49	66	47
1/1 Blend	1.0		58	45	59	42
	1.5		64	50	65	49
LAS	1.0		35	21	37	22
	1.5		53	43	58	43
LAEO	1.0	Dacron	29	42	76	70
1/1 Blend	1.0		28	47	69	78
LAS	1.0		17	24	32	33
LAEO	1.0	PP	41	40	61	49
1/1 Blend	1.0		33	44	55	53
LAS	1.0		21	28	38	35
LAEO	1.0	Nylon	49	72	76	79
1/1 Blend	1.0		22	63	60	77
LAS	1.0		7	25	12	31

[a] See Table II.

TABLE IV

Soil Removed After Three Washes
15% Surfactant, 1.5 g/l Product

Surfactant	Hardness, ppm	Temp., F	Soil Removed, %					
			Cotton			PP		
			Lube oil	Cholesterol	Clay	Lube oil	Cholesterol	Clay
LAEO	50	120	93	94	68	92	97	97
	250		97	92	64	89	92	92
LAS	50		91	91	66	88	96	96
	250		86	85	64	83	96	90
LAEO	50	60	87	84	60	82	91	90
	250		77	76	58	63	83	78
LAS	50		89	85	60	88	91	88
	250		61	68	45	57	81	74

Experimental Procedures

Washing tests were carried out in a Tergotometer for 10 min at 100 cycles/min. A typical linear alcohol ethoxylate (LAEO[3]), the sodium salt of a linear C_{13} alkylbenzene sulfonate (LAS) and a 1/1 mixture of the two were used as surfactants in typical built formulations described later. Water hardness was obtained from a stock solution of calcium and magnesium chlorides, having a 60/40 Ca^{++}/Mg^{++} ratio. Four soiled swatches of a given fabric, each 10 cm sq, were washed in 500 ml of wash liquor. The following fabrics were obtained from Testfabrics Inc., New York: Cotton, bleached sheeting, S/405; Nylon 66, spun, type 200, S/354A; Dacron, spun, type 54, S/754AW; Dacron 54/cotton, 65/35 with permanent press finish, S/7406WRL.

Radiolabeled sebum having the composition shown in Table I was applied and counted by the method of Shebs and Gordon (11). In the two series of rewashing tests, only the lube oil and cholesterol components were tagged and the correspondence between these tests and the single wash tests is not exact because of selective removal of sebum components. The method of Gordon and Shebs (7) was used to apply the tagged clay portion of the soil. In summary, the test methods are as follows:

Clay, if used, was applied to 10 cm square swatches of the desired fabric from an aqueous suspension. After appropriate rinsing and air drying, the clay content of swatches in groups of four was determined by gamma ray counting. One ml of a benzene solution of the doubly labeled sebum was applied to each swatch and allowed to air dry. The swatches were washed in the Tergotometer at the desired conditions, rinsed by hand in 105 ml of distilled water and again gamma ray counted to determine the amount of clay remaining. Aliquots of the combined wash and rinse waters were counted in a three channel liquid scintillation counter to determine the tritium and carbon-14 contents of the sebum removed. Computer programs translated the various counting data to percent soil removal.

[3] Based on a NEODOL detergent alcohol and containing 68% polyoxyethylene by weight.

Results and Discussion

Single Wash Tests

A number of Tergotometer tests involving a single wash of swatches soiled with 28 mg of the seven component sebum (Table I) were carried out using our customary method (11) in order to study such basic laundering variables as temperature, surfactant structure, concentration, water hardness and fabric type. The detergent formulation used is shown in Table II. Washing conditions are given in Table III, which presents a selection of the results of this work and demonstrates the main responses found.

With cotton fabric similar amounts of polar and nonpolar sebum fractions were removed at a given condition, indicating little selectivity. Detergency was generally less efficient at 60 F than at 120 F. At 60 F in 150 ppm hard water, LAEO and the 1/1 LAEO/LAS blend performed at approximately 70–80% of their 120 F level. At a product concentration of 1.5 g/l, the LAS formulation showed a similar temperature sensitivity, but at a level of only 1.0 g/l, the 60 F detergency was only about 60% of the 120 F value. Furthermore, at 120 F and 1.0 g/l, only 60% as much sebum was removed by LAS as by LAEO. We have consistently found that an increase in water hardness or a decrease in product (hence sodium tripolyphosphate) concentration reduces detergency, but that LAEO formulations are much less affected than those based on LAS.

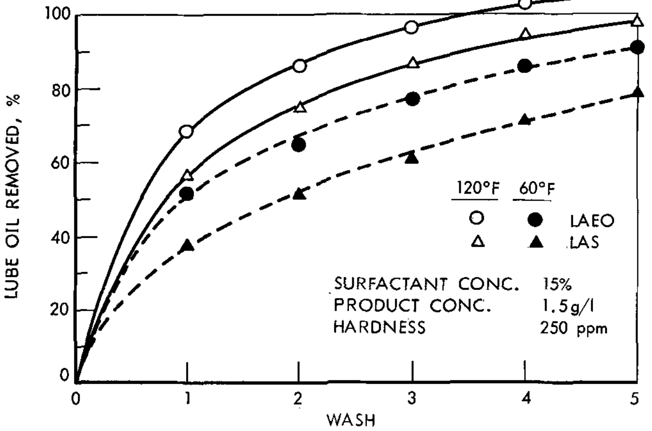

FIG. 1. Cumulative lube oil detergency in rewashing of cotton—effects of surfactant and temperature.

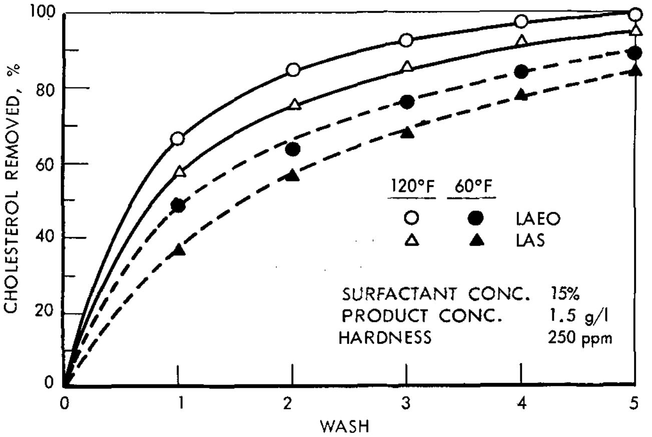

FIG. 2. Cumulative cholesterol detergency in rewashing of cotton—effects of surfactant and temperature.

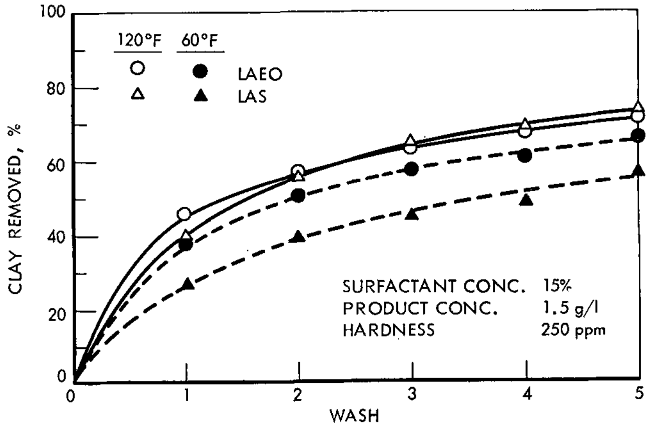

FIG. 3. Cumulative clay detergency in rewashing of cotton—effects of surfactant and temperature.

The synthetic fabrics, Dacron, permanent-press Dacron/cotton 65/35 (PP) and nylon, behave quite differently than cotton. Considerable selectivity in soil removal was observed in that the polar sebum was as much as three times more readily removed than the nonpolar sebum. A reverse temperature sensitivity was found, especially with the more difficultly removed nonpolar sebum, indicating that cold water washing of synthetic fabrics may be advantageous. The relative diffusion rates of the sebum into and out of the synthetic fibers during soiling and washing steps are thought to be important in the detergency processes, and appear to require further study.

Under the test conditions, where water hardness is only about 65% sequestered, LAEO was roughly twice as effective as LAS in removing sebum from the polyester fabrics and even more effective with nylon. Other work has shown that surface deposits on the nylon, even though it was supposedly scoured by the supplier, may be responsible at least in part for the wide range in results found with this fabric. Blending of the LAEO and LAS at a 1/1 ratio resulted in performance close to or even better than that of the LAEO alone.

Rewashing Tests

A series of tests was carried out to study the effect of rewashing of soiled cloths. Swatches of cotton and PP were soiled with about 4 mg of clay and 28 mg of the seven component sebum. In these tests only the lube oil and cholesterol components were radiolabeled; previous work (6) had shown these materials to be the most difficult to remove from these fabrics.

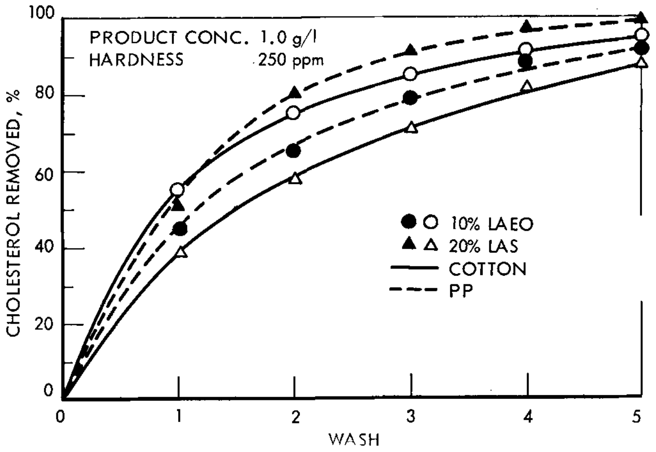

FIG. 5. Cumulative cholesterol detergency in rewash tests at 120 F.

The swatches were washed at the desired condition, gamma-ray counted to determine unremoved clay, air dried, and rewashed for a total of five cycles. Analyses of the wash and rinse waters gave the sebum removed. The composition of the detergent formulation used is given in Table II.

Washing conditions are as indicated in Table IV and Figures 1 to 6 which give the results. Curves showing the progressive washing of cotton in hot and cold 250 ppm water using 1.5 g/l of products containing 15% of LAEO or LAS are to be found in Figures 1 to 3. In all cases detergency was greater at 120 F than at 60 F. LAEO was more efficient than LAS at both temperatures with all three soils. With LAS in cold water, only about 80% of the sebum components was removed after five washes whereas with LAEO more than 90% was removed. Clay was appreciably more difficult than sebum to remove from cotton, in at least partial agreement with Powe's (12) observation that clay is the major soil found on cotton garments. Both clay and cholesterol were more readily washed from PP than from cotton. With PP, LAEO was again better than LAS except in cholesterol removal at 120 F. As is shown in Table IV washing of both fabrics was more efficient in 50 ppm water than in 250 ppm water, and the effects of temperature and surfactant were smaller at 50 ppm. In general, the detergency with LAEO was reduced only slightly by a reduction in product concentration or an increase in water hardness, while LAS was much more sensitive to these variables.

At a lower product concentration, 1.0 instead of

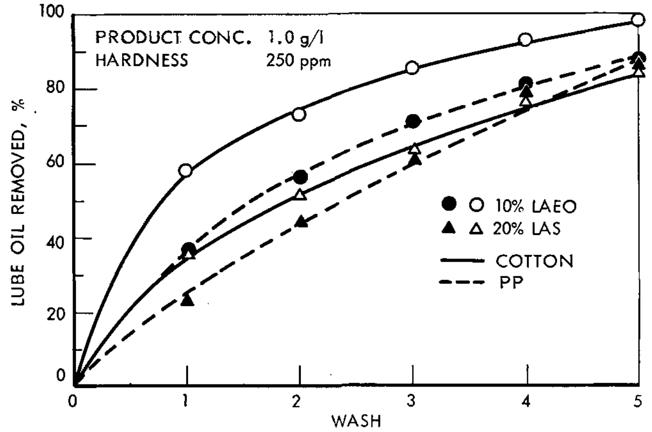

FIG. 4. Cumulative lube oil detergency in rewash tests at 120 F.

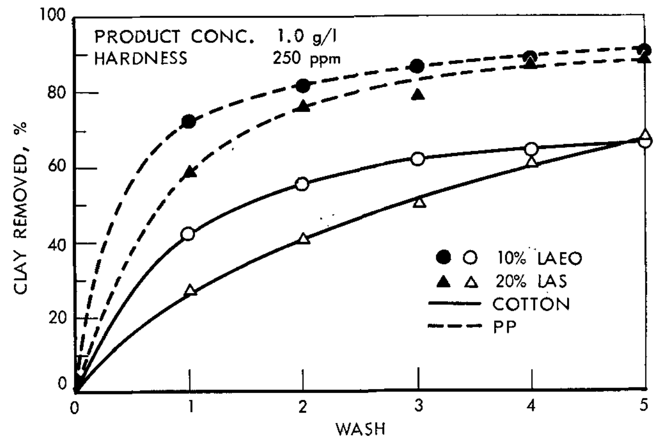

FIG. 6. Cumulative clay detergency in rewash tests at 120 F.

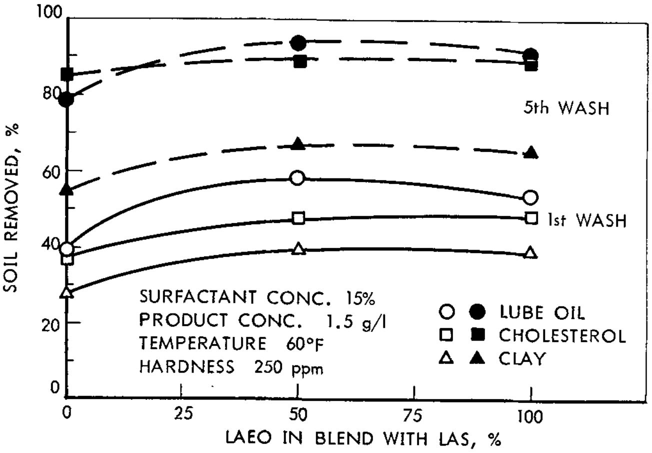

FIG. 7. Effect of surfactant composition on soil removal from cotton at 60 F.

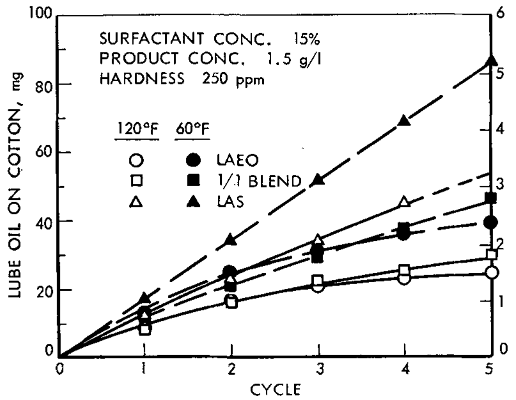

FIG. 8. Lube oil buildup on cotton during resoil-rewash tests.

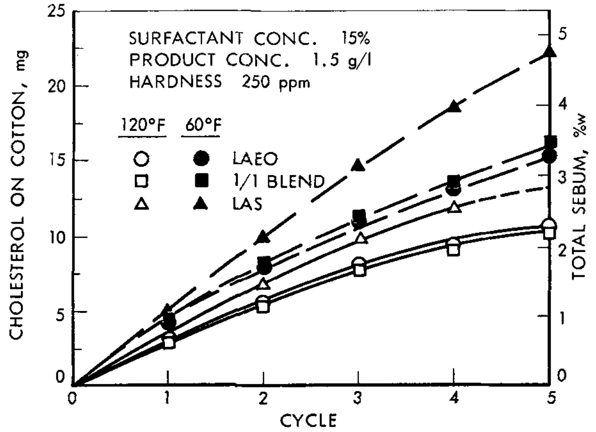

FIG. 9. Cholesterol buildup on cotton during resoil-rewash tests.

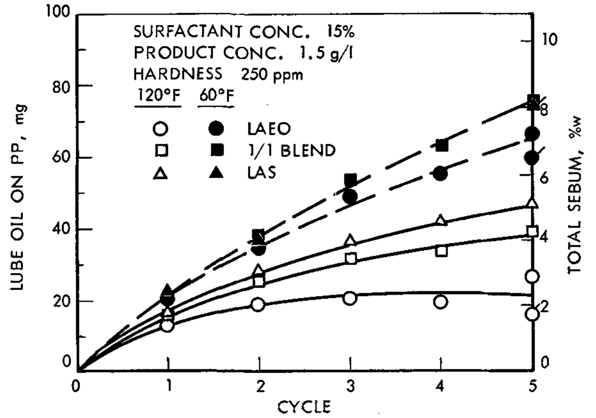

FIG. 10. Lube oil buildup on PP during resoil-rewash tests.

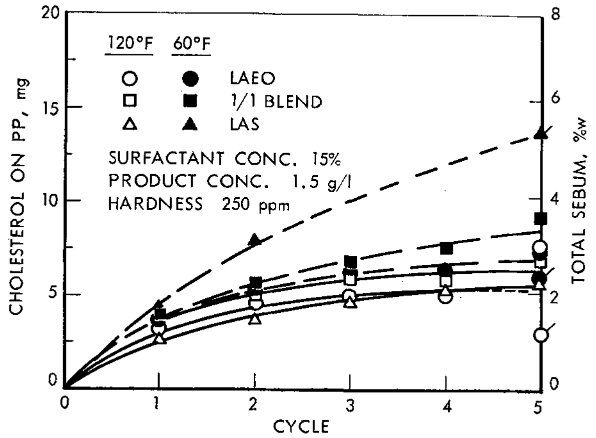

FIG. 11. Cholesterol buildup on PP during resoil-rewash tests.

1.5 g/l, 10% LAEO is compared with 20% LAS in washing tests in 250 ppm water at 120 F, in Figures 4 to 6. In spite of the twofold difference in surfactant concentration LAEO was more effective than LAS in removing all soils from both fabrics except cholesterol from PP.

Detergency increased with increasing LAEO content of blends with LAS. Slight synergism for a 1/1 blend was observed with cotton in cold, hard water, as shown in Figure 7. The blend retained most of the insensitivity to low concentration and high hardness of LAEO, and thus would offer an economic advantage in many cases.

Resoiling-Rewashing Tests

In a related series of tests, swatches were resoiled with sebum, again containing lube oil and cholesterol as the labeled components and then rewashed. Before the first wash the cotton and PP fabrics were soiled with both clay and sebum. In soil-wash cycles two through five, sebum only was applied because of the uncertainties involved in applying clay to a soiled swatch, and the probability that some sebum would be lost in the clay padding step. The sebum, 100–116 mg/set of four swatches (containing 25–29 mg of lube oil and 6.9–7.9 mg of cholesterol) was applied in the usual manner by automatic pipet to air dried swatches which had been washed and gamma ray counted.

The weights of lube oil and cholesterol remaining on the four swatches after each wash are shown in Figures 8 to 11. The values are calculated from wash

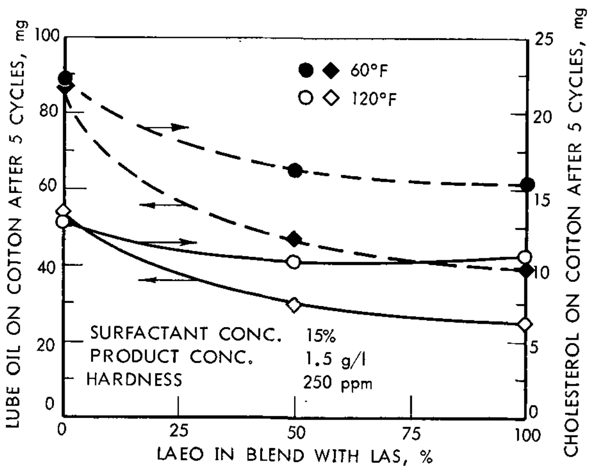

FIG. 12. Effect of surfactant composition on sebum buildup on cotton.

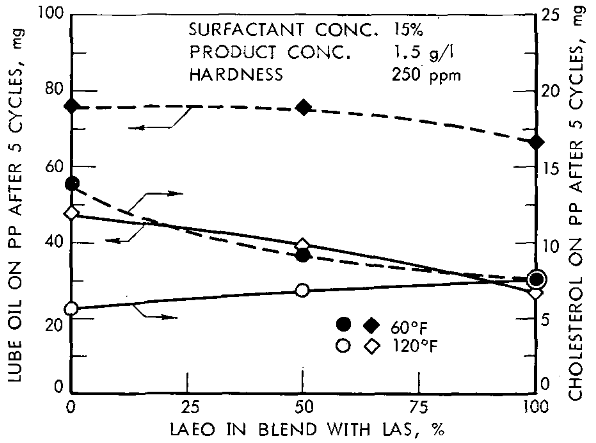

FIG. 13. Effect of surfactant composition on sebum buildup on PP.

water analyses, except for occasional values after the fifth cycle which were obtained by extracting the swatches with 1/1 benzene-methanol. These data are shown as tagged points in the figures. The right hand scale in Figures 8–11 gives the order of magnitude of the percentage of total sebum on the cloth, calculated by assuming that each of the labeled components represents the whole sebum. This is a faulty assumption, since these are the most difficultly removed components, and the true values may be as much as 25% less than those shown. The calculated range of sebum buildup was 2% to 8%, in agreement with the 2.2% to 7.6% range found by Powe and Marple (13) for naturally soiled garments.

The sebum content of swatches repetitively soiled and washed increased regularly in most cases. A steady state was reached after three to five cycles when PP was washed in soft water and also in hard water with LAEO at 120 F. As was found in the rewashing tests, detergency was better at 120 F than at 60 F, resulting in correspondingly less sebum buildup at 120 F. With cotton, for example, the content of either sebum component on the cloth at 120 F was roughly two-thirds that at 60 F. Less sensitivity to temperature was observed with LAEO than with LAS.

The effect of increasing the LAEO concentration from 0 to 50 and 100% in blends with LAS is shown in Figures 12 and 13. With cotton, the 1/1 blend was nearly equivalent to pure LAEO in limiting sebum buildup, and such a blend could offer an economic advantage. With PP fabric, however, LAEO was the preferred surfactant, especially for the nonpolar lube oil soil.

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