Statistical Approach to Detergency. III. Effect of Artificially Soiled Test Cloth

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Abstract

The relative effectiveness of several proprietary detergents is measured in cleaning "standard" soil cloths. Quantities of soil removal are related to detergent type, and to polarity or hydrophilicity of the soil and cleaning media. Various calculation methods and statistical treatments of detergency data are discussed.

Introduction

EARLIER STUDIES at our laboratories dealt with variables in detergency evaluation such as mechanical action, water hardness and detergent composition (1,2). This paper is an extension of these studies to include the influence of widely used "standard" soil cloths on detergency results for various commercial detergents. Other workers have noted that soil is the most critical variable in detergency evaluation and have conducted similar studies (3).

In detergency evaluation, there has been considerable controversy regarding the type of soil applied to fabric (4). Should the soil simulate actual soil or be synthetic in nature? The choice of "standard" soil cloth is known to be fairly critical and less important are differences in mechanical action, load to liquor ratio and other test variables. It is frequently stated that soils utilized in the laboratory evaluations should yield results consistent with large scale laundry testing (5).

In recent years, there has been considerable research in the area of soils and detergency testing (6). More sophisticated test methodology has evolved, for example, utilizing radiotracer techniques. There has been considerable effort to employ soils more representative of natural soil. Clay and sebum soils have been described as important or universal problem soils, and methods have been proposed incorporating their use in synthetic soils (7–9). One very recent paper describes the use of synthetic sebum combined with natural airborne particulate matter from air-conditioning ducts, and use of multiple soil-wash cycles (9). The trend toward natural soil is further illustrated by another method which utilizes vacuum cleaner soil and a cumulative wash-soil-wash technique (10). And finally, many workers still argue that only tests simulating actual washing conditions provide useful information (5). These workers rely on multiwash laundry tests with actual family bundles.

With all the objections and alternatives to commercial soil cloths, it remains an actual fact that many organizations currently employ these in research and quality control of detergent products. Such organizations frequently do not possess the proportionate sales volume in detergents to justify a test soil program. This is particularly true in the area of private label detergents where firms may be limited in research, but still require reliable evaluations.

An analysis of the types of results obtained from using commercial soil cloths therefore remains meaningful. In this paper, comparative results are given for 16 commercial detergents in performance on three soil cloth types: from U.S. Testing, Testfabrics and Foster D. Snell, Inc. Results are categorized in relation to detergent sudsing type, i.e., high or low sudsing, and according to the ionic type of detergent active ingredients.

Experimental

Listed below are the various detergent systems tested:

Laundry Detergents Tested. Commercial Products: 11 high-sudsers (A–K); 5 controlled sudsers (L–P).

Reference Materials. Alkylphenol + E.O. adduct (APEO), (nonionic) (R); 10-APEO, 90-builders [1] + water (built nonionic); Sodium tridecylbenzenesulfonate (NaTDBS) (anionic); 20-NaTDBS, 80-builders + water (built anionic); APEO/NaTDBS, 4/1 (nonionic/anionic); 10-APEO, 2.5-NaTDBS, 87.5-builders + water (built nonionic/anionic).

Of the 16 commercial products, 11 were high sudsers, 5 were low or controlled sudsers. For reference or control purposes, we employed an unbuilt nonionic detergent, namely an alkylphenol-ethylene oxide adduct, coded R. This material was also combined at 10% level with conventional detergent builders. As an anionic detergent, we employed sodium tridecylbenzenesulfonate run unbuilt and built at a 20% active level. Blends of nonionic with anionic detergent were also tested. Detergents employed in this study were not of the "biodegradable" type. However, later work has shown that biodegradable and nonbiodegradable detergent actives yield similar results.

Soil components of the three test cloths are described in the literature (4,11). We are apparently dealing with three distinctly different soiling systems. From composition, U.S. Test cloth would appear to be the most hydrophobic, with only carbon and primarily high molecular weight hydrocarbon and fatty oils present. Testfabrics soil appears less hydrophobic because of the presence of aromatics, cellulosics and emulsifiers. FDS cloth contains lower molecular weight fatty acids and esters and by including a modified clay, provides a different chemical entity in the soil mixture. This modified clay, of course, is not at all similar to the natural clay found in ordinary clothing soil. Bentone 34, in containing demethyldioctadecylammonium groups, is much more hydrophobic than natural clay.

Experimental conditions of detergency testing are as evolved from the earlier studies in our laboratories (1,2). These are outlined below.

Procedures

Conditions

Fifty and 300 ppm water hardness (as $CaCO_3$, Ca/Mg–60/40); 750 ml detergent solution at 0.2% concentration; 120F; Terg-O-Tometer, 150 cycles/minute; 15 min wash time.

[1] Conventional detergent builders: including STP, Na-silicate, Na_2SO_4, CMC, etc.

Cloth Loading

Single Fabric Type. Three swatches U.S. Test (4½ × 5 in.); Testfab (3½ × 3¾ in.) *or* FDS Cloth (4 × 4 in.).

Mixed Fabric Load. One of each swatch type above added to test beaker. (All runs were made in duplicate). Conditions are fairly conventional for laboratory screening. The Terg-O-Tometer was employed and detergents were tested at near use concentration or 0.2% in soft and hard waters. Cloth loadings were of two types. In the first case which is more usual, three swatches of one soil cloth type were introduced into the wash solution. In this way detergencies by first one cloth, then another were measured in separate washings. In the second case, one of each soil cloth type was introduced so that the three cloth types were simultaneously washed in the same detergent solution.

Calculations used in expressing the results are:

a) $\Delta R = R_w - R_s$
where R_w = reflectance after washing
R_s = reflectance before washing

b) "Soil Removal" $= \frac{R_w - R_s}{R_o - R_s} \times 100$
(% Whiteness Return)
where R_o = reflectance of original cloth before soiling.

c) Kubelka-Munk equation:

$$\%\ SR = \frac{(K/S)_s - (K/S)_w}{(K/S)_s - (K/S_o)} \times 100$$

where $\frac{K}{S} = \frac{(1-R)^2}{2R}$

All are based on reflectance of soil cloths. The first, by ΔR, or simply the difference between reflectances of washed and unwashed cloths. The second is an apparent per cent soil removal value calculated from reflectance differences; and the third method utilizes Kubelka-Munk equations to approximate actual per cent soil removal from the same reflectance measurements.

Conventional statistical methods were used to calculate precision from the data:

Statistical Treatment

Standard Deviation (S) of Test

$$S = \sqrt{\frac{d^2}{2k}}$$

where: d = difference between duplicate values
k = degrees of freedom
(= no. of duplicate pairs in this case)

Precision of Each Reported Mean

$$95\%\ \text{Confidence Limits} = \pm t \frac{S}{\sqrt{n}}$$

where: t = critical value of "Student's t" at the 0.05 probability level for *k* degrees of freedom
n = no. of replicates in each mean = 2

Least Significant Difference Between Means (LSD)

$$LSD = \bar{x}_a - \bar{x}_b = t \frac{S}{\sqrt{n/2}} = t\,S \quad (\text{since } n = 2)$$

In addition to standard deviation and 95% confidence limits, we calculated the least significant differences (LSD) between any two results or mean values. Thus, at the adopted 95% confidence level, if two means differed by less than the LSD, the values were judged not significanty different. Of course, the converse was used to detect significant differences.

TABLE I
Sample of Detergentcy Data—Single Coth Type/Wash
(50 ppm water hardness)

Detergent	U.S. Test			Testfab.			FDS		
	a[a]	b	c	a	b	c	a	b	c
G	14.0	24.1	57.6	27.6	46.4	81.6	28.0	42.5	82.8
K	16.2	27.2	62.6	28.8	48.6	83.0	28.3	42.8	83.2
L	12.2	21.3	54.3	26.5	44.0	80.4	26.3	39.6	81.4
M	18.6	31.2	67.6	26.8	44.2	80.6	20.9	31.6	73.6
Water	4.4	7.4	24.3	8.4	14.3	40.4	8.0	12.1	42.0
(LSD) 16,0.05P	(1.1)	(1.9)	(2.7)	(1.1)	(1.6)	(1.3)	(1.6)	(2.1)	(1.9)

[a] Calculation methods: a = ΔR, b = [$(R_w - R_s)/(R_o - R_s)$] × 100, c = KM equation.

Data and Discussion

Typical detergency data by the single cloth type method are given in Table I. Comparing calculation methods for each cloth, we note that the magnitude of the values varies with equation employed, but relative ranking of detergents remains unchanged. For example, for U.S. Test cloth Δ R's ranged from 12–19 units for detergents while percent whiteness returns were 21–31 units and K-M soil removals were higher at 58 to 68 units. This latter result illustrates the fact that a low reflectance increase actually corresponds to a relatively high degree of soil removal. Comparing detergencies among cloths, we note that U.S. Test cloth yielded lowest values; hence, it appears to be the most difficult to clean. Testfabrics and FDS cloths yielded substantially higher detergency values. These differences were also reflected in water removal values obtained in the absence of detergent. Thus, if removal by water is used as a criterion, we conclude that U.S. Testing is less hydrophilic than Testfabric or FDS cloth.

Similar data obtained by running mixed cloth loadings are given in Table II. In this case, different lots of each cloth were used, so that the magnitude of the values between single and mixed cloth type loadings cannot be compared. However, certain very interesting similarities are apparent, particularly in relative results. U.S. Test cloth again yielded lower removals for detergents and water compared to Testfabrics and FDS cloths. FDS cloth yielded higher removals than Testfabrics, but other work on other lots of cloths suggest that this is not necessarily a general rule.

Relative ranking of the detergents by each cloth appears similar, comparing single and mixed load data. This is shown in Table III.

The rank order is not exactly the same from single to mixed loads: for example, by U.S. Test cloth M was better than K in single loading while they appeared equal in mixed loading. While certain differences do arise, no major interactions appear evident among the three soils. This indicated that mixed loading could be employed in laboratory evaluations

TABLE II
Sample of Detergency Data—Mixed Cloth Soil Load
(50 ppm water hardness)

Detergent	U.S. Test			Testfab.			FDS		
	a	b	c	a	b	c	a	b	c
G	11.4	19.0	50.2	19.3	30.5	69.9	27.3	41.2	82.0
K	14.6	24.3	59.0	23.8	37.8	76.8	29.0	44.0	83.8
L	9.4	15.8	43.9	15.1	23.9	61.2	26.2	39.3	80.9
M	15.0	25.3	59.8	16.2	25.8	63.4	22.9	34.4	76.6
Water	1.0	1.7	6.2	6.0	9.6	32.8	10.6	15.8	51.2
(LSD) 8,0.05P	(0.9)	(1.0)	(1.9)	(1.8)	(2.8)	(3.4)	(1.2)	(1.7)	(1.2)

TABLE III

Rankings (50 ppm water hardness)

	U.S. Test		Testfab.		FDS	
	Single	Mixed	Single	Mixed	Single	Mixed
1)	M	1 } M,K	1) K	1) K	1 } K,G	1) K
2)	K	2	2) G	2) G	2	2) G
3)	G	3) G	3 } M,L	3 } M,L	3) L	3) L
4)	L	4) L	4	4	4) M	4) M

without introducing highly specific and artificial results.

Distinct differences in ranking did occur between soil cloths. For example, M was *most effective* according to U.S. Test cloth, *but* poorest by Testfabrics and FDS cloths. G ranks third by U.S. Test cloth and first or second by the other two cloths. Some similarities do exist, for example, K and L rank fairly high and low, respectively, throughout the results. However, the reversals in effectiveness suggest that rather profound differences in soil removal characteristics exist among these cloths.

A graphical presentation of data for all 16 samples tested is shown in Figure 1. Plotted here are Δ R values for detergents arranged simply in aphabetical order for 50 and 300 ppm water hardness.

High sudsers are A-K; low sudsers are L through P. The shapes of the curves have no absolute significance within a cloth type but comparing curves for one cloth versus another cloth reveals impoitant differences.

Here we see the relatively low removals for U.S. Test compared to Testfabrics and FDS cloths. The difference is especially true for high suds detergents which relatively are highly effective on Testfabrics and FDS cloths.

With high sudsers, all three cloths show relatively small differences among the various products. This is true for low sudsers only in the case of Testfabrics cloth. With U.S. Test and FDS cloth, wide differences among the low sudsers are evident. The interesting thing here is that FDS cloth results are virtually the exact opposite of the U.S. Test cloth results.

It is also interesting to compare high suds versus low suds results. According to Testfabrics and FDS cloths, high sudsers are more effective than low sudsers, the difference being especially pronounced with FDS cloth. U.S. Test cloth shows one low sudser to be inferior while others are equal to or better than the various high sudsers.

In Figure 2, apparent percent soil removals are plotted. The placement of the curves is somewhat altered but relative results and conclusions from the

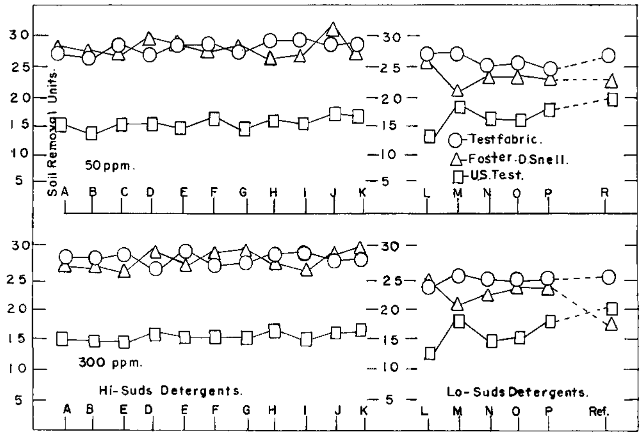

FIG. 1. Soil removals by reflectance (R_w–R_s).

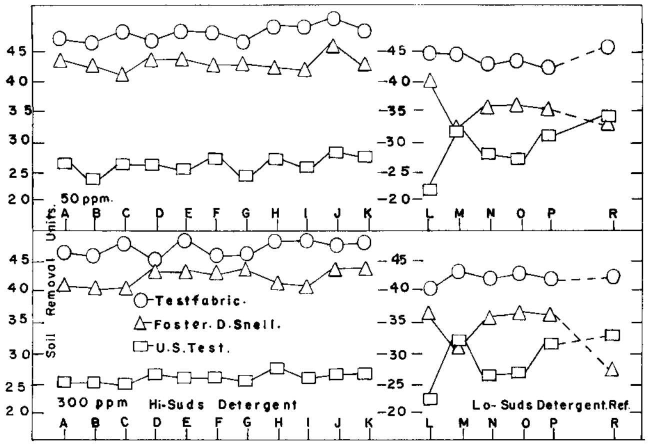

FIG. 2. Soil removals by (R_w–R_s)/(R_o–R_s) × 100.

data are identical with those obtained from the Δ R values. This is also true for the Kubelka-Munk values which are given in Figure 3. K-M expressed data appear to show wider differences among samples, but again relative rankings are unaltered.

Data given in Table IV for laboratory prepared detergents provide some interesting insights. Detergencies are given for unbuilt and built detergent actives including a nonionic low sudser, a mixed nonionic/anionic low sudser and an anionic high sudser. Detergency by U.S. Test cloth shows the straight nonionic active as highest performing. On the other hand, Testfabrics and FDS cloths indicate the straight anionic to be most effective. The mixed active material tends to fall intermediate in detersive action.

A detergent formulator might tend to prefer one detergent ionic type or another depending on which soil cloth was employed in screening.

Based on this limited study it is not possible to draw definite conclusions regarding the causes of these specific results. Certain interesting points are however evident. U.S. Test cloth is the most hydrophobic of the three soils and tends to favor nonionic detergents. Nonionics tend to form highly developed micellar solutions and are excellent solubilizers of oily and fatty soils (12,13).

Testfabrics and Foster D. Snell are more hydrophilic soils and tend to favor anionic detergents. Detersive action of anionics is enhanced by ionic charge and dispersive effects which may operate especially strongly on polar soils. The specific response of FDS cloth apparently stems from the presence of modified

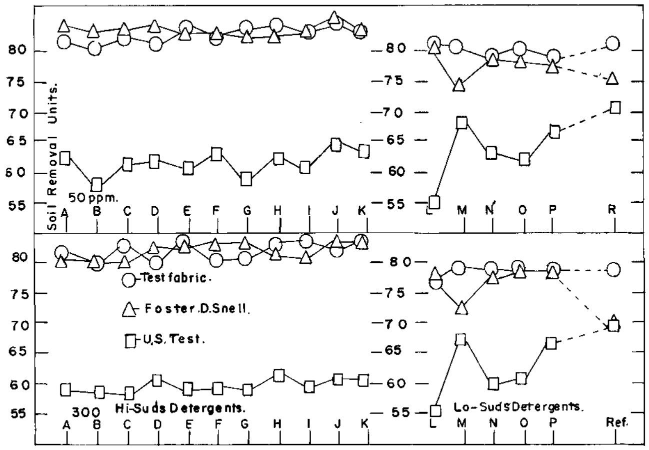

FIG. 3. Soil removals by Kubelka-Munk equations.

TABLE IV

Detergent Effect on Soil Removal
(0.2% total detergent concentration, 135 ppm water)

Detergent	Active type	ΔR		
		U.S. Test	Test-fab.	FDS
APEO	Nonionic	14.0	15.0	22.4
APEO/NaTDBS, 4/1	Nonionic/anionic	10.0	15.0	26.0
NaTDBS	Anionic	9.6	25.9	30.9
APEO/builders, 10/90	Built nonionic	16.1	15.4	24.0
APEO/NaTDBS/bldrs., 10/2.5/87.5	Built nonionic/ anionic	14.0	17.0	28.0
NaTDBS/bldrs. 20/80	Built anionic	13.2	22.9	31.8
	(LSD)	(1.0)	(1.8)	(1.5)

clay in the soiling mixture. In addition to the practical implications of this work, further studies of these and other soils and relation to detergent structure could be used to elucidate detergency mechanisms.

In summary, we have shown that relative effectiveness of various laundry detergents depends on the soil employed in evaluation. Commercial soil cloths yield highly specific results, apparently depending on the sudsing and ionic nature of detergent active ingredients and on the hydrophilicity and chemical nature of soiling components.

REFERENCES

1. Linfield, W. M., E. Jungermann and J. C. Sherrill, JAOCS *39,* 47 (1962).
2. Jungermann, E., G. A. Davis, E. C. Beck and W. M. Linfield, Ibid. *39,* 50 (1962).
3. Harris, J. C., and E. L. Brown, Ibid. *28,* 96 (1951).
4. Harris, J. C., "Detergency Evaluation and Testing," Interscience Publishers, Inc., New York, 1954.
5. Wagg, R. E., Second International Congress Surfactants Acta *4,* 35 (1957).
6. Ginn, M. E., JAOCS *40,* 662 (1963).
7. Davis, R. C., Soap Chem. Specialties *39,* 47 (1963).
8. Hensley, J. W., and C. G. Inks, ASTM Special Technical Publication No. 268 (1959).
9. Spangler, W. G., H. D. Cross, III, and B. R. Schaafsma, JAOCS *42,* 723–727 (1966).
10. Schwarz, A. M., and J. Berch, Soap Chem. Specialities *39,* 78 (1963).
11. Technical data sheet from Foster D. Snell, Inc.
12. Ginn, M. E., R. M. Anderson and J. C. Harris, JAOCS *41,* 113 (1964).
13. Ginn, M. E., E. L. Brown and J. C. Harris, Ibid. *38,* 605 (1961).

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