A Realistic Soil Cloth and Test Procedure for Detergent Evaluation

B. J. RUTKOWSKI, Whirlpool Corporation, Research Laboratories, St. Joseph, Michigan

Abstract

The preparation of a uniformly soiled cloth for detergency studies is described. The soil, chosen for its realistic nature, consists of a colored clay as the particulate portion and triolein as the fatty or oily portion. The particulate portion of the soil is applied by tumbling the fabric in a horizontal axis washing machine containing a suspension of clay. The fatty portion is then applied by allowing the fabric to adsorb a known quantity of solvent-dissolved triolein with subsequent evaporation of the solvent.

An evaluation test procedure for measuring the relative efficiencies of proprietary detergents is also described. Using this procedure, soil removal, soil redeposition and optical brightener effectiveness of a detergent are determined simultaneously. Detergents can thus be given a numerical rating according to their over-all performance. This rating is calculated from the equation: Overall Performance = Soil Removal − Soil Redeposition + Optical Brightener.

Typical detergent evaluation data obtained with this soil cloth and test procedure are given, along with a statistical treatment of the data.

Introduction

The purpose of this work was the development of ways and means to keep abreast of the ever-changing science of laundry detergent formulation. The objective was the continual monitoring of detergent performance through a long-range detergent evaluation program.

Attainment of this objective required the development of a standard soil cloth and standard evaluation method which would meet certain specifications. The soil cloth and method had to be relatively realistic and sensitive. Both had to be very reproducible so that results could be compared with meaning over a long period of time. The method had to be simple enough to allow a large number of detergents to be evaluated, and finally the method had to lend itself to an expression of the total detergency picture as one value. This one value would include the three most important functions of a detergent: soil removal, prevention of soil redeposition, and optical brightening.

Success in obtaining a realistic and sensitive soil cloth hinged on proper selection of soiling materials and proper application to a test fabric. What, however, comprised a realistic soil? Current literature is in agreement that carbon-based soils are inadequate for detergency studies and equally in disagreement as to what does constitute a reliable soil (1–6). Choice of soiling materials here was a clay and triolein. Justifications for this choice were several. Various analyses (7–9) of the oily portion of laundry soils have skin fats or residues of skin fats as a common denominator. Analyses of airborne and ground soils (10) and of street dirt (11) show clay as a component common to all. Most significant, has been the work of Powe (7, 12) who showed "buildup" or problem soils to be clay minerals and residium of sebum, i.e., lime soaps and esters. Thirty to forty percent of these esters were as triglycerides. It followed that clay and fats or oils, representative of sebum, would comprise a meaningful soil for detergency studies.

A kaolinite type clay was chosen as the particulate portion of the soil. For the fatty portion, easily removable soils were not considered. This decision was based on the assumption that a detergent's laboratory performance against a difficult soil provides more confidence in prediction of field performance. Further work by Powe (13) has shown the ease of fatty soil removal from a cotton substrate by several surfactants and builders. Free fatty acids are easily removed, as are mono- and diglycerides. The most tenaciously held fatty soils are triglycerides. Triolein, a representative triglyceride was therefore selected. Initially, a lime soap was also thought to be desirable because it too is a "problem" or difficult-to-remove soil. In preliminary experiments cotton fabric was soiled with this material by several techniques. However, because of nonreproducible soil removal characteristics of these soil cloths, lime soap was eliminated as one of the soil components.

Uniformity of soil application and batch to batch reproducibility were the criteria for an acceptable soiling procedure. Simultaneous clay and triolein application was not used simply because an acceptable procedure could not be devised. Soiling with both components from a solvent suspension had two disadvantages. Ambient humidity conditions influenced degree of particulate and fatty soil pickup and the amount of triolein that could be applied was limited. Simultaneous soiling from an aqueous system was also unacceptable. In this case an emulsifying agent would be required to handle the fatty soil. This defeats the purpose of applying a fatty soil in the first place. The procedure as finally developed, which met the criteria of uniformity and reproducibility, consisted of applying the clay soil to the fabric from an aqueous suspension, drying and then applying triolein in just sufficient solvent to wet out, but not soak, the fabric and then evaporation of the solvent.

The goal in developing a detergent evaluation test procedure was a method which simultaneously evaluated soil removal, soil redeposition and optical brightening. Simultaneous evaluation was desired because of the interdependence of these three detergent functions. Under home laundering conditions each has an influence on the others. The basic requirement for this type of test is use of sufficient soil cloth to provide a realistic soil level in the bath for soil redeposition measurement.

Because a complete study of detergent performance under all possible field conditions is an impossible task, average practical conditions were used. Wash time was 10 min and water hardness was 135 ppm—the US average. A somewhat higher than average wash temperature was used because of its positive effect on soil redeposition. Hopefully this would increase sensitivity of the test.

Each detergent was evaluated at two concentration

TABLE I

Laundry Detergents—General Information

	Cost/pound ¢	Recommended Concentration %	Recommended Cost/wash ¢	7 Cent concentration %
Manufacturer A				
Best	24	0.12	4.1	0.21
Average	24	0.16	4.4	0.21
Poorest	22	0.17	5.3	0.23
Manufacturer B				
Best	28	0.18	7.0	0.18
Average	26	0.18	6.5	0.19
Poorest	31	0.19	8.5	0.16
Private Label				
Best	24	0.15	5.1	0.21
Average	20	0.16	4.6	0.25
Poorest	20	0.15	4.4	0.25

levels. The first, and usually lowest, was the concentration recommended by the detergent's manufacturer themselves. That amount recommended for a top loading automatic washer with an approximate 17 gallon fill was used. The second was that amount, also for a top loading automatic, equivalent to a cost of seven cents. Thus, detergent concentration varied according to recommended use level and cost.

Experimental

Soil Cloth Preparation

Materials. The standard soil cloth was prepared from white, bleached, unsized indianhead cotton; style 405, Testfabrics, Incorporated; New York, New York. Soiling materials were a kaolinite clay; Bandy Black, Spinks Clay Company, Paris, Tennessee and technical grade triolein; Matheson, Coleman and Bell. A front loading, tumble action washing machine was used to apply the clay soil to the test fabric.

Procedure. The preparation of the soil cloth involved three separate steps; pretreatment of the fabric and clay, soiling with clay and finally triolein soiling.

Ten 36-in. × 56-in. pieces of cloth—sufficient for 1040 4-in. × 4-in. swatches— were stripped twice in 0.25% Calgon at 150F, rinsed twice and extracted. Pretreatment of the clay consisted of grinding 100 g in a colloid mill under controlled conditions. The clay was then diluted to 4 gal with water at 100F containing 70.4 g of $CaCl_2 \cdot 2H_2O$. Total calcium content of this water was 50 g as $CaCO_3$.

The cloth, while still wet from the pretreatment, was placed in the washing machine and tumbled 1 hr in the 4 gal of soiling slurry. The fabric was then extracted, rinsed for 3 min in 4 gal of clear water at 100F, extracted again and tumbled in a wet condition for 1 hr. Tumbling while still wet uniformly evened out the clay distribution on the fabric. The cloth was dried in a large commercial-type dryer. After drying, the clay-soiled cloth was folded and placed in a stainless steel beaker. Triolein, 5% by weight of the fabric, in sufficient perchloroethylene to make a total volume in milliliters equal to 90% of the fabric weight was added to the clay-soiled fabric. This volume of triolein and solvent was experimentally found to be just sufficient to wet the fabric. The beaker was tightly covered and allowed to stand 24 hr. The soil cloth was then air dried, rolled up and stored at refrigerator temperature until use.

TABLE II

Ranking of Detergents

Detergent	Rank based on soil removal data only: Soil removal %	Redeposition	Brightener %	Rank based on overall performance: Detergent	Performance
P-1	64.6	5.0	11.8	P-1	65.5
A-1	63.0	5.7	13.6	A-1	64.1
B-1	62.3	6.1	12.2	B-1	62.3
P-2	59.4	9.1	8.2	B-2	54.8
A-3	58.8	13.6	12.8	P-2	54.4
A-2	58.4	11.0	12.0	A-2	53.4
B-2	57.4	9.2	13.2	A-3	51.6
P-3	54.0	11.7	8.2	B-3	47.7
B-3	51.7	10.2	10.4	P-3	46.5

Detergent Evaluation

Materials. Unsized, bleached indianhead cotton and pure polyester fabrics were used for redeposition swatches. The detergents evaluated were purchased locally through regular retail outlets. Reflectance of test swatches before and after washing was measured on a Hunter D-40 reflectometer. A Terg-O-Tometer was used as the washing device.

Procedure. Sufficient soil cloth swatches for the entire evaluation study to be conducted were cut and systematically randomized at one time. Each detergent was evaluated in triplicate at two concentration levels. Each test required 10 swatches. Therefore, 60 swatches per detergent were needed. The initial reflectance readings of the swatches were made. One liter of 135 ppm naturally hard water was placed in each of two Terg-O-Tometer beakers and allowed to come to a temperature of 140F. The appropriate amount of detergent was added and agitated exactly 30 sec. Five soiled swatches and four redeposition swatches (two cotton and two polyester) were added to each beaker and agitated at 100 strokes per minute for exactly 10 min. The wash solution was decanted and excess water squeezed from the swatches by hand. The swatches were soaked-rinsed 5 min in 2 gal of 135 ppm naturally hard water at 100F with no agitation. The rinse water was decanted and excess water squeezed from the swatches which were then dried in a domestic type modulated heat dryer. The preceding was repeated twice more. Ten new soiled swatches were used for each test, but the same redeposition swatches were carried throughout the three washes. Final reflectance readings were then made.

Discussion

Reporting of Results

Test results were reported as percentage of soil removal, soil redeposition, optical brightener effectiveness and over-all performance. Soil removal values were obtained from reflectance measurements made of the original and washed soiled swatches and applying the Kubelka-Munk Equation. Soil redeposition was reported as reflectance units lost by the redeposition swatches in three washings. With the test procedure used for this study, soil removal and soil redeposition are directly related. Redeposition is, to a certain degree, dependent on soil content of the wash bath; this, in turn, is dependent on the soil removal ability of the detergent. As a result, detergents poor in soil removal could appear to be good in preventing soil redeposition simply because little soil was available to redeposit. To compensate for this variation in soil content of the wash bath, redeposition values were arbitrarily corrected to a theoretical 100% soil removal level. This correction is reasonably valid because soil redeposition has been shown to be a linear function of soil content of the wash bath when soil level in the bath is low (1). Such was the case for these tests.

TABLE III

Laboratory and Field Performance of Three Laundry Detergents

	Laboratory tests			Home laundry tests		
	Redeposition			Redeposition		
Detergent	Cotton	Dacron	Optical brightener %	Cotton	Dacron	Optical brightener %
A	2.7	0.7	11.0	5.7	3.8	11.0
B	4.7	+0.8	6.4	7.8	4.3	9.1
C	6.8	3.1	8.2	9.3	6.1	9.7

Optical brightener effectiveness was reported as percent of the total reflectance due to fluorescence. Although soil redeposition influences optical brightener adsorption by cotton, no attempt was made to correct or adjust these figures for the amount of soil redeposited.

The detergents were ranked according to their soil removal ability and to their overall performance for cotton detergency. Performance, the total detergency picture expressed as one value, of each detergent was determined from the summation of its soil removal, soil redeposition and optical brightener results according to the equation:

Performance = (Soil Removal) − (Soil Redeposition) + ½ (Optical Brightener)

This equation places more weight on soil removal and prevention of redeposition than on optical brightener effectiveness. It is felt that under home laundering conditions, i.e. repeated washing of primarily cotton fabrics, high soil removal and low soil redeposition are more important than optical brightening. Optical brighteners improve the appearance of a wash. They are important for this reason but they cannot cover up poor detergent performance over any extended period of time.

Data

Typical general information for a number of detergents is shown in Table I. These detergents, selected from a total of 37 which have been evaluated, represent those rated best, average and poorest from each of two manufacturers and a group of private label brands.

Detergency data at the seven cent concentration level for these detergents are given in Table II. Two methods of presenting test results are shown. The first lists the detergents in order of decreasing soil removal ability. The second lists them in order of decreasing overall performance with soil removal, soil redeposition, and optical brightener data combined. Detergents that show high soil removal, low soil redeposition, and a good optical brightener rank high under either system. Detergents that are poor in preventing redeposition, such as A-3, or have a poor or insufficient optical brightener such as P-2 lose position. Detergent B-2 which exhibited excellent optical brightening gained in position.

The distinct advantage of this overall performance method for summarizing the test data is that it gives a single, numerical value for the housewife's criterion of judging detergent performance. "How white and how bright do my clothes look?"

As a check on the reliability of the test procedure for determining a detergent's soil redeposition and optical brightener characteristics, three detergents were laboratory and field evaluated. Table III is the result of these laboratory and practical wash tests. Detergent concentration for both was the manufacturer's minimum recommended level. Soil redeposition on cotton and polyester and optical brightening were noted. These data are the change in reflectance and effect of optical brightener after three washes for the laboratory evaluation and after ten washes for the practical wash tests. There is a difference in magnitude, but not in order, between these two sets of data. Visual appearance of the fabrics corresponded to reflectometer measurements. The agreement shown here, although based on limited data, indicate a certain degree of reliability in the laboratory evaluation procedure.

TABLE IV

Statistical Analysis
Eight Detergents—Three Replications

I. Analysis of variance

Source of variation	Degrees of freedom	Sum of squares	Mean square	F-Ratio
Replications	2	149.44		
Detergents	7	4367.19	623.88	
Error	229	743.75	3.25	192.08
	238	5260.38		

II. Ranking of detergents

Least significant range for adjacent values = 0.974%

	Rank							
	1		3	4		6	7	8
Detergent	A	B	C	D	E	F	G	H
% Soil removal	58.5	58.2	56.1	53.8	53.6	51.9	50.6	44.6

Statistical Analysis

To determine the significance of differences in percentage of soil removal between detergents, a complete analysis of variance was made of these data for each group of detergents evaluated. The analysis was that of a "Randomized Complete Blocks Design." It was appropriate because the detergent tests were run in a different random order for each of the three replications. The detergents were then ranked according to a "Multiple Range" test (14). It consisted of determining, as a function of the Error Mean Square, Least Significant Ranges. In the example given in Table IV the Least Significant Range for adjacent average percent soil removal values was 0.974%. Thus, detergents A and B tie for first place and Detergents D and E tie for fourth place. There is a significant difference between all other detergents.

Test Standardization

Correlation of tests run at different times and with different batches of soil cloth required a standardization procedure. Therefore, a standard detergent was included with each group of detergents evaluated and test results were adjusted on the basis of data obtained with this standard. Table V shows the magnitude of this adjustment. These data were obtained over a period of nine months for four different batches

TABLE V

Soil Cloth and Procedure Reproducibility

Soil cloth batch	Test number [a]	Soil removal %	Adjustment factor
4 (July 1965)	1	52.2	1.000
	2	51.6	1.010
5 (August 1965)	1	53.0	0.985
	2	52.6	0.990
10 (January 1966)	1	50.6	1.030
	2	51.6	1.010
15 (March 1966)	1	53.6	0.973
	2	53.6	0.973

[a] Each test represents 3 replicates.

of soil cloth. Difference in results among the four batches cannot be assumed to be entirely due to batch to batch soil cloth differences. Technician and test condition variation also are factors. The very small difference between tests using soil cloth from a single batch indicate good uniformity of soil application and good reproducibility of the test procedure.

REFERENCES

1. Hensley, J. W., and C. G. Inks, ASTM Special Technical Publication, No. 268 (1959).
2. Ginn, M. E., G. A. Davis and E. Jungermann, JAOCS *43*, 317 (1966).
3. Davis, R. C., Soap Chem. Spec. *39*, 47 (1963).
4. Spangler, W. G., H. D. Cross, III, and B. R. Shaafsma, JAOCS *42*, 723 (1966).
5. Schwarz, A. M., and J. Berch, Soap Chem. Spec. *39*, 78 (1963).
6. Schmolka, I. R., and J. W. Hensley, "Variations in Nonionic Detergent Evaluations with Different Soiled Swatches," paper presented at 51st Mid Year Chem. Spec. Manu. Assoc., May 18, 1965.
7. Powe, W. C., and W. L. Marple, JAOCS *37*, 136 (1960).
8. Brown, C. B., Research *1*, 46 (1947).
9. Oldenroth, O., Fette Seifen Anstrichmittel *61*, 1220 (1959).
10. Morris, M. A., and B. Wilsey, Textile Res. J. *29*, 971 (1959).
11. Sanders, H. L., and J. M. Lambert, JAOCS *27*, 153 (1950).
12. Powe, W. C., Textile Res. J. *29*, 879 (1959).
13. Powe, W. C., "Detergency Studies on Removal of Triglycerides, Diglycerides, Monoglycerides and Free Fatty Acids from Cotton." Paper presented before the Division of Colloid and Surface Chemistry, ACS September 2, 1964.
14. Harter, H. R., Biometrics *16*, 671 (1960).

[Received October 27, 1966]