A Double Label Radiotracer Approach to Detergency Studies[1]

B. E. GORDON, J. RODDEWIG and W. T. SHEBS, Shell Development Company, Emeryville, California

Abstract

The comparative detergency of a series of built detergents of commercial interest has been measured via the use of a doubly labeled multi-component synthetic soil. Four test fabrics: cotton, nylon, Dacron, and Dacron/cotton were soiled with the seven-component soil, which was in turn almost completely and then individually labeled. The fabrics were washed in a conventional Tergotometer under cold-water and hot-water conditions. Analyses of the fabrics before and after washing were made by liquid scintillation counting.

Two sets of experiments were run, the first based on cold-water detergent formulation (heavy-duty liquid), the second based on hot-water detergent formulation (heavy-duty powder). A number of nonionic surfactants were compared with linear alkyl aryl sulfonate in the first set, and two anionics were compared with two nonionics in the second set.

Expressing results as total detergency, i.e., amount of soil removed from all four fabrics, it was found that, under cold-water conditions, LAS (average side chain C_{13}) is significantly less effective than the nonionics investigated. The linear primary alcohol (C_{12}-C_{15} and C_{14}-C_{15}) ethoxylates removed slightly more soil than the ethoxylates of a Ziegler alcohol (C_{14}, C_{16}, C_{18}) and random secondary alcohols (C_{11}-C_{15}).

The same tabulation for the heavy-duty powder formulations under hot-water conditions showed LAS to be least effective over-all, sulfated linear primary alcohol somewhat more effective, and ethoxylated linear, primary alcohol slightly more effective still.

Redeposition of the various soil components onto unsoiled cotton was found to be slight, ranging from 0.2% to 1.7% of the amount in the wash water.

Introduction

THE EFFECTIVENESS of different detergent formulations is usually measured by their ability to remove soil from selected fabric during a washing cycle in an automatic washer or Tergotometer.[2] The choice of an appropriate soil has varied widely indeed over the years, ranging from carbon black to naturally soiled articles of clothing. Carbon black (1), clay suspended in lubricating oil (2), and other colored soils have been widely used because of their ready determination on white fabric by reflectance measurements. This technique lends itself very well to automated analyses and data handling, an important feature because of the large numbers of samples generated during detergency studies.

However, with increasing knowledge of the composition of natural mammalian wax (3) and the publication of experiments which cast some doubts on carbon black as a reliable representative of the organic and inorganic material likely to occur in soils (4,5), there has been a trend toward the use of more sophisticated soils together with a trend toward more accurate methods of analysis for the soil used. Thus Harris et al. (5) in 1950 used a carbon-14 tagged amide and hydrocarbon on metal as one of the earliest labeled soils in detergency studies. Ashcraft (4) used carbon-14 labeled tristearin and carbon black in a study of the relative removal of these two soil components from cotton fabric. Hensley and Inks (2) impregnated clay with calcium-45, which was then suspended in lubricating oil, and used this mixture as a particulate-bearing soil.

Ehrenkranz (6) used tagged tripalmitin in olive oil as a test soil, and Spangler (9) employed a nine-component soil much closer to natural sebum than the above authors. In 1955 Hensley et al. (1) properly pointed out that the use of radioactive soils would prove to be a powerful tool in evaluating detergency with artificial soils much closer to the natural condition than had heretofore been possible.

Wagg and Britt (7) in 1964 made one of the most comprehensive studies of detergency, using an eighteen-component soil in which five of the components were carbon-14 labeled in turn. They compared several fibers and several detergents in a series of time studies which demonstrated, in general, rapid removal (2–5 min) of the bulk of the trapped compounds, followed by a slow removal rate. Analysis was done by end-window Geiger counting, and no indication was given of the radiochemical purity of the labeled compounds. Recently Fort et al. (8) studied soiling and detergency with several detergents, four fabrics and four carbon-14 labelled soils. They, too, used end-window Geiger counting as the method of detection.

Thus there is no doubt that tagged compounds will continue to play a most important role in detergency studies. However some problems have impeded this application of tracers and particularly of multi-component soil in this area. First, the limited availability of required tagged components; second, the lack of rapid, accurate analytical methods for multi-component soils on fabric swatches and, third and most serious, the high probability that the tagged components were not radiochemically pure, thus yielding erroneous data (10).

In recent years these limitations have been the subject of considerable work with salutary results. First, there has been a steady increase in the availability of tagged organic compounds and in the development of new, convenient methods of synthesis (11,12). Second, end-window counting of radioactivity on swatches with its inherent errors of self-absorption is being replaced by the more accurate liquid scintillation counting (13). Finally, concern for radiochemical purity is now forcing users of labeled compounds to examine more carefully all compounds, purchased or prepared, for the presence of contaminants (13). This situation has recently prompted an editorial (14), stating that the policy of the journal would henceforth require authors to specify what they have done to investigate and insure the purity of radioactive compounds used in their study.

It therefore seemed appropriate to take advantage of modern radiochemical technology and to apply

TABLE I
Composition of Synthetic Soil

Component	Weight, %	Label	Source
Hydrocarbon oil (medium viscosity lubricating oil)	25	³H	Synthesized in this laboratory (see Ref. 15)
Tristearin	10	³H	New England Nuclear Company, Boston, Mass.
Arachis oil	20	None	....
Stearic acid	15	¹⁴C	NENC
Oleic acid	15	¹⁴C	NENC
Cholesterol	7	¹⁴C	NENC
Octadecanol	8	¹⁴C	NENC

modern techniques of radiochemical synthesis and analysis to a study of detergency by using a multi-component soil. The soil chosen resembles to some extent that of Spangler (9), but its composition was dictated in part by the commercial availability of the components. Doubly labeled soil was prepared to reduce the number of runs to be made and to investigate the selectivity of removal while reducing the possible effect of irreproducibility between runs. The fatty or oily components were tritium-tagged, and the polar components were carbon-14 tagged. The soil composition is shown in Table I.

Labeled arachis oil was not obtainable, but tristearin-³H was thought to behave in a manner similar to arachis oil (peanut oil). In the studies using completely labeled soils (except for arachis oil) the data were computed by assuming that this oil was represented by the tristearin-³H.

Radiochemical Purity

Considerable effort was expended in this part of the study. The lubricating oil was purified by multiple passes over activated silica gel, using hexane to elute the saturates and benzene to elute the aromatics. Each fraction was counted to determine its specific activity, and the total recovered activity was calculated. When no significant change in either was noted between two successive passes, the fractions were combined and used. The main purpose of this step was to remove any polar components which might have arisen during the labeling run (15).

Oleic acid and stearic acid-¹⁴C were converted to methyl esters and analyzed by gas-liquid radio-chromatography (GLRC) (10). The criterion of radiochemical purity was that greater than 95% of the radioactivity was to be present in the major peak. One batch of stearic acid was rejected on this basis; the other was satisfactory, as was the methyl oleate. Thin-layer chromatograms were run on the second batch of stearic acid and on the oleic acid as well. The areas with the acids contained more than 95% of the radioactivity on the plate (by liquid scintillation counting). The stearic acid was 98.7% pure, the oleic 99.2% pure. Octadecanol was examined by GLRC and found to have 18% radioactive contaminants. It was purified by preparative scale GLC,

TABLE II
Selectivity of Removal of Soil Components

Surfactant	Ratio ¹⁴C/³H Fractions Left							
	Cotton[a]		Nylon		Dacron		Dacron/ cotton	
	60F	120F	60F	120F	60F	120F	60F	120F
LPA-12	0.70	0.63	0.37	0.37	0.29	0.37	0.63	0.62
LAS	0.65	0.65	0.53	0.52	0.51	0.57	0.66	0.58

[a] Ratio of ¹⁴C/³H fractions in cloth before washing:
Cotton = 0.82
Nylon = 0.77
Dacron = 0.81
Dacron/cotton = 0.82

TABLE III
Removal of Soil Under Cold-Water and Hot-Water Conditions, %[a]

Surfactant and T, °F		Cotton		Nylon		Dacron		Dacron/cotton		All fabrics
		³H	¹⁴C	³H	¹⁴C	³H	¹⁴C	³H	¹⁴C	Total soil
LPA-	60	43	47	76	85	36	76	40	55	55 ± 3
12	120	52	59	74	86	26	79	44	67	60 ± 3
LAS	60	22	33	15[b]	32	16[b]	49	29	45	29 ± 4
	120	47	57	7[b]	25	17[b]	58[b]	32	53	38 ± 3
ZA-	60	42	49	66	76	28	65	34	51	51 ± 3
9.5	120	42[b]	53	54	80	34	84	40	67	55 ± 6
RSA-	60	43	48	63	75	33	66	40	52	51 ± 1
13	120	56	63	41	75	31	75	41	62	55 ± 3

[a] All data are averages of at least four replicates, others of eight.
[b] Data noted have unduly large deviations (i.e., ±30–40% relative). These arise from irreproducibility between Tergotometer runs. Precision within runs is generally less than ±10% relative for values below 60%, and generally less than ±4% for values above this.

was examined again by GLRC and found to be pure. Cholesterol-¹⁴C was purified by column chromatography over silica gel (Adsorbosil), and the purified fraction tested by thin-layer chromatography. About one-half of the original activity was present in the cholesterol peak; the remainder appeared later in the eluent and remained fixed to the column. Such gross impurity is unfortunately not rare. The TLC test of the purified fraction showed high radiochemical purity (>99%). Tristearin-³H was examined by TLC and found to be 93% radiochemically pure. The bulk of the impurity was tentatively identified as the diglyceride. Because of the limited quantity of tritiated tristearin at hand then and because purification usually results in a small percentage of handling losses, the compound was used at this level. Subsequent work with tristearin-³H will be at a higher purity level.

Analytical Method

The detailed method is the subject of a forthcoming report. Briefly it involves direct immersion of a swatch (0.25 to 0.5 g) of fabric in a toluene-based liquid scintillator and analyses of both tritium and carbon-14 by *beta*-ray spectrometry in a Packard liquid scintillation counter, Model 3003 (Packard Instrument Company, Downers Grove, Ill.). The efficiency of the system for tritium and carbon-14 is determined by the external standard method, in which a pellet of a *gamma*-emitting nuclide is injected into the counter chamber near the sample vial and the count rate of the Compton electrons, induced in the liquid scintillator, is obtained. By prior calibration the relationship between tritium and carbon-14 efficiency and the external standard count rate had been established and the entire computation programmed in FORTRAN IV for the IBM 7040, thus avoiding excessive calculations. In practice the three-channel liquid scintillation counter is set so that two of the channels look at tritium and carbon-14 while the third looks at the external standard. The machine then counts a sample for a preset time, enters the data on an IBM card, introduces the external standard, counts again for one minute, and punches out the data

TABLE IV
Comparison of Total Soil Removal from Completely Labelled and Individually Labelled Runs, % Removed

Surfactant	Completely labelled run		Sum of individual runs	
	³H	¹⁴C	³H	¹⁴C
LPA-S₁	51	77	55	79
LPA-S₂	45	73	47	73
LAS	42	65	42	66
LPA-12	57	70	62	76
RSA-13	56	72	60	73

TABLE IVa

Formulations and Wash Conditions

Active matter—anionics	0.3 g/l or 0.225 g/l
—nonionics	0.15 g/l
Sodium tripolyphosphate—anionics	0.525 g/l
—nonionics	0.60 g/l
Sodium silicate	0.075 g/l
Sodium sulfate	0.45 g/l
Carboxymethylcellulose	0.0075 g/l
The use concentration of the built detergents was 1.5 g/l.	
Water hardness	150 ppm as CaCO₃
	(Ca/Mg = 60/40)
Temperature	120F
Time	10 min
Agitation	100 rpm
Volume/Fabric	500 ml/5.3 g, approx. 100/1

The surfactants tested were:

LPA-S₁ — C₁₄₋₁₅ sulfate[a]	0.3	g/l
LPA-S₂ — C₁₄₋₁₅ sulfate[a]	0.225	g/l
LAS — alkyl aryl sulfonate		
LPA-12 — C₁₂₋₁₅ alcohol[b] ethoxylated to 12EO average.		
RSA-13 — C₁₁₋₁₅ alcohol[c] ethoxylated to 13EO average.		

[a] Linear, primary alcohol, NEODOL 45-S, Shell Chemical Company.
[b] Linear, primary alcohol, NEODOL 25-12, Shell Chemical Company.
[c] Random secondary alcohol.

again. The IBM program ignores the counts accumulated in the third channel during the first counting period and in the first two channels during the second counting period.

All computation is then done by machine, and the final results are expressed as mg/g of each fraction for each compound, as percentage remaining or percentage removed, etc. Thus sample and data manipulation end once the sample is introduced into the counter.

Detergency Studies

Padding

Preparation of soiled swatches is of paramount importance in a study involving very large numbers of samples. Sections of fabric 8 ft × 9 in. were prepared by several procedures. Radioactive soil was used because of the ease of measuring padding uniformity with the same method used in the detergency studies.

First, continuous padding was tried wherein a section of each cloth was dipped through a trough containing a soil solution in warm n-heptane, then passed through wringers and finally to a roller. Analysis of sections of the fabric (about 1½ × 3 in.) at various positions showed poor uniformity, about ±25–50%.

Second, a total absorption method was tried wherein the fabric was allowed to absorb completely a known volume of a soil solution. Vigorous agitation assisted the dispersal of the solution. About one-fourth of the fabrics so prepared were acceptable, i.e., had a uniformity of ±10% or less. This high mortality rate led to its discard after several months of use.

The third and current method consists of total immersion of the fabric 8 ft long by 9 in. wide in 400 ml of a 2% solution of soil in benzene/heptane (20/80) for several minutes for complete equilibration. The fabric is then removed, the excess liquid expressed with a hand wringer, and the cloth draped over a wire in a hood to promote air circulation. Generally this method has given uniformity to better than ±10%

TABLE VI

Individual Component Removal, Nylon, % Removed

Sur-factant	Lube oil	Tri-stearin (plus arachis oil)	Stearic acid	Oleic acid	Octa-decanol	Choles-terol
LPA-S₁	77	73	96	86	85	93
LPA-S₂	65	57	93	79	74	91
LAS	56	37	77	73	67	66
LPA-12	92	94	97	91	89	94
RSA-13	90	91	97	90	87	92

on analysis of at least six swatches. Recent experiments have shown that, if the ends of the fabric are cut off (one foot), uniformity seems to be improved. For nylon and Dacron a 1.75% solution was used, for cotton and Dacron/cotton a 2.05% solution. These gave padded fabrics with the same soil concentration (about 2%w).

Storage tests with the fabric showed no migration or evaporation of the soil after one month at ambient temperature. However drying at 250F with heated air results in the loss of some of the tritium fraction.

Washing

Before the study of soil removal from the various test fabrics was begun, a brief study was made to determine whether selectivity of removal occurred and, if so, whether it was affected by such factors as cloth, detergent, and temperature. The completely labeled soil was used (except for arachis oil), and the specific activities were adjusted so that the two tritiated components had the same specific activity (in dpm/mg), and the five carbon-14 components had the same specific activity. The tritiated materials had a specific activity about five times that of the carbon-14 components because the efficiency of counting the former is much lower than that of the latter. Thus a loss of activity because of the removal of either fraction could be translated into weight regardless of the particular component being removed.

Conditions for this first set of washing experiments (heavy-duty liquid formulation) were as follows: active matter, 0.15 g/l; potassium pyrophosphate, 0.375 g/l; sodium silicate, 0.0525 g/l; water hardness, 150 ppm as CaCO₃ (Ca/Mg = 60/40).

The use concentration of the built detergent was 1.5 g/l. Fabrics: cotton, nylon, Dacron, Dacron/cotton (one soiled 10 cm × 10 cm swatch of each in a beaker plus one unsoiled swatch of cotton, same size). Temperature, 60F and 120F. Time, 10 min. Agitation, 100 rpm. Volume/fabric, 500 ml/5.3 g soiled fabric approx. 100/l.

The surfactants tested were: linear primary alcohol C₁₂₋₁₅,[3] ethoxylated to 12EO average (LPA-12); linear alkyl aryl sodium sulfonate, C₁₃ side chain (LAS); normal primary alcohol, Ziegler process C₁₄₋₁₈, ethoxylated to 9.5EO average (ZA-9.5); random sec-

[3] NEODOL 25–12, Shell Chemical Company.

TABLE V

Individual Component Removal, Cotton, % Removed

Sur-factant	Lube oil	Tri-stearin (plus arachis oil)	Stearic acid	Oleic acid	Octa-decanol	Choles-terol
LPA-S₁	41	57	73	63	70	49
LPA-S₂	41	49	72	62	54	49
LAS	37	43	67	52	52	43
LPA-12	51	67	70	60	64	47
RSA-13	50	63	68	59	62	46

TABLE VII

Individual Component Removal, Dacron, % Removed

Sur-factant	Lube oil	Tri-stearin (plus arachis oil)	Stearic acid	Oleic acid	Octa-decanol	Choles-terol
LPA-S₁	37	45	96	92	88	97
LPA-S₂	31	33	94	86	87	94
LAS	44	39	96	81	81	76
LPA-12	37	44	92	84	68	67
RSA-13	31	38	83	80	53	54

TABLE VIII

Individual Component Removal, Dacron/Cotton, % Removed

Sur-factant	Lube oil	Tri-stearin (plus arachis oil)	Stearic acid	Oleic acid	Octa-decanol	Choles-terol
LPA-S₁	50	56	89	72	82	63
LPA-S₂	53	54	88	71	83	65
LAS	51	51	82	63	78	56
LPA-12	51	56	82	67	84	49
RSA-13	49	54	78	65	84	44

ondary alcohol C_{11-15}, ethoxylated to 13EO average (RSA-13).

Table II clearly demonstrates selectivity. In all cases the polar (^{14}C) fraction is preferentially removed. Selectivity is affected in large part by the fabric and to a lesser extent by the surfactant. Temperature has a minor effect on the relative polar compound removal, enhancing it for cotton and Dacron/cotton, decreasing it for Dacron, while nylon remains unaffected. This establishes that a single tracer would be unacceptable for a multicomponent soil where the components were chemically or physically quite different. The $^{14}C/^3H$ ratios in the footnote for Table II may be compared with the value of 0.82 of the solution used to soil the fabric. This indicates little selectivity in the soiling step.

It was next of interest to compare a number of nonionic surfactants with a widely used anionic at equal active-matter concentrations under conditions of heavy-duty liquid detergent concentrations, i.e., cold-water washing.

The fully labeled soil (except for arachis oil) was again used. The four fabrics were padded, and replicates of at least six of each of the four soiled fabrics (often 12) were run to determine padding uniformity, usually better than ±10% relative standard deviation.

Table III provides information for a number of statements. Hydrocarbon and triglycerides (tritium fraction) were more difficult to remove than polar materials from all farbrics and with all surfactants. Higher temperature generally increased removal of soil from cotton, Dacron, and Dacron/cotton but had very little effect on nylon. The anionic surfactant LAS was definitely poorer than the nonionics under cold-water conditions for all fabrics. LAS is also significantly poorer in soil removal at the higher temperatures. There are no remarkable differences among the nonionics for any of the fabrics tested except that the linear, primary alcohol ethoxylate, LPA-12, appears to be somewhat more effective for the nonpolar fraction on nylon than the random secondary alcohol ethoxylate and the higher boiling ethoxylated alcohol ZA-9.5. There is no explanation for the consistently higher removal of the nonpolar fraction (^3H) from nylon at 60F compared with 120F for the last two surfactants.

The data in Table III can also be expressed as total soil removed from all cloths for each surfactant to provide an indication of total detergency, as shown in the last column.

TABLE IX

Removal of Total Soil, All Fabrics

Surfactant	Removal, %
LPA-S₁	66 ± 2[a]
LPA-S₂	59 ± 2
LAS	53 ± 2
LPA-12	68 ± 2
RSA-13	66 ± 2

[a] Absolute standard deviation.

The linear, alkyl aryl sulfonate is definitely poorer over-all in the removal of total soil. It shows the greatest improvement with temperature. The nonionics are quite similar to each other with possibly slightly better performance for the LPA-12. The difference however is not great. Temperature apparently does have an effect, generally resulting in 5–10% more removal at 120F compared with 60F.

It was next of interest to apply the double label approach to individual component removal in the full synthetic soil under heavy-duty powder formulations. The double label approach reduced the number of runs needed. A study was made, composed of one run where the fully labeled soil (except for arachis oil) was again used as in the earlier experiments, followed by a set of four additional runs where two labeled components were present in the soil in each run, one tritium, and one carbon-14. The formulations and wash conditions were as shown in Table IVa.

The fully labeled run was included in this study to determine whether repeatability of the Tergotometer between runs was such as to permit inter-run comparisons. This was done by summing the percentage of each tritium and each carbon-14 component removed in the individual labeled runs (basis the complete soil) and comparing the value with that obtained from the fully labelled soil. The data were totalled for all four fabrics and are shown in Table IV.

The data in Table IV indicate fair reproducibility between the two types of runs, that is, to within 2–11% relative. Comparison of the data shows that the sum of the individual runs tends to be somewhat higher than the values from the composite runs. This is mostly on account of a disagreement between the two sets of data for cotton where the sum of the individual values is consistently high compared with the composite on this fabric (about 8–20%). The simplest explanation is that the value for the soiled, unwashed cotton on the composite run was too low. Because agreement for the other fabrics was better, the systematic error in the cotton value was reduced by about one-third (the fraction of total soil it contained) when averaging values over all fabrics. One probably cannot achieve much better agreement until both padding and washing can be made more precise.

The results of the individual soil removal runs from each fabric are expressed in Tables V–VIII. The same detergents were used as in Table IV. All data are averages of at least four replicates. The fully formulated soil was used in all cases.

A study of Tables V–VIII leads to several interesting conclusions. The most obvious one is that fabric composition plays an important role in detergency. On this basis it is reasonable to discuss the relative performance of the five detergents on a fabric-by-fabric basis.

Cotton. The nonionics (detergents LPA-12 and RSA-13) are superior to the anionics in their ability to remove hydrocarbon and triglycerides. The two nonionics are similar. Among the anionics the LAS is consistently lower in detergency than the two alkyl sulfates. The higher concentration (LPA-S₁) increases the removal of alcohol and the triglycerides only. The two acids and octadecanol are more easily removed than cholesterol or the nonpolar fraction.

Nylon. This fabric is characterized by a remarkable susceptibility to laundering, particularly by nonionics where all components are removed to better than 85%.

Of the anionics, the alkyl sulfates, in either 0.3 or 0.225 g/l concentration, are markedly superior to

the LAS. Again the higher concentration of active matter (LPA-S$_1$) yields consistently higher removal of all components. In fact, except for the low polarity components, LPA-S$_1$ is comparable with the nonionics for this fabric.

Dacron. This fabric demonstrates the greatest resistance to removal of the hydrocarbon and triglycerides of the four tested. The removal of the polar fraction, i.e., the acids, octadecanol, and cholesterol, is comparable with nylon for the anionics, notably the alkyl sulfates (LPA-S$_1$, LPA-S$_2$). For this fabric LAS is somewhat superior for hydrocarbon removal, inferior for cholesterol removal, and comparable for the rest. The nonionics are comparable with the anionics for the hydrocarbon, triglycerides, and the acids but are inferior for octadecanol and cholesterol. It is interesting to note that for this fabric, as for the other three, LPA-12 is slightly but persistently superior to RSA-13 for all components.

Dacron/Cotton. This fabric should present a picture somewhere between cotton and Dacron. This is approximately the case for removal of the acids, octadecanol, and cholesterol; but removal of hydrocarbon and triglyceride is a bit higher than would be expected from the results in Tables V and VII. For this fabric anionics and nonionics are, in general, comparable for all the components. LAS again is the lowest of the three anionics, though not to the extent noted with nylon. Again the nonionics (LPA-12 and RSA-13) remove cholesterol rather less effectively than do the anionics. Also, removal of polar materials is greater than that of nonpolar.

Tables V–VIII lead also to a few general comments. First, over-all, LAS removes the least amount of each soil component from the four fabrics. Second, there is a slight but persistently higher detergency with the alkyl sulfate at 0.3 g/l over 0.225 g/l. Third, there is a slight but persistently higher detergency with the linear primary alcohol ethoxylate over the random secondary alcohol ethoxylate. Fourth, fabric composition affects detergency remarkably, both on an over-all basis (see Table VI for nylon) and on an individual soil component basis (compare Tables V and VII).

One can combine the data in Tables V–VIII to obtain an over-all picture of total detergency of the five formulations tested similar to that in Table III. The results are shown in Table IX.

Table IX bears out the general statements made above. The two surfactants at concentrations common to Tables III and IX are the nonionics, LPA-12 and RSA-13. The higher removal in the heavy-duty powder formulations compared with the heavy-duty liquid may be based on the difference in inorganic builders in the two formulations, notably the phosphate, or on the fact that the padding procedure was different for the two sets of experiments. In any case, comparisons within one set of experiments (i.e., heavy-duty liquid or heavy-duty powder) are the most meaningful.

Redeposition

As noted previously, one unsoiled cotton swatch was placed in each beaker containing the four soiled swatches in order to study redeposition of the soil. These were analyzed in the usual way. The concentration (as percentage of soil removed by the detergent) on the unsoiled cotton is expressed in Table X.

The values are all very small, indicating that no great problem in redeposition is present under these conditions. In terms of concentration the values range from about 0.01 to 0.1 mg/g.

General Comments

The method as applied above is fairly reliable when comparing surfactants which differ in detergency by >15% relative standard deviation. It is less so, the smaller these differences, and one requires greater precision in the experimental work to see such differences. The analytical method is better than ±5% relative standard deviation and can easily be improved to ±3%. It is in the padding and particularly the washing steps that major improvements are required.

As suggested above, the padding step may be significantly improved (to ±3%) by removing the ends of the large padded fabric section. However some comments must be made on the Tergotometer operation.

Occasionally very large errors have appeared in the analyses of the four replicates. These errors (>40%) were almost always attributable to one of the four replicates containing two to five times the soil that the other three had. Such a result can be caused by poor padding, by nonuniform distribution of the soil on the washed sample from which the counting sample is cut, or by inadequate washing in the Tergotometer. Careful analyses of the padded fabric eliminated padding as a cause of errors of such magnitude. The second possibility, nonuniform distribution of soil on the washed sample, was investigated by the destructive sampling of a large number of washed samples. It was shown that nonuniformity of soil on the sample fabric after washing accounted for a minor, but significant part of the over-all variation in the results, as much as ±20% in some cases. By far the major cause of the occasional, very erratic results was a washed sample which had an abnormally high soil content, rather uniformly distributed over the swatch. This suggested poor washing reproducibility.

To avoid these two sources of error, two changes in procedure should be made. First, the cause of the occasional unwashed swatch should be eliminated, perhaps by insuring immersion and agitation throughout the wash cycle. Second, the effects of nonuniform soil distribution after washing can be eliminated by analyzing the wash water only. This, of course, would require the same fabric in each beaker rather than four different fabrics, as in this work. It would also require good agreement between beakers, which seems to be no great problem. In anticipation of this approach a liquid scintillation method for the analysis of wash water, based on the emulsion method of Patterson and Greene (16), has been developed and found to be satisfactory.

With these changes the Tergotometer should become as precise an instrument as the analytical method for soil.

TABLE X
Soil Redeposition on Unsoiled Cotton, %

Surfactant	Lube oil	Tristearin (plus arachis oil)	Stearic acid	Oleic acid	Octadecanol	Cholesterol
LPA-S$_1$	1.2	0.4	1.0	1.3	1.1	0.2
LPA-S$_2$	1.4	0.7	0.7	1.5	1.6	0.2
LAS	1.1	0.8	0.5	1.7	1.3	0.3
LPA-12	1.1	0.5	0.6	1.0	1.1	0.5
RSA-13	1.0	0.5	0.4	1.2	1.2	0.5

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