Establishment of a Standardized Detergency Evaluation Method[1]

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This paper describes a standardized laboratory procedure for determining the fabric soil-removal efficiency of heavy-duty detergents. A careful analysis of machines, standard soil fabrics, operating times, and water hardness had led to the standardization of technique. The precision of the method has been presented for tests carried out in hard and soft water on two anionic heavy-duty detergents at a concentration of 0.2%. Standard deviations of 0.74% for a water hardness of 50 p.p.m. and 1.03% for a water hardness of 135 or 300 p.p.m. have been obtained.

A STANDARDIZED laboratory procedure for the evaluation of detergents for laundering fabrics has, as its basic requirements, at least the following: a) the process must be valid, that is to say, it must measure accurately the natural function for which a product is being developed; b) it must be rapid; and c) it must be precise.

Detergency procedures vary from laboratory to laboratory, and the validity of any one method is under constant scrutiny and attack by workers in the field. Most depend upon the use of bench-scale detergency testers and standardized techniques for simulating natural soil. A few studies involving full-scale home and commercial washers have been reported. The problem faced by the research laboratory is one in which numerous formulations representing rather subtle differences in components must be evaluated rapidly, and a bench-scale procedure of reasonable accuracy and reproducibility is needed.

Practically all detergency procedures in common use are based on the utilization of one or more standard soil cloths, all of which are controversial in nature. While these standard soil cloths do indeed leave something to be desired in this area of evaluation, nevertheless, in the hands of skilled observers, standard soils remain the most rapid and economical means of estimating fabric detergency. One of the most widely used of these has been described by Harris and Brown (2).

Radiotracer techniques also have received considerable study in the period following the second great war when tagged elements entering into the detergent process, for example, carbon 14, phosphorus 32, and others in kind, became available for nonmilitary laboratory purposes. Hensley and co-workers (6) have described radiotracer techniques for detergency evaluation. Diamond and Levin (1) also have described a technique for assessing the soil-removal efficiency of detergents by precipitation in fiber substrates of the extremely insoluble substance, zirconyl phosphate, prepared by using phosphorus 32 as a tracer.

A number of bench-scale mechanical detergency testers have been used, or proposed for use, for detergency evaluation. One of the earliest examples is the Atlas Launderometer.[2] Wollner and Freeman (8) have described the development and operation of the Deter-Meter, a bench-scale tester possessing very carefully controlled mechanical action in the form of impact of fabric against retaining screens. Perhaps the most widely used laboratory detergency tester at the present time is the Tergotometer, considered in detail by Harris *et al.* in a number of comprehensive studies (3,4,5). Ludeman, Balog, and Sherrill have outlined a novel technique for detergency evaluation, utilizing an ultrasonic cone transducer (7). This ultrasonic device, capable of an output of mechanical action of very precise magnitude, has been utilized for critical comparisons of chemical structures of alkylbenzene sulfonates.

While many papers have appeared dealing with the theory underlying detergency performance and the evaluation thereof, few workers have written comprehensively of the selection of mechanical factors in methodological development. Furthermore there is little to be found in the literature on the statistical appraisal of detergency evaluation procedures. Since the task of the detergent development laboratory is one primarily of critical comparison of essentially similar materials, the basis for discrimination between products and processes must necessarily hinge upon statistical estimates of variance. This paper describes the steps involved in the selection of a procedure and systematically assesses the over-all variability of the component parts and the whole.

In this paper the Tergotometer and cotton standard soil cloth supplied by the U. S. Testing Company have been employed. Choice of the Tergotometer in this instance has been an expedient one. Rapid, routine analyses are an everyday requirement in the detergent evaluation laboratory. The Tergotometer provides rapid evaluation and good precision at a level of mechanical action sufficient to reveal relatively small differences between formulations. Aside from the fact that standard soil cloths combine prototypes of ingredients generally agreed to be present in naturally soiled cottons and that these are in widespread general use in all detergent laboratories, the validity of the standard soil approach is beyond the scope of this writing.

Experimental

Equipment. A Tergotometer was employed for providing mechanical action. A Hunter Multipurpose Reflectometer[3] was used to assess the reflectance of test pieces before and after washing.

Materials. Cotton standard soil cloth was employed in these studies. Water hardness was simulated by the addition of appropriate amounts of calcium and magnesium salts in the ratio 60:40.

Procedure. Standard hard water was prepared by dissolving 13.3 g. of anhydrous calcium chloride and 16.2 g. of magnesium chloride hexahydrate per liter. The resulting solution assays 20,000 p.p.m. total hardness at a Ca./Mg. ratio of 60/40. Hardness in these studies was simulated, employing 1.88, 5.06, and 11.25 ml. of standard hard water in 750 ml. of distilled

[1] Paper I in a series entitled: "Detergency Evaluations." Presented at spring meeting, American Oil Chemists' Society, St. Louis, Mo., May 1–3, 1961.

[2] Atlas Electric Devices Company, Chicago, Ill.

[3] Gardner Laboratories.

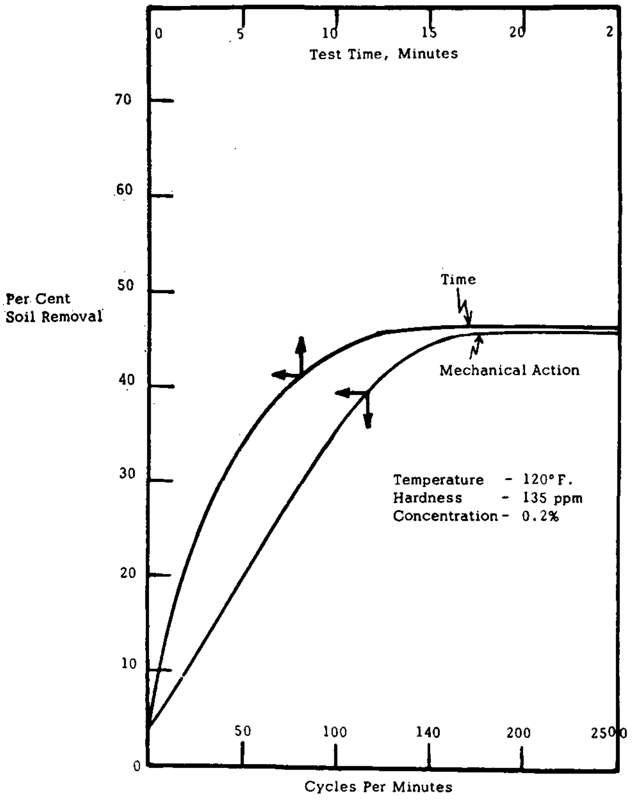

FIG. 1. Soil removal values in Tergotometer as function of mechanical action and time.

water to produce 50, 135, and 300, respectively, p.p.m. total hardness.

In actual practice three standard soil swatches, each four by five in., were entered into each Tergotometer cup together with 750 ml. of water at 120°F. A weighed amount of detergent was added. The Tergotometer then was run for 15 min. at 150 cycles per minute. The test pieces then were given four hand-squeezes under running tap water as a rinse. The swatches were ironed dry and reserved for assessment of soil removal.

Soil removal is determined from reflectance measurements made of the original soil cloth and the laundered piece. These reflectance readings then are treated as follows:

$(R_w - R_s)/(R_o - R_s) \times 100$ = percentage of soil removal

where R_w = reflectance of washed sample
R_s = reflectance of original soil
R_o = reflectance of unsoiled Indian Head

Indian Head fabric currently has a reflectance of 84.5 to 88.5% (magnesium oxide = 100% by definition). A value of 86.5% has been used for R_o in this work. Reflectance readings have been made by using four thicknesses of fabric, employing the green tristimulus filter (5550 ± 1000 Å).

Results and Discussion

Methodological

In any detergent process there are many variable factors, less than a dozen of which can be controlled with any degree of certainty. The variables considered in the method developed here are the following: mechanical action (type of detergency device), liquor/fabric ratio, test time, test temperature, number of washings, water hardness, and soil cloth type.

Mechanical Action. The Tergotometer simulates home washing-machine action in a bench-scale unit. It comprises four stainless steel cups mounted in a thermostat, each cup fitted with an agitator of the type found in top-loading, home-washing machines, into which washing liquor and fabric are placed. Its speed can be varied over a wide range. The Tergotometer provides simple and rapid evaluation and produces a level of soil removal sufficient in one wash to reflect reasonably small formulation differences.

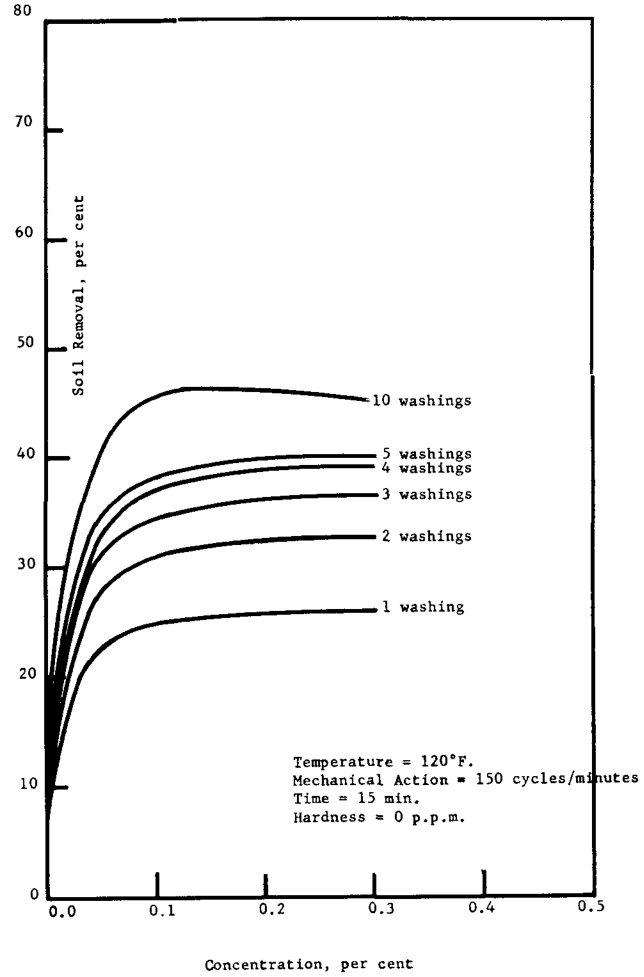

FIG. 2. Soil removal values, using U.S.T. cotton standard soil cloth in a Tergotometer as a function of number of replicate washings.

Liquor/Fabric Ratio. The liquor/fabric ratio was set arbitrarily at 75/1. This ratio was chosen for convenience since the practical home laundry ratio of 15/1 was impossible to achieve.

Test Time. Studies of soil removal as a function of time are shown in Fig. 1; all variable factors relating to machine operation are fixed. Soil removal rises rapidly up to a test time of 10 min., leveling off beyond this point. A test time of 15 min. was chosen, At this point change in soil removal with increasing time is small, and precision changes with small changes in time are minimized.

Test Temperature. A test temperature of 120°F. was chosen for these studies. Such a choice is obvious. The great bulk of the work reported on the evaluation of detergents and detergency procedures has been carried out at this temperature.

Number of Washings. Much detergency testing is done on the basis of replicate washings. As a matter of fact, virtually all industrial detergency evaluation is based on 20- and 50-wash test pieces. Laboratory screening however usually must be accomplished

TABLE I
Fabric Soil Removal Efficiency at 0.2 Percentage of Detergent Concentration

Replicate	Detergent T						Detergent C					
	Soil cloth Lot 1			Soil cloth Lot 2			Soil cloth Lot 1			Soil cloth Lot 2		
	T_1	T_2	T_3	T_1	T_2	T_3	C_1	C_2	C_3	C_1	C_2	C_3
	Total Water Hardness = 50 p.p.m.											
1	23.6	24.1	26.4	25.3	26.5	26.8	22.3	19.4	18.8	22.6	16.9	16.9
2	25.1	24.4	28.7	25.9	24.5	25.8	22.8	19.8	19.3	19.7	16.0	16.4
3	24.7	24.8	27.4	23.6	24.4	26.4	23.6	19.9	19.5	20.5	15.8	16.5
4	24.9	25.1	28.1	24.8	24.4	26.1	22.9	20.2	19.0	21.7	16.9	17.4
$\bar{x}$	24.6	24.6	27.6	24.9	25.0	26.3	22.9	19.8	19.2	21.1	16.4	16.8
	Total Water Hardness = 135 p.p.m.											
1	25.4	26.6	25.4	26.8	25.8	26.4	23.2	19.7	18.1	20.8	19.6	18.7
2	25.9	26.8	23.6	26.5	26.9	27.7	21.1	17.6	16.1	23.7	19.0	20.2
3	24.7	26.7	26.5	28.5	26.6	26.0	22.3	18.4	18.6	21.7	18.6	20.6
4	25.2	26.1	26.7	27.5	28.2	26.2	23.0	18.8	19.0	20.6	19.0	17.8
$\bar{x}$	25.3	26.6	25.6	27.3	26.7	26.6	22.4	18.4	18.0	21.7	19.0	19.3
	Total Water Hardness = 300 p.p.m.											
1	26.6	26.4	27.4	25.6	26.4	25.6	25.1	23.1	19.3	28.3	25.3	19.0
2	24.5	25.0	25.7	27.2	24.7	27.1	27.3	22.2	19.6	29.3	22.3	17.5
3	24.5	25.9	27.1	24.3	27.9	28.1	25.1	21.8	17.7	28.6	24.3	19.6
4	25.2	25.5	26.7	25.1	26.2	29.8	26.4	21.0	17.9	28.1	23.9	18.5
$\bar{x}$	25.2	25.7	26.7	25.6	26.3	27.7	26.0	22.0	18.6	28.6	24.0	18.6

much more rapidly than this. The family of curves shown on Fig. 2 represent the soil removal curves for one, two, three, four, five, and 10 washings; all other variables in the evaluation are the same. Note that five replicate washings produce a value of soil removal about 60% higher than the soil removal achievable in one wash. Ten replicate washings do not quite double soil removal values. From these data it was concluded that, for purposes of rapidity of evaluation, one wash is sufficient.

Water Hardness. Detergency data are reported at a number of levels of water hardness. Some standardization has been effectuated at 50, 120, and 300 p.p.m. total hardness. The water hardness range of 50 to 120 p.p.m. represents natural hardness found in eastern seaboard areas and in the major municipalities of the nation, where water conditioning down to a threshold hardness is practiced. A water hardness of 300 p.p.m. is typical of deep well waters utilized in rural areas. Fig. 3 shows the variation of soil removal with total water hardness for two synthetic detergent formulations.

Soil Cloth Type. A number of standard soil cloths currently are available in this country. Preliminary screening of four examples of cotton standard soil cloth led to the selection of one prepared by the United States Testing Company. This material is a fat-carbon black-oil cloth made by immersion of Indian Head fabric in the soiling medium. It was chosen for reasons of magnitude of soil release under the conditions in this method and for the overt reproducibility achievable in single wash tests.

Statistical

A preliminary investigation was made to isolate and assess the probable sources of error which would contribute loss of precision in the evaluation method outlined in the foregoing. A detergent concentration of 0.2% was chosen, and four replicate evaluations per variable were made among two types (T and C) of built anionic spray-dried heavy-duty detergents, three different lots of each of these detergent types, three water hardnesses, and two different lots of standard soil cloth. Detergent T contained a mixture of 10% dodecylbenzenesulfonate, 9% tallow alcohol sulfate, and 2.5% amide on an as-is basis while detergent C contained 18% dodecylbenzenesulfonate and 2% amide. Both were built with 40% phosphates and 1% carboxymethylcellulose. These studies were undertaken to determine the effect of each variable upon the reproducibility or precision of the test method and are not indicative of variations of detergency under

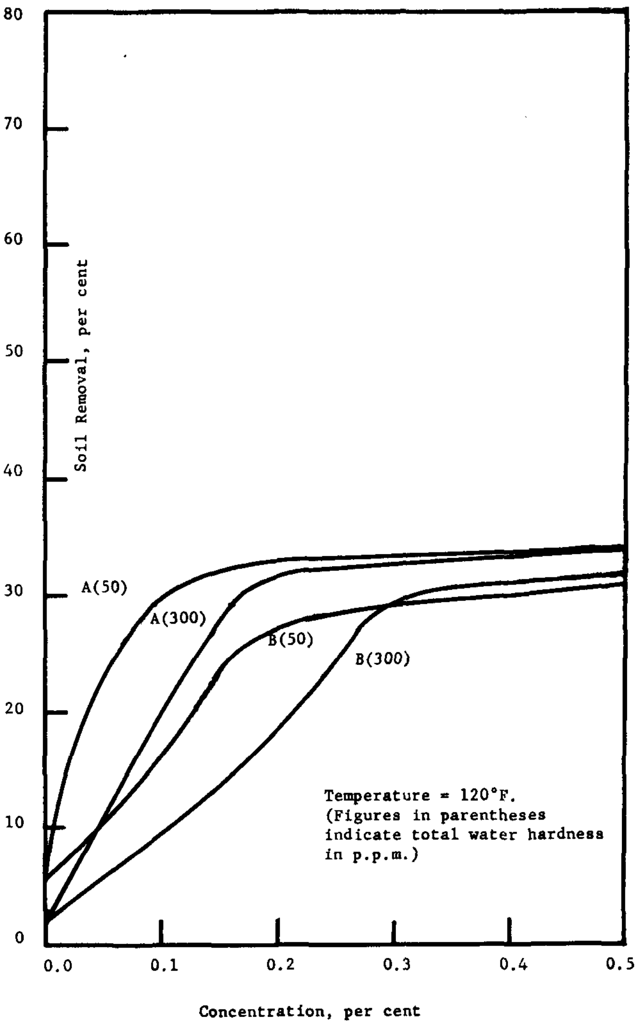

FIG. 3. Soil removal values for two anionic heavy-duty detergents (A and B) using U.S.T. cotton standard soil cloth in a Tergotometer.

different conditions. In Table I are shown the results of this series of tests. Analysis of variances, isolating possible sources of variations, and the application of the F-ratio test for homogeneity of variances are shown in Table II.

The following facts emerge from examination of these data. In the comparison of two different lots of soil cloth involving some 54 degrees of freedom, an F-ratio of 1.56 was indicated against the critical value of 1.57. This is a borderline situation. It is doubtful that different lots of soil cloth will produce different levels of precision of this method, based on these data.

Greater reproducibility occurs at 0.2% of detergent concentration in water of 50 p.p.m. total hardness than in harder waters. Since the ratio of the mean squares obtained at 135 p.p.m. and at 300 p.p.m. water hardness failed to exceed the critical value of F for the number of degrees of freedom involved, these mean squares are different estimates of the same variability. Thus the data from these hardnesses can be pooled for a better estimate of the hard water variance.

Different lots of the same type of detergent give the same reproducibility, and the same precision can be obtained from different types of anionic detergents.

These data indicate that the method of reproducibility at a concentration of 0.2% in soft (50 p.p.m.) water is as follows: standard deviation equals 0.74% soil removal; precision equals 1.5% soil removal at a 95% confidence level. The data for hard water (135 or 300 p.p.m.) is as follows: standard deviation equals 1.03% soil removal; precision equals ± 2.06% soil removal at a 95% confidence level.

In a subsequent paper the precision of the method outlined herein will be presented at detergent concentrations other than at 0.2%.

TABLE II
Analysis of Variance of Soil Removal at 0.2% of Detergent Concentration

Variable	Mean square	Degrees of freedom	F-ratio	Critical value of F
1. Soil cloth				
Lot 1	0.6956	54	F 2-1 = 1.56	1.57
Lot 2	1.0884	54		
2. Total hardness				
50 p.p.m.	0.5422	36	F 300-50 = 2.10	
135 p.p.m.	0.9944	36	F 135-50 = 1.83	1.75
300 p.p.m.	1.1394	36	F 300-135 = 1.15	
3. Detergent sample				
T_1	0.8192	18	F 1-2 = 1.11	
T_2	0.7371	18	F 3-1 = 1.51	2.29
T_3	1.2374	18	F 3-2 = 1.68	
C_1	1.0446	18	F1-2 = 1.69	
C_2	0.6168	18	F 1-3 = 1.16	2.29
C_3	0.8970	18	F 3-2 = 1.45	
4. Detergent type				
T	0.9312	54	F T-C = 1.09	1.57
C	0.8528	54		

Acknowledgment

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Statistical Approach to Detergency Evaluation. Correlation of Performance Data with Gas Chromatographic Patterns of Alkylbenzenes[1]

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The precision of a standardized detergency test based on the use of a Tergotometer and U.S. Test Cloth was found at a concentration of 0.4 and 0.5%. At these concentrations, the standard deviation was 0.56% soil removal units, and precision at a 95% confidence limit was ± 1.12% soil removal units.

The detergency of some built spray-dried detergents was examined by this method and found to differ significantly, though chemical compositions were identical. Gas chromatographic analysis of the alkylbenzenes obtained by desulfonation of the alkylbenzene sulfonates indicated small structural variations which correlated with the observed variations in the detergency.

IN A PREVIOUS PAPER (3) a standardized procedure for determining the detergency of built detergent powders was described utilizing the Tergotometer and U.S. Test Cloth. It was found that when this test was run at a concentration level of 0.2% the precision was dependent on the hardness of the water being used. With soft water (50 ppm) the precision at a 95% confidence limit equalled ± 1.5% soil removal units; on the other hand at the 135 ppm and 300 ppm water hardness level the precision was ± 2.6% soil removal units. This indicates that for evaluating the relative cleaning ability of detergents, the 0.2% concentration level might lead to misleading results. This point is illustrated in Fig. 1, which shows typical soil removal *vs.* concentration curves. At the 0.2% concentration, the slope of the curve is still quite steep, and errors are readily magnified.

The purpose of this investigation was to determine whether the precision of our method could be improved by running the test at higher concentrations

[1] Paper II in a series entitled Detergency Evaluations, presented at the meeting of the American Oil Chemists' Society, St. Louis, Missouri, May 1–3, 1961.