by Hofgaard (4) and by Kraemer and Bailey (5). It is apparent from their volume-temperature curves for cottonseed and peanut oils that the slope, or the change in volume per degree, is about the same for the two oils in the liquid state but that below the temperature at which solid separates the slope is very much greater for cottonseed than for peanut oil.

Filtration

The use of filtration as a means of separating the solid from the chilled oil-acetone mixtures was examined briefly by means of a small-scale "filter leaf" test, with and without filter aids. These experiments were limited to oil-solvent ratios ranging from 20 to 50% and a chilling temperature of −9.0°C. with a 3-hour holding-time and were only roughly quantitative.

In general there was an extreme contrast between the ease of filtration of the cottonseed oil mixtures and the difficulties encountered with the peanut oil mixtures. The former proved readily filterable over the entire range of concentrations investigated while the latter could be filtered clear at a reasonable rate up to an oil-solvent ratio of only 30%. Successful filtrations of the cottonseed oil-acetone mixtures were made without filter aids while the only satisfactory tests made on peanut oil mixtures involved the use of filter aids either as a precoat or added to the solution.

The most successful filtrations were made by using a No. 8 duck as the filter cloth. The initial rate of filtration (duration one minute) of a 35% solution of cottonseed oil containing about 1% of filter cel kept in suspension by gentle agitation during chilling and using a vacuum of 10 inches of mercury was approximately 530 pounds of oil per square foot per hour. Using the same cloth or a heavy twill with a precoat of the filter aid about one-sixteenth inch thick a 30% solution of peanut oil in acetone filtered at the initial rate of approximately 350 pounds of oil per square foot per hour. A 30% solution of the same oil containing a small amount of filter aid and agitated while cooling filtered at approximately the same rate.

Summary and Conclusions

Systematic physical chemical data on the solvent-winterization behavior of cottonseed and peanut oils with acetone have been obtained which should serve as a basis for selecting the conditions necessary for the effective solvent winterization of these oils in acetone.

Cottonseed and peanut oils are only partially miscible with acetone below certain temperatures which have been determined. In peanut oil this phenomenon may interfere with the winterization process within a certain range of concentrations. For cottonseed oil however the separation into two liquid phases does not occur until some 5°C. below the temperature required for adequate winterization.

Complete data for a 3-hour holding-time have been obtained for three cottonseed oils ranging in iodine value from 106.1 to 116.4. Tables and graphs have been constructed to show the effect of oil-solvent ratio, chilling temperature, holding-time, agitation, and iodine value of the original oil on the percentage of solid removed and on the degree of winterization and iodine value of the winterized oil.

Similar data have been obtained for a refined peanut oil insofar as possible without interference from separation into two liquid phases. It seems probable that if acetone were used as the winterization solvent for peanut oil, the separation into two liquid layers and the sensitivity of this phenomenon to moisture might be a source of processing difficulties especially if filtration instead of centrifugation were used to separate the solid from the supernatant.

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Detergency Evaluation. I. Wash Test Methods[1]

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SURFACE-ACTIVE agents can be evaluated by many different tests, some of which were described in a previous paper (4). Of the many possible, a method for estimation of cleansing ability is necessary since one of the very important uses of these agents is the cleansing of surfaces such as soiled wearing apparel, which alone represents a multi-million pound market in the United States.

Not all surface-active agents possess the same degree of cleansing action, and differentiation between them is a serious problem which becomes more complex when the multitude of mechanical means used to produce washing action are considered. These have varied from hand cleaning to use of mechanical washers and now includes fully automatic washing machines installed both in homes and in power laundries. Duplication of these washing processes in the laboratory on a small scale, under controlled conditions, proves fairly difficult. Mechanical action and its mode of application must be controlled since it directly affects the degree of soil removal, as demonstrated by Bacon and Smith (2) for the Laun-

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derometer. Apparently there are almost as many different wash test procedures in use as there are laboratories performing such evaluation work.

Disregarding the machine for the moment, but considering the washing and rinsing sequence, many investigators use a single wash period of varying duration, followed by an arbitrary rinse cycle, perhaps designed to approximate practical rinsing conditions. Other investigators have used a multiple wash system, but again the treatment of the fabric in the wash and rinsing system has varied widely. With this lack of standardization of wash test method (including rinsing) it is understandable that radically different results can be obtained by different investigators in detergent evaluation even though only a single soil test fabric were to be used.

The purpose of this work was to determine the extent of correlation obtainable between several different wash test methods. Factors controlled as constants were the detergents used, their concentration, temperature of wash, water hardnesses, and a standardized soiled test fabric.

No attempt will be made to review the many wash test methods revealed in the literature since they are arbitrary in nature. The wash test methods used in the present work are believed to be sufficiently representative to cover single wash, single or multiple rinse systems, and multiple wash, single or multiple rinse procedures.

Contrary to many views, a wash test requires as much attention to detail as does an involved analytical procedure. Well-trained operators are a necessity, and it is a mistake to entrust the wash test to unskilled personnel if reliable and reproducible data are to be obtained.

Wash Test Machines. No attempt will be made to review the many machines used in the washing operation. Those used in this work are widely recognized and representative. The Launderometer (7) has been fully described in many papers and is probably one of the most widely used laboratory machines. In some respects it is admirably suited to laboratory work because of size and availability and because it can be made to control many of the mechanical variables involved. Unfortunately the mechanical action involved seldom closely approximates practical conditions. It can hold as many as 20 sample jars at a time and requires small volumes of solution.

Less well-known is the Terg-O-Tometer (11) because of its more recent introduction. In effect this machine is a gang of four small conventional washers. One of its advantages is the possibility of using several individual swatches of test fabric per wash to increase the reliability of the wash data.

The advent of the fully automatic washer has broadened the availability of modes of mechanical action and washing and rinsing cycles. Better known however is the conventional agitator washer. In our tests a machine representative of this type washer was used (12). The characteristics of these machines are compared in Table I.

TABLE I

Machine Operating Characteristics

Characteristic	Launderometer	Terg-O-Tometer	Conventional
Loaded capacity—liters	0.1 or 0.2	1.0	64
Weight of fabric (g.)/liter soln	37 or 15[1]	6-12[2]	56[3]
Rotation—degrees	360	350	150
Cycle-rate/minute	40	144	122

[1] One 6 x 5" swatch; one 3 x 4" swatch. [2] Four or eight 3 x 4" swatches. [3] Eight lb./17 gal.

It was to be expected that the machines would differ, but perhaps the most noticeable variations, other than solution capacity, are the weight ratios of fabric to solution, and the degree and rates of rotation of the agitators. It is important that the fabric to solution weight ratio is greater in the conventional washer than in the laboratory equipment.

Other variations of these methods for applying mechanical action have been described, including models of power washing wheels, conventional home washers, or the use of pony wash wheels. Regardless of the machine, it will be difficult for two laboratories to check exactly with the same type of machine unless the procedure used is fully described and followed exactly.

Soils. Examination of the literature will probably indicate that there are as many soil test fabrics in use as there are investigators. The thinking on soil test fabrics varies widely from the "realistic" school which uses actual soils to dirty their fabrics, the "quasi-realistics" who compound their soils based upon chemical analyses of actually encountered dirts, and the "arbitraries" whose soils are arbitrarily chosen for the method of evaluation or tenacity of character. In any event the soil must provide a realistic evaluation of commonly recognized and effective materials and must provide a degree of reproducibility. Part I of this paper is not concerned with soil test cloths in general but is specifically concerned with a single test fabric which has been fully described elsewhere (5). Briefly, the test cloth is Indianhead fabric which has been soiled with a suspension of Oildag and Wesson Oil in carbon tetrachloride and subsequently standardized to a definite soil removal range.

Detergents Tested. The detergents chosen for this work were limited to four, and they were chosen for their rather wide variation in structure and character. They were:

a) A built nonionic agent.
b) A built alkyl aryl sulfonate.
c) A pure soap of moderate titer.
d) Loralkyl sodium sulfate.

Both the built compositions may be considered as moderately heavy-duty materials whereas both the other two have met most success in the light-duty field. All are widely used detergents from commercial production lots.

The solution concentrations chosen were those optimum for soap. In the usual detergency evaluation, concentration and water-hardness curves would be developed, which would show the relative effectiveness of the agents over ranges covering practical usage. The object of this work was not a direct comparison of detergents as such but an evaluation of wash test methods so that the data developed concerning relative detergency ratings are restricted to the range which follows:

50 ppm. water—0.2% concentration;
300 ppm. water—0.4% concentration except for loralkyl sulfate which remained 0.2%.

The water used covered soft and hard water conditions and was constituted to give a calcium to magnesium ratio of 60 to 40 as parts per million

$CaCO_3$. The salts used to provide hardness were calcium chloride and magnesium sulfate.

Wash Test Procedures

The wash test procedures used are detailed below.

Test 1. Launderometer. Four 10-minute washes.

Equipment. Launderometer with attached loading table, pint jars with glass lids and rubber gaskets, and rubber balls for the jars. The speed of the jar rack was adjusted to 40 ±2 rpm. at full load.

Test Cloth Preparation. Five by six-inch swatches of the standardized soil test fabric were cut from the length of the roll. The six-inch length was nicked ¼ inch at 1½-inch intervals with scissors. The four pieces thus marked off were identified with indelible marking ink for purposes of identification. Two solid pieces were prepared for each sample to be tested.

Charging the Launderometer. 1. A 1-liter stock solution of the detergent under test was prepared, and from it were poured about 220-ml. amounts of solution into 250-ml. beakers. These were preheated on a hot plate to 120°F. The beakers were removed from the hot plate and the solutions were poured into 100-ml. graduated cylinders. This amount of solution was poured into the corresponding jar on the loading table. Ten rubber balls (Launderometer specification) were placed in each jar. When the jars had attained the temperature of the machine, the previously marked swatches of soil test fabric were placed in the corresponding jar, the jars sealed and tested for leaks, and loaded into the Launderometer.

2. These were washed for exactly 10 minutes at 120°F.

3. While the first wash was in process, another set of jars was placed in the loading tray, and except for the soil test fabric all preparations were made for a second wash.

4. After 10 minutes in the Launderometer, the jars were opened and the contents dumped into a perforated copper catch-box in the sink. Both swatches for each detergent sample were removed from the box before the contents of the next sample jars were dumped. The swatches were squeezed out by hand and laid aside until all of the swatches had been removed. The fabric samples were then spread out and the pieces representing the first wash (the first 1½-inch pieces) were cut off. The remainder of the cloth was returned to the corresponding jars in the loading table.

5. The second 10-minute wash was made in exactly the same manner as the first. Fresh jars and rubber balls were prepared for the loading table while the wash was in progress.

6. The cloth swatches representing the first wash were rinsed in two portions each of approximately 500 ml. of distilled water. This was done by dousing the cloth swatches into each water three times and squeezing them out after each dip. The same procedure was repeated in the second rinse water.

7. The third and fourth 10-minute washes were made in exactly the same manner as for the second wash.

8. The rinsed swatches were squeezed free from water by hand and spread on an aluminum sheet which was immediately transferred to an oven at 65°C. equipped for circulation. The swatches were removed when dry.

Test 2. Launderometer. Single 20-minute wash.

Since the procedure for Test 2 was essentially the same as for Test 1, only variation in method will be mentioned.

1. Only a single wash of 20 minutes' duration was given.
2. The flat swatches were squeezed in a manually operated wringer after the wash.
3. The swatches were rinsed once for 5 minutes in the Launderometer jar containing the 10 rubber balls, and with a volume of 100 ml. of water of the hardness in use at 120°F.
4. Repeat 2.
5. The swatches were spread out upon an aluminum sheet and transferred to an oven at 65°C. and were removed when dry.

Test 3. Terg-O-Tometer. Single 10-minute wash.

1. 1,000 ml. volumes of the detergent solution in use were preheated and transferred to the Terg-O-Tometer.
2. The machine was started and, with assistance, the four individual 3 x 4-inch swatches were quickly added one at a time to the beaker.
3. These were washed for exactly 10 minutes at 120°F.
4. The beakers were removed from the water bath and the solution discarded.
5. The swatches were individually wrung through a hand wringer.
6. The swatches were returned to the beakers as described under (2) above and rinsed for exactly 5 minutes in water of the hardness in use at 120°F.
7. Repeat (4) and (5).
8. The swatches were spread on an aluminum plate to dry and transferred to a circulatory oven at 65°C. When the swatches were dry, they were removed.

Test 4. Terg-O-Tometer. Single 20-minute wash.

The procedure was exactly as in Test 3, except that the wash time duration was 20 minutes, and 8 swatches were used instead of 4.

Test 5. Conventional Washer.

The water capacity of the machine with an 8-pound load was found to be 17 gallons. The load was weighed into the machine and consisted of normally soiled fast-colored or white garments. Each load contained, in addition to the soiled garments, five 5 x 6-inch swatches of standard soiled fabric.

1. The machine was filled to the predetermined level with water at 120°F.
2. The detergent was added with the agitator in motion to permit rapid solution.
3. The 8-pound weighed load was added.
4. The load was washed for 10 minutes.
5. The garments were then wrung into a stationary tub of 9 gallons of water of the same hardness as the wash, at 100 ±5°F.
6. A hand rinse was administered in the water of Step 5 by thoroughly moving the garments up and down in the water.
7. The rinsed garments were wrung into the machine filled with 17 gallons of fresh water of the hardness in use at 100 ±5°F.
8. A machine rinse was made for 5 minutes.
9. The garments were wrung from the rinse.
10. The soil swatches were removed and pressed dry at a low iron temperature in a flat work press.

Test 6. Launderometer. Steel ball technique.

1. Test pieces were 3 x 4" in size, and each jar contained one swatch of soil, and one piece of white unsoiled fabric of the same size.
2. The concentration for each detergent solution was 0.2% in 50 ppm. water and 0.4% in 300 ppm. water except for the fatty alcohol sulfate, which was 0.2% in 300 ppm. water. The stock solutions were preheated to 120°F. before adding to the jar.
3. In each pint Launderometer jar were placed ten ¼-inch stainless steel balls, 200 ml. of test solution, at 120°F., and the swatches in this order.
4. The closed jars were tested for leaks, transferred to the loading table for 10 minutes to attain temperature, and then loaded into the machine.
5. The jars were rotated for 30 minutes at 40 ±2 rpm.
6. After the wash period the jars were poured successively into a strainer in the sink. The pieces were then dropped into a pail of distilled water at 110°F. and stirred for one minute, removed individually, and laid on a towel lying on the bench. They were then blotted dry with a clean dry towel and laid out on an aluminum sheet and dried as in Test 1.

Reflectance Readings. Reflectance readings were made by placing duplicate swatches from the same wash and detergent, one upon the other and stretching them between small brads on a board painted battleship gray. With Indianhead fabric and the background described, background reflectance is minimized and essentially constant.

The Photovolt model 610 meter (9) was adjusted to 0% reflectance for the soil actually used and then adjusted to 100% reflectance for the white fabric used in preparing the soil test cloth. This is an arbitrary procedure and gives immediate percentage soil removal readings for the washed swatches. Three methods of attaining reflectance values have been made:

1. The preferred method just described.
2. Adjustment of the Photovolt to absolute zero and to 90% (or other) reflectance with a suitable working standard.
3. Measurement with the Hunter Photometer (6) using working standards.

TABLE III

Percentage Soil Removal Data

Detergent	%	ppm.	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6
1. Built nonionic	0.2	50	47	39	43	51	35	35
2. Built alkyl aryl sulfonate	0.2	50	45	38	41	45	36	28.5
3. Pure soap	0.2	50	53	52	60	49	21	48
4. Loralkyl sodium sulfate	0.2	50	37	29	34	36	....	24
1. Built nonionic	0.4	300	47	41	46.5	54	33	37
2. Built alkyl aryl sulfonate	0.4	300	48	43	48	54	34	38
3. Pure soap	0.4	300	51	48.5	60	49	38	45
4. Loralkyl sodium sulfate	0.2	300	38.5	26.5	39	39.5	....	30

Test 1, multiwash Launderometer method.
Test 2, single wash Launderometer method.
Test 3, Terg-O-Tometer 10-minute wash.
Test 4, Terg-O-Tometer 20-minute wash.
Test 5, conventional wash.
Test 6, Launderometer single wash with steel balls.

The preferred method provides percentage soil removal data (percentage reflectance) immediately and directly. Both methods 2 and 3 require arithmetic calculations to obtain comparative soil removal:

$(A - B)/(C - B) \times 100 = \%$ soil removal, where,
A = Soiled fabric after wash,
B = Soiled fabric before wash,
C = White fabric before soiling.

The following data are illustrative of the values obtained for a single set of swatches of the four previously described detergents washed under identical conditions of test. The columns headed "% Soil Removal" were obtained as previously described, and the other columns are the comparisons between products referred to one sample as a standard. Differences for the three methods between the comparison with the standard for a given detergent can be attributed to experimental error in the operation of the photometers, including the fact that "% soil removal" values are recorded only to the nearest significant 0.5 unit by methods 1 and 2.

TABLE II

Comparison of Reflectance Methods

Detergent	Method 1 Soil Standard		Method 2 Working Standard		Method 3 Hunter	
	Soil Removal	Comparison With Std.	Soil Removal	Comparison With Std.	Soil Removal	Comparison With Std.
1	45.5	100	43	100	38	100
2	46.5	102	44	102	40	105
3	60.5	133	54	126	50	132
4	35	77	33	77	27.5	72

Statistical Methods

The methods used to assist in interpretation of the data are all recognized ones: standard deviation (1), standard error, $\sigma_{\bar{x}}$ (10), coefficient of variation (1), and coefficient of correlation (7, 8).

A significance level was used for this work of 0.05 (five chances out of 100 of being wrong). These calculated values are available from Fisher's Table V. A. (3).

Comparison of Two Mean Values (3). Two mean values may be compared by the process used by Fisher, who shows that if the difference between two mean values is equal to, or greater than twice the larger standard error, the chances are 95.45 out of 100 that the two materials are actually different.

Duplication of Tests. Each value shown in the tables was the average of at least duplicate samples in two separate wash series for Tests 1, 2, and 6, quadruplicate swatches for at least two wash series for Test 3, eight swatches for at least two wash series for Test 4, while Test 5 comprised the average of 10 washes, each containing five soil swatches.

Discussion

Examination of Table III shows the considerable variation in extent of soil removal which exists from test to test. This should be expected, considering the differences in method of handling and in the washing machines used. In one general level are Tests 1, 3, and 4. Test 1 is a multi-wash Launderometer method, Test 3 is a 10-minute Terg-O-Tometer method, and Test 4 is in the same machine, but for a 20-minute washing period. A generally lower level of soil removal was attained by Tests 2, 5, and 6, which are respectively a single 20-minute Launderometer wash, the wash in the conventional washer, and Test 6 the Launderometer method, using a double volume of solution and steel balls. It might have been expected that a closer coincidence of values should have been found between the conventional washer and the Terg-O-Tometer, or between the various Launderometer tests.

Table IV presents the same data using the loralkyl sulfate detergent as a basis for comparison. It again becomes evident that there are several different levels of detergency, and this method for investigation offers no clarification over the percentage soil removal data. A question that should be answered is whether the test methods show variation in the detergent samples tested and if they do, whether the variation is significant and whether the samples are rated in the same order of effectiveness. This may be accomplished by use of the statistical data given in Table V and by determination of statistical correlation between methods. Using the twice standard error method previously described, the detergents can be arranged in order by test method as shown in Table VI.

TABLE IV

% Detergency

Basis of Loralkyl Sulfate

Detergent	%	ppm.	Test 1	Test 2	Test 3	Test 4	Test 5
1	0.2	50	127	134	127	141	146
2	0.2	50	122	131	120	125	119
3	0.2	50	143	179	176	136	200
4	0.2	50	100	100	100	100	100
1	0.4	300	122	155	119	137	123
2	0.4	300	125	162	123	137	127
3	0.4	300	132	183	154	124	150
4	0.2	300	100	100	100	100	100

A further method for examining the degree of correlation between tests is to determine their coefficients of correlation in general comparing the meth-

TABLE V

Standard Deviation and Standard Error
Based on Table II—% Soil Removal

Detergent	%	ppm.	Test 1		Test 2		Test 3		Test 4		Test 5		Test 6	
			σ	$\sigma_{\bar{x}}$	σ	$\sigma_{\bar{x}}$	σ	$\sigma_{\bar{x}}$	σ	$\sigma_{\bar{x}}$	σ	$\sigma_{\bar{x}}$	σ	$\sigma_{\bar{x}}$
1	0.2	50	2.90	1.68	1.79	1.03	1.87	0.71	2.05	0.51	4.51	0.64	1.87	1.08
2	0.2	50	3.10	1.79	4.60	2.64	0.93	0.35	2.86	0.69	4.78	0.68	1.14	0.66
3	0.2	50	0.63	0.36	2.74	1.58	1.66	0.63	3.30	0.83	5.72	0.81	2.60	1.50
4	0.2	50	2.55	1.47	1.50	0.87	0.79	0.30	2.70	0.67	......	......	1.73	1.00
1	0.4	300	3.10	1.79	3.58	2.06	4.24	1.61	2.50	0.63	3.62	0.53	1.22	0.71
2	0.4	300	2.90	1.67	2.40	1.38	1.37	0.52	0.55	0.14	5.90	0.83	2.69	1.55
3	0.4	300	1.16	0.67	1.52	0.88	3.75	1.42	4.75	1.19	5.58	0.79	1.50	0.87
4	0.2	300	1.98	1.14	1.52	0.88	1.70	0.64	1.92	0.48	......	......	2.96	1.71

ods with Test 1. A significance level of 0.05 was believed to fall within the limits of reproducibility of these methods. The data resulting from these comparisons are given in Table VII. The following characterizations are revealed from Tables VI and VII:

50 ppm.

SignificantCorrelation
Tests 1 and 2
Tests 5 and 6

Close Correlation
Tests 1 and 3
Tests 1 and 6

Significantly Negative
Tests 1 and 5

300 ppm.

Significant correlation
Tests 1 and 2

Tests 1 and 5

Tests 1 and 6
Tests 5 and 6

The possible reason for a significantly negative correlation in 50 ppm. water between Tests 1 and 5 is that the soap in a conventional washer has a much greater soil load thrown upon it than in the comparatively small laboratory tests hence reacts less favorably. (Note the differences in weight of fabric to volume of solution as shown in Table I.)

Significant correlation might be expected between Tests 1 and 2 because one is a simple variant of the other. Since Tests 1 and 6 are accomplished in the same machine with variation in some of the control factors, it should not be surprising to find significant correlation between them. Less clearly defined is correlation between the results obtained in the Launderometer and the Terg-O-Tometer. Test 3 for a single 10-minute wash in the Terg-O-Tometer gives closer correlation with Test 1 than does Test 4 for a 20-minute wash.

TABLE VI

Statistical Rating (2 $\sigma_{\bar{x}}$ Method)

Test 1	Test 2	Test 3	Test 4	Test 5	Test 6
50 ppm. Water					
3	3	3	1	1, 2	1
1, 2	1, 2	1	3	3	2
4	4	2	2	....	3
....	....	4	4	....	4
300 ppm. Water					
3, 2	3	3	1, 2	3	3
2, 1	2, 1	2, 1	3	1, 2	1, 2
4	4	4	4	....	4

NOTE: The ratings given in this table are subject to additional interpretation according to concentration levels observed. See Text.

Detergents—No. 1, built nonionic; No. 2, built alkyl aryl sulfonate; No. 3, pure soap; No. 4, loralkyl sodium sulfate.

In Table VIII where water hardness was disregarded and the results combined, only one lack of correlation between Test 1 and the other tests was found. This occurred with the conventional washer. Again this lack of correlation can be attributed to the poor showing of pure soap under the practical test conditions. The question as to whether any of the tests correctly align the products according to their known capabilities is one which should be answered in the light of the conditions observed. The solution concentrations are sufficiently high to permit soap to act at its point of maximum effectiveness *except* in the conventional washer in soft water. It is known however that built soaps are more economical and more effective than straight soaps and that built synthetic agents are superior in heavy-duty characteristics to unbuilt, light duty products such as the loralkyl sodium sulfate used in these tests.

TABLE VII

Coefficient of Correlation
(Basis Table II)

Comparison	Water Hardness	
	50 ppm.	300 ppm.
Test 1 and 2	0.976	0.999
Test 1 and 3	0.937	0.900
Test 1 and 4	0.833	0.784
Test 1 and 5	0.982	0.949
Test 1 and 6	0.938	0.954
Test 3 and 4	0.672	0.405
Test 5 and 6	0.962	0.991
Test 2 and 3	....	0.905
Test 4 and 6	....	0.566

Significance level P = 0.05, for 1 and 5 = 0.997, others 0.950.

The wash tests methods in general show pure soap to be most effective, followed by the built synthetics. The exception was the practical test in soft water where soap showed up poorly, due probably to the heavy soil load thrown upon it. In this sense these laboratory tests are unrealistic since the conditions chosen were at levels which provided effective cleansing for all the agents. A normal evaluation would include concentration and water-hardness evaluations which quickly would re-align the products in a realistic manner. The test conditions chosen for this

TABLE VIII

Correlation Coefficient
Combination of Water Hardness Data

Comparison	r
Test 1 and 2	0.967
Test 1 and 3	0.908
Test 1 and 4	0.802
Test 1 and 5	0.708[x]
Test 1 and 6	0.917
Test 3 and 4	0.551
Test 5 and 6	0.593[x]

Significant correlation when r = 0.7067 or greater (0.05 significance level).

[x] Significant correlation when r = 0.811 or greater.

work therefore favored pure soap, and it should have shown effective cleansing, as it did. With few exceptions the alignment of products by test methods under the conditions observed is in the order: pure soap, built nonionic and built alkyl aryl sulfonate, and loralkyl sodium sulfate.

Note that none of the test methods used corrects for redeposition of soil which may cause marked change in the actual net soil removal. This factor is receiving increasing attention and can be evaluated either concurrently with soil removal, or separately. One of the reasons for difficulty in discerning differences between products lies in test method variation. Table IX shows the coefficient of variation data for these tests. The "average" values indicate that greatest variation occurred with the practical wash test in the conventional washer. This could have been expected because of the variety of soils encountered. Nevertheless when the extent of variation is known, it can be taken into consideration and a correction made when comparing test results, and valid conclusions may then be drawn. Aside from the rather high variation of the conventional method, according to these test conditions, there seems to be little choice between any of the other methods.

TABLE IX

Coefficient of Variation

Detergent	%	50 ppm.	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6
1	0.2		6.2	4.6	4.3	4.0	12.9	5.3
2	0.2		6.9	12.1	2.3	6.4	13.3	4.0
3	0.2		1.2	5.3	2.8	6.8	27.2	5.4
4	0.2		6.9	5.2	2.3	7.5	......	7.2
		300 ppm.						
1	0.4		6.6	9.0	9.1	4.6	11.0	3.3
2	0.4		6.0	5.6	2.9	1.0	17.4	7.1
3	0.4		2.3	3.1	6.3	9.7	14.7	3.3
4	0.2		5.2	5.7	4.4	4.9	......	9.9
		Average	5.2	6.3	4.3	5.6	16.1	5.7

Discussion

The degree of correlation between these tests is good, considering the range of methods and machines used. Variation in correlation between tests was discerned between soft and hard water, perhaps attributable more to variation within tests than to water hardness effect, since solution concentrations were sufficiently high to obviate this as a factor.

The degree of soil removal for a given detergent varied from method to method. Only in the hard water washing tests did a majority of the tests rate the detergents in the same general order, Test 4 being the only exception.

Pure soap was so effective in these tests because essentially optimum concentrations for soap usage were observed. Had lower solution concentrations or harder water been used, soap effectiveness would have been greatly impaired. The effective ratings of detergents are generally determined by preparing detergency curves based upon concentration and water-hardness variables, but such tests were precluded in the present work. The comparatively poor detergency for soap in the practical test under soft water conditions and 0.2% solution concentration appears to be attributed to the soil load thrown upon it. In hard water, at 0.4% solution concentration, soap performs quite effectively. Consequently the sensitiveness of soap at a critically low solution concentration and high soil content of the load appear to be the most acceptable explanation for the divergence of the practical from the laboratory tests.

Redeposition of soil can markedly affect detergency values, and relatively few tests at present include this important factor. Redeposition values can be ascertained simultaneously with soil removal, or arbitrarily determined separately. This factor will undoubtedly receive more emphasis in future work.

Test variation for the five laboratory methods was of the same degree. The practical conventional washer test gave a variation roughly triple that for the laboratory methods, attributable largely to the wide variety of actual soils encountered and to degree of soiling found in normally worn or used garments.

From these tests it would appear that control of factors such as time of wash, or ratio of fabric to solution, might permit adjustment to give closer correlation of data between methods. The use of primary or primary and secondary samples for comparison purposes is to be recommended for observation of control over both wash test method and soiled test fabric.

As exemplified by the wash test results in the conventional washer, the ratio of soil load (soil or dirt in the garments), to the fabric weight and detergent solution volume can be very important in evaluation technique. Laboratory wash test methods should approach observed practical ratios to provide comparable data.

Choice of wash test method will depend largely upon the reliability experienced. If one method consistently produces results which correlate closely with known practice, then that method probably will be followed. Many methods are probably designed to closely duplicate practical conditions, but some will provide greater ease of control, larger volume of data, or simplification of test procedure. Choice of wash test machine is many times a matter of availability, recognized usage, or duplicability of a recognized procedure. In any event the machine should be readily controlled though some will provide a greater volume of useful data than others.

The use of statistical methods as tools in the evaluation of data cannot be emphasized too greatly. Where variation in data is as great as it is, only a statistical method will assist in arriving at reasonably valid conclusions. Thorough training of operators of wash test methods and close attention to operational details are necessary in producing reliable data.

Summary

Soil removal data were developed for five laboratory methods and one practical wash test method, utilizing a single standardized soil test fabric. The degree of correlation between the methods is good considering the variety of machines and procedures used. Better correlation between methods was obtained in hard than in soft water, attributable to the higher solution concentration used in the hard water tests.

The rating given the four detergents by the test methods was fairly uniform; the hard water data again were more concordant. Under the conditions used which were optimum for soap, the order of effec-

tiveness was: soap, built nonionic and built alkyl aryl sulfonate, and loralkyl sodium sulfate. Ordinarily, solution concentration-water hardness curves would be developed for complete evaluation, but the scope of this work precluded this procedure.

The test variation for the five laboratory methods was of the same degree. The practical conventional washer test gave coefficients of variation roughly triple those for the laboratory methods. This difference is largely attributable to poorer test control of conditions such as degree and kind of soil of the test load. Even though different test washing machines were used, it appears that adjustment of factors such as wash time and ratio of fabric to solution might provide closer correlation between methods.

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Notes on the Determination of Photometric Colors

SEVERAL points concerning the determination of photometric colors have arisen as more and more spectrophotometers come into use and more and more operators use the method. In some instances the Model B instruments seem to be giving on refined oils results which are somewhat higher than those obtained on the instruments used by the Color Committee in the original work on which the equation for calculating photometric color was based. In other instances extremely good checks between Lovibond colors and photometric colors are obtained. There does not seem to be any tangible trouble at low color levels. Photometric colors well below Lovibond red values can be and have been obtained. Even negative photometric colors are encountered. In extremely green oils the green correction ($-56.4D_{670}$) can be greater than the combined values at 460, 550, and 620 millimicrons. Photometric colors using the present calculation are of course meaningless on very green oils. Lovibond red values however are equally meaningless.

Anomalous results obtained by some operators are directly traceable to faulty Lovibond red readings. Many uncalibrated sets of Lovibond type are in use as well as many Wesson or Stevenson Colorimeters which are in bad repair and poor optical balance. Faulty spectrophotometers, faulty calibration standards, poor techniques, samples which are not clear, and cuvettes which are of the wrong type or which are dirty or etched, all are factors in affecting the individual's ideas on how well his laboratory checks Lovibond and photometric colors.

In determining photometric colors many wrong conclusions can be avoided if the method is followed carefully. Some of the points to observe are:

1. Calibrate the spectrophotometer between 25° and 30°C.
2. Check the instrument at all indicated wavelengths. If the specifications cannot be met by proper adjustment, the instrument should be returned to the factory.
3. The cylindrical cuvettes must be type B and must check not only each other but must check the Coleman CCl_4 standard. Cuvettes should be kept free from dirt and free from scratches.
4. The oil samples must be clear. If the oil is not clear when filtered through paper, 0.5 gm. of diatomaceous earth in 300 gms. of oil should be used to insure clarity.
5. Voltages to the spectrophotometer must be controlled to the point where fluctuation in readings does not occur.
6. Care in calculating photometric color is essential.

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