A Detergency Test Method Using Radioactive Carbon Black Soil[1]

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For many years inadequacies have been apparent in laboratory test methods that have been used for evaluating detergency in the laundry field. This is testified to by the large volume of published criticisms of various methods and the lack of agreement among different laboratories on test methods and results. The difficulty in arriving at adequate laboratory test methods appears to arise in large part from the nature of standard test soils that have been used, and the nature of these standard soils has been governed largely by the methods available for measuring soil removal.

Tests with particulate type of soils (usually carbon black) have depended on measurements of light reflectance from the cloth before and after washing, or on the light transmission through the detergent solution after washing to determine the degree of soil removal. Both of these methods are capable of good precision and have yielded much useful information when properly correlated with field experience. However the test soil must be designed to give light reflectances or transmissions in ranges most suitable for accurate measurement. This has placed rather severe limitations on standard soils, especially with respect to soil loading range. Most commonly used standard soiled cloths are rather heavily loaded with carbon black, alone or combined with other soil components, deposited in the cloth from aqueous or non-aqueous suspensions. The soil loading and methods of application, although suited to the measurement methods, perhaps are not representative of the more commonly encountered natural soils. The need has been apparent for a more flexible method of soil measurement, which would permit the study of much lower soil loadings, different soiling mechanisms, and different types of soil components.

Tagging of soils with radioactive isotopes appears to provide the sensitivity of measurement and flexibility that has been needed. Sensitivity of course depends on the specific activity of the isotope used and dilution of radioactive with inactive material in the soil. Currently available specific activities of isotopes of principal interest in soil studies permit accurate measurements at very low levels where soil would hardly be detectable with other methods. The variety of available radioisotopes, in numerous chemical forms, makes it possible to study most soil types of interest.

It appears that difficulties, real or imagined, involved in the use of radioactive tracers have retarded the application of radioactive soils to detergency testing; however several approaches to the problem have been reported. Ridenour (5) has employed bacteria tagged with phosphorus-32 as soil in wash tests. Lambert and co-workers (4) have reported the use of fission products and radiocarbon black as soils on cloth. Vegetable oils containing carbon-14 are being used as laundry test soils (1). In the metal cleaning field fatty acid (3) and mineral oil (2) containing carbon-14 are being used as test soils. In the laundry field few actual wash test data have appeared, reports being mainly of a preliminary nature.

During the past five years this laboratory has developed laundry test procedures, using several types of soil tagged with radioactive isotopes. These soils include carbon black and other particulate materials, mineral oils, fatty acids, and insoluble soaps. This report is limited to carbon black soil. During the course of developing these tests, numerous methods of soil application and many variations of the wash procedure have been tried, but all of these variations cannot be covered in this paper. The procedures described are being used regularly to provide basic information and to supplement detergent evaluations by the more conventional methods.

A detergency test method which uses radioactive soil must be designed so as to take full advantage of the potentialities of radioactivity measurements. Also procedures must be designed so as to minimize the possibilities of health hazards. These two considerations make it apparent that there is little point to using a radioactive tag in a conventional type of standard soil, merely substituting radioactivity measurement for reflectance measurement, and employing soiling and washing procedures otherwise the same. Such a procedure would retain many of the limitations of the conventional tests, and the soiling procedures, usually carried out on a large scale, are not suited to the use of radioactive materials. Soiling and test procedures preferably should be carried out on a small scale so as to minimize the amount of radioactivity involved. Efficient use should be made of the radioactive material with a minimum of waste. Soiled cloth should carry a low level of activity, consistent with accurate measurements. Soil should be sufficiently adherent to permit safe handling in the open, without the hazard of air-borne radioactive particles. Soil should have sufficiently uniform characteristics and the wash method sufficient precision to permit the use of a minimum number of replicates of small size so as to limit the amount of activity involved.

With these considerations in mind, it was decided to undertake a fresh approach to the detergency test problem, independent of the more or less established test methods. Preliminary trials with soiling baths containing radioactive colloidal particles indicated that such soiling baths would not be the most suitable approach. Utilization of soil material is of necessity inefficient, and close control of radioactivity is difficult. It was felt further that some of the difficulties experienced with conventional laboratory test soils perhaps stemmed from mechanisms involved in deposition of soil from suspensions. Consequently ways were sought to apply a soil such as dry carbon black or carbon with oil to cloth by rubbing it into the surface in a reproducible manner. Such procedures have been worked out, and currently the preferred soil consists of a combination of radiocarbon black

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and mineral oil rubbed into the cloth surface.[2] Dry carbon soil applied in the same way has been used extensively also, and it has been found that the presence of a small amount of mineral oil with the carbon black has no effect on the relative rating of various detergent types. Data will be presented in a later section supporting this statement. Use of oil with the carbon improves soiling action and minimizes the production of radioactive dust.

Preliminary trials indicated that commercially available laboratory wash test apparatus would not be entirely suited for the type of test desired with radioactive soil. The Launder-Ometer, for instance, employs a random type of wash action and requires a relatively large number of replicate soiled swatches for adequate precision. It was considered desirable to provide for closer control of the washing action on individual swatches in order to reduce the number of replicates required. Consequently two types of wash test apparatus have been developed specifically for use with small disc swatches. The first type employed a very high solution to cloth ratio, two 1.5-in. discs being washed in 300 ml. of detergent solution. A second, miniature type of apparatus was then developed, in which three of the disc swatches, two soiled and one clean, are washed together in 7 ml. of detergent. This gives a solution to cloth ratio of 13.7 to 1 by weight, which is within the range used in home-washing machines, and somewhat higher than that used in commercial wash wheels (4 or 5 to 1). The relatively low solution to cloth ratio in the miniature washer, in addition to being closer to practice, permits sufficient soil loading in the solution to give a measurable redeposition of the radioactive soil on a clean swatch washed with the soiled ones. This makes it possible to determine whiteness retention values simultaneously with soil removal results. At the same time the soil removal and whiteness retention values are essentially independent as the extreme sensitivity of radioactivity measurements makes it possible to determine redeposition at such a low level that redeposition on soiled swatches has no very significant effect on relative soil removal values, determined at a much higher counting level.

Characterization of Radioactive Carbon Black

The carbon black used in this work was prepared by reduction of carbon dioxide containing carbon-14. Three lots of the radiocarbon have been used, two obtained from Tracerlab Inc., and one from Nuclear Instrument and Chemical Company. Specific activity of most of the material used has been about 0.07 mc. per mg. The carbon black has been used as received, without dilution with inactive carbon. Electron micrographs have been obtained for radiocarbon lots 1 and 2, with some difficulty because of problems involved in getting good dispersions on the mounts starting with very small quantities of the active carbon. Particles are irregular in shape, similar to graphite particles rather than the spherical particles found in colloidal blacks. Any accurate estimate of particle size distribution is difficult to make as the irregular shape of particles makes it difficult to distinguish between larger particles and agglomerates. However most of the particles are less than 0.5 micron, ranging down to less than 0.05 micron.

Different lots of carbon black prepared in small amounts by reduction would not necessarily have the same physical properties. Lots 1 and 2 have somewhat different appearances under the electron microscope, particles of lot 1 appearing to be coarser and more jagged than those of lot 2. However the three lots of carbon, from two sources, have given the same relative soil removal evaluations with different types of detergents.

Preparation of Soiled Cloth

Oily Carbon Soil. Initial handling of the radioactive carbon black is carried out in the small filter hood shown in Figure 1, set inside a large conventional hood. A blower at the back of the unit produces a moderate movement of air, carrying any loose carbon particles to the disposable cotton filter at the back. When the dry carbon black is to be transferred, it has been found helpful to wet it down with alcohol to prevent flying. A small amount of the carbon is dispersed in a trace of Nujol mineral oil by working them together with a spatula on a glass plate. The quantities of carbon and oil cannot be specified as it is not feasible to weigh the very small quantity of carbon used. Trials with inactive carbon have indicated that a milligram or less of carbon is used with perhaps twice as much of the oil. In practice, just sufficient oil is worked into the carbon to form a smooth dispersion. The dispersion is worked thoroughly with the spatula to ensure uniformity.

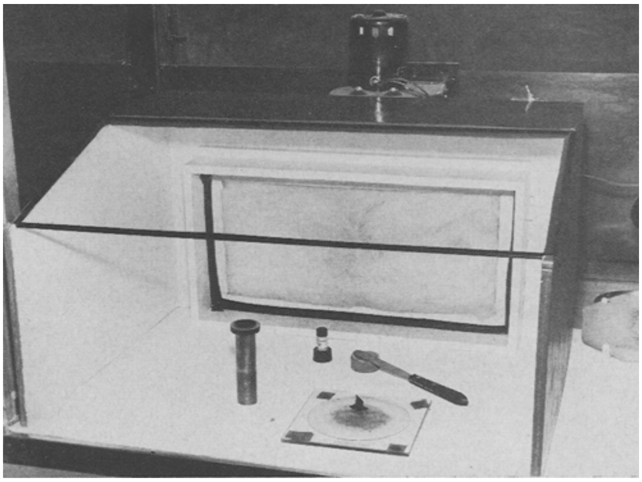

FIG. 1. Filter hood for handling radioactive carbon black. Soil applicator assembly for soiling machine on the left.

Cloth swatches are 1.44-in. discs, cut from bleached, unfinished Indian Head muslin. This is the standard test cloth used in our other laundry test procedures. The cloth is used without pretreatment and without preconditioning. Swatches are stored, before and after soiling, under regular laboratory conditions.

The soil mixture is applied to the cloth swatches with the machine shown in Figure 2. The soil is carried by a 6-in. sq. Pyrex glass plate, the surface of which has been very lightly etched with hydrofluoric acid. The glass plate is clamped to an aluminum plate, which is moved in a 1.5-in. circle by a crank mechanism underneath and kept from rotating by the parallelogram linkage at the end. The plate and linkage ride on plastic bearing surfaces. The cloth disc is backed by a 1-in. felt disc cemented to a 1.5-in. alu-

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[2] Lambert (4) also has reported a rubbed-in soil for laundry detergency testing, in which the soil mixture is applied to cloth as a water slurry.

minum disc and pressed against the glass plate by the weight (398 g.) of a 4-in. length of 1-in. steel shafting, riding in a ball-bearing sleeve. The aluminum backing disc is fixed by a pin in the center, fitting a depression in the end of the steel shaft. The cloth disc is held in position by friction against the felt disc, which is coated lightly with latex.

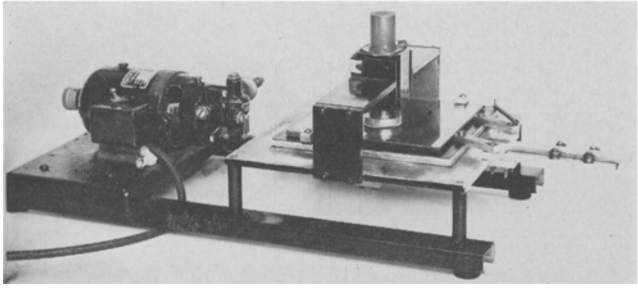

Fig. 2. Soiling machine for rubbing radioactive soil into the surface of cloth discs.

The carbon-oil dispersion is applied to the glass soiling plate with an applicator assembly, which is visible in the hood in Figure 1, supported by the steel shaft which has been removed from the soiling machine. The applicator consists of a 1-in. disc of tracing paper, cemented to a felt backing disc which in turn is cemented to a 1.5-in. aluminum disc similar to that used in the backing assembly for cloth discs.

A small amount of the carbon-oil dispersion is applied to the applicator disc with a spatula. The applicator assembly is then placed on the glass soiling plate, the steel shaft lowered into place, and the machine run for 10 turns at a rate of 160 per min. A clean cloth disc is then substituted for the soil applicator and the machine run for 20 turns, the shaft being given a quarter circle rotation each 5 turns. Soiling of cloth discs is continued in this way until the counting level falls below about 5,000 counts/min., when fresh carbon-oil dispersion is applied. Normally 12 or more cloth discs can be soiled with each application of dispersion to the soil plate. The first cloth disc soiled after each application of soil to the plate is discarded. As a final step, the soiled surface of each cloth disc is brushed for 20 strokes with a 1-in. camel-hair brush. The cloth disc is rotated during the brushing process, which is carried out in the filter hood.

Dry Carbon Soil. The above procedure for preparing oily carbon soil is the preferred current method, but some wash test data are given in a later section for a dry carbon soil as well as for the oily carbon. The radiocarbon can be applied dry with the same soiling machine, using a different type of soiling plate. The best soiling results with dry carbon have been obtained by using a stainless steel soiling plate (highly polished but with microscopic pits) and applying the carbon as a dispersion in hexadecane. The dispersion is spread as a thin film with a spatula, and the plate is then heated to remove the hexadecane. Any loose carbon is wiped off the surface of the plate before it is assembled in the soiling machine. Cloth discs are then soiled and brushed as described above, the first few soiled on the freshly loaded plate being discarded. Generally, about 50 discs can be soiled at a suitable loading before it is necessary to reload the plate with carbon.

Glass soiling plates have also been used in preparation of dry carbon soil, with the carbon applied as a dispersion in glycerol, which is removed by heating. The same relative detergency results were obtained with this type of plate, but soiling action for dry carbon was not so satisfactory as with the steel plate. Generally, the type of solvent used in dispersing the carbon appears to have no effect on relative detergency ratings provided by the dry soil so long as the solvent gives good dispersion of the carbon, wets the soil plate, and can be removed by volatilization.

Radioactivity Measurements

Measurements of radioactivity on cloth swatches are made with end-window Geiger counters having window thicknesses of less than 2 mg./sq. cm. The cloth discs are supported about 5 mm. from the window by means of the type of mount shown in Figure 3. Top surfaces of the mounts are coated with latex cement, which is allowed to dry before use. Cloth discs, pressed lightly onto the mount, remain flat for counting. The latex cement coating is renewed after a dozen or so discs have been counted.

In soil removal tests, initial and final counts are generally taken for sufficient time to give a statistical standard deviation of about 1%. In measuring the redeposition of soil on clean cloth, counting levels are much lower, and limitations on counting time generally result in a statistical standard deviation of 2 to 3%. Precision of redeposition counts could, of course, be improved considerably by the use of a windowless counter.

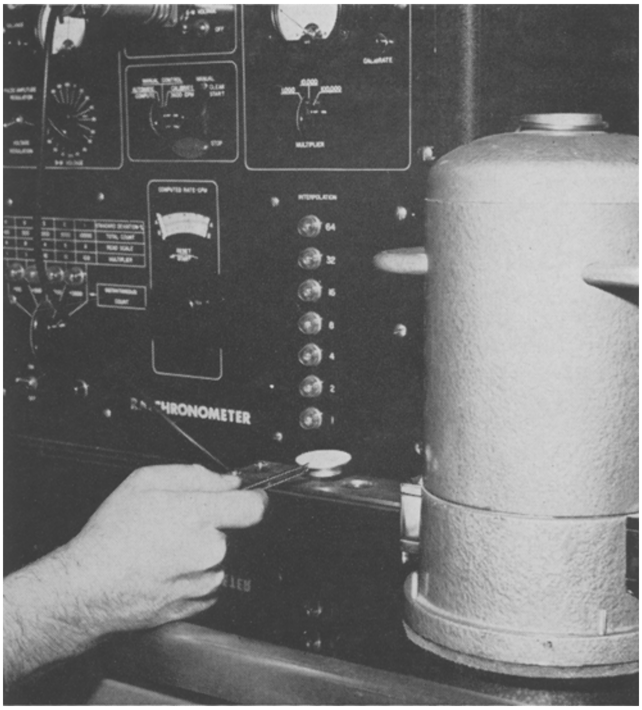

Fig. 3. Arrangement for measuring radioactivity of soiled cloth discs.

Wash Test Equipment

The first type of washer developed for this work is shown in Figure 4. The detergent solution, generally 300 ml., is held in the stainless steel beaker

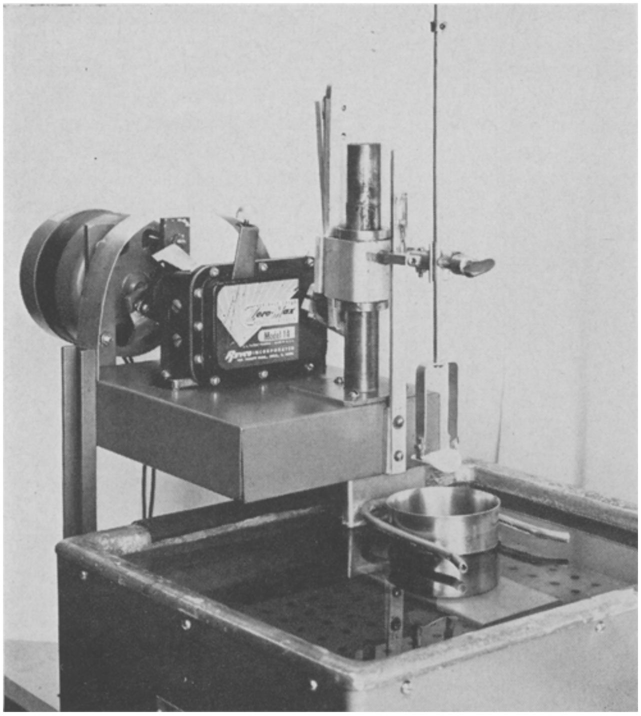

FIG. 4. Type 1 laboratory washer. Cloth discs agitated under the surface of a detergent solution in the beaker.

immersed in the constant temperature bath. The soiled cloth discs are clamped at opposite edges in the fork assembly as shown, with some slack in the cloth. The cloth is lowered into the detergent solution to a depth determined by a stop on the fork support rod. The machine drives the fork through a vertical stroke of one in. at 300 cycles per min. Because of the slack in the cloth, it flops up and down with the motion, producing a flexing action and friction between fibers. The soiled cloth discs normally are washed in pairs, with soiled surfaces apart. Placing the soiled surfaces together greatly increases the the soil removal level, with corresponding loss in spread among different detergents.

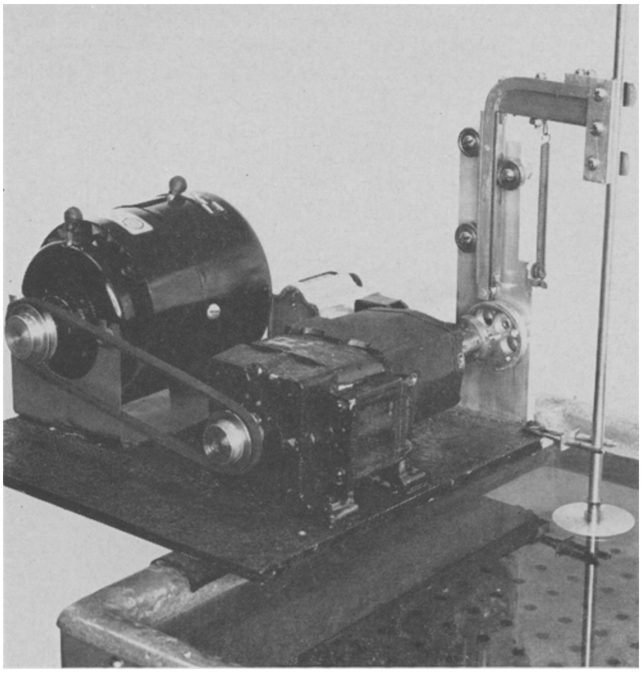

FIG. 5. Type 2 laboratory washer (miniature type). Small wash vessel agitated in constant temperature bath.

The miniature washer apparatus currently in use is shown in Figure 5. The wash vessel proper is the small cylindrical portion attached to the support rod and immersed in the constant temperature bath during a test. The remainder of the machine, having a cam-driven, spring-loaded action, provides a vertical oscillating motion to the wash vessel, with a stroke of five-eighths in. at 600 cycles per min. The wash vessel is shown disassembled in Figure 6. Two soiled discs, soiled surface together, are held in the ring assembly as shown. Small irregular shaped agitator pieces of stainless steel are placed on top of the cloth inside the upper ring. They provide friction between the cloth surfaces as the ring assembly moves with relation to the wash vessel. The motion also forces detergent solution through the cloth. A clean cloth disc, for measuring soil redeposition, is held at the bottom of the cup portion by a snug-fitting ring. A 1-in. screen disc is placed under the center of the clean cloth disc to permit circulation of the detergent solution through the cloth. All metal parts of the washer are of stainless steel, and a polyethylene gasket is used in the cap. The cup portion has an inside diameter of 1.563 in. and a depth of 0.5 in. The ring assembly has an outside diameter of 1.5 in., thickness of 0.25 in., and a center opening of 1.125 in. Since the soiled area in the center of a cloth disc is 1 in. in diameter, the soil is not covered by the ring assembly. Total free volume of the wash vessel, with the ring assembly in place is 13.5 ml., and a 7-ml. portion of detergent solution is used.

Wash Test Procedure

Similar procedures have been used with the two types of apparatus described, aside from the difference in detergent solution volumes and the use of a redeposition swatch with the miniature (type 2) washer. All data in this paper are for a wash period of 5 min. in 0.25% solutions of detergents in demineralized water at 60°C.(140°F.). The effect of washing time with various detergents has been studied to some extent, but there appears to be no advantage to extending the wash time past 5 min. Normally no rinse is used as with this type of soil rinsing appears to have no significant effect on relative values or the precision of results. After swatches are removed from the detergent solution, they are pressed for 5 min.

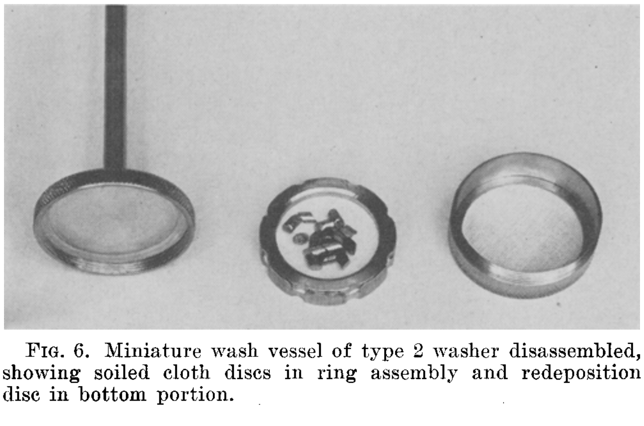

FIG. 6. Miniature wash vessel of type 2 washer disassembled, showing soiled cloth discs in ring assembly and redeposition disc in bottom portion.

between filter papers under a 1-kg. weight before drying. The count on a swatch that can be due to dispersed soil in the retained solution has been found to be insignificant.

When several detergents are to be evaluated, a sufficiently large group of soiled swatches is prepared to provide six swatches per detergent. Swatches for each detergent are then selected from throughout the soil group (in order of soiling) by a standard sampling method so as to compensate for any gradual variation in soil characteristics through the group. At least one standard reference detergent is always included in each group of detergents being evaluated. Generally two such evaluations, each involving six swatches per detergent, are made, using two separate groups of soiled discs and running detergents in a different order in each evaluation.

Statement of Results

Soil Removal. Wash tests are always run in comparison with a reference detergent, which is a sodium alkylarylsulfonate (40% active agent) from a selected and homogenized stock. Soil removals are expressed as percentage of this reference detergent, thus assigning the latter an arbitrary value of 100. From the counts per minute values as determined on each soiled swatch before and after washing, the percentage soil removal is calculated. Since initial and final counts are obtained under fixed geometry conditions, the only correction required is subtraction of background count. The soil removals for the six replicate swatches are averaged, and this average value is divided by the average percentage soil removal obtained with the standard reference detergent for swatches from the same soil group and multiplied by 100 to give the "percentage of reference detergent" value.

Whiteness Retention. Soil redeposition values are obtained from the soil pick-up in counts per minute by a clean cloth disc washed along with two soiled ones in the miniature washer. The amount of soil redeposition depends upon the soil loading of the detergent solution, and the soil loading of the solution depends upon the soil removal efficiency of the detergent. Consequently the soil redeposition values for two detergents of differing soil removing abilities would not be directly comparable even if initial soil levels of swatches were equal. It has been found however that at the low soil level used in these tests the soil redeposition is very nearly a linear function of the total soil in the detergent solution. Consequently redeposition values obtained at any known soil loading in the bath can be corrected by simple ratios to a standard bath loading for comparison of different detergents. Figure 7 shows redeposition values obtained with alkylarylsulfonate reference detergent plotted against bath soil loading, both stated as counts per minute. The values plotted are for individual redeposition swatches run with a number of different soil groups. The detergent bath soil loading is determined from the counts per minute of soil removed from the soiled swatches during washing, that is, the difference between the combined initial counts of swatches washed together and the combined final counts. The soil loading value for the solution and redeposition on a swatch, as stated in counts per minute, of course have no absolute significance. However so long as counting is carried out under fixed conditions, these numbers are proportional to the actual quantities and serve just as well for relative evaluations of redeposition on an arbitrary scale.

The redeposition values stated as counts per minute of soil pick-up are corrected to a standard soil loading in the bath as indicated above, and then converted to a percentage whiteness retention value based on the standard reference detergent. A level of 10,000 counts per minute of soil in the detergent solution, i.e., 10,000 counts per minute removed from the soiled swatches, has been selected arbitrarily as the standard bath loading. A redeposition value is corrected to the standard bath loading by multiplying by 10,000 divided by the counts per minute lost by the soiled swatches to the detergent solution. The corrected redeposition value for the reference detergent is obtained in the same way. Assuming that the whiteness retention property of a detergent is inversely proportional to the soil redeposition, then relative whiteness retentions of two detergents should be inversely proportional to their redeposition values. Then a whiteness retention value for Detergent A as percentage of the reference detergent is equal to 100 times the corrected redeposition in c.p.m. for the reference detergent divided by the corrected redeposition in c.p.m. for Detergent A.

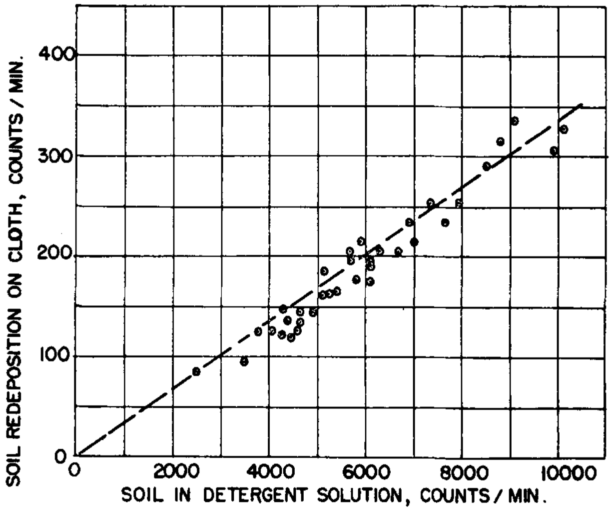

FIG. 7. Soil redepositions on individual cloth discs (initially clean) washed with two soiled discs.

Although there is no basic need for converting redepositions to whiteness retention values for comparisons of detergents, it has been done as a matter of convenience in comparing results of the tracer test with those of our conventional procedure, where results are expressed as whiteness retentions related to the standard reference detergent.

Effect of Initial Soiling Level

With the type of rubbed-in soil employed in this work, it is not feasible to hold the initial soiling level on swatches at a constant value although the range of the soiling level can be controlled without difficulty by adjusting the quantity and frequency of soil applications to the plate. It has been found that variation of the soil level over a rather wide range has no significant effect on the percentage of soil removal by a given detergent. Figure 8 shows soil removal values obtained with a relatively ineffective detergent composition at initial soil levels, covering the range normally found in a soil group. Soil removal values shown are for individual swatches taken from a group of 100 swatches, every fifth swatch being run in this detergent. Actually initial soil level can vary over several times the range shown in Figure 8 without significant effect on soil removal values, but the soil normally has been held approximately within the indicated range.

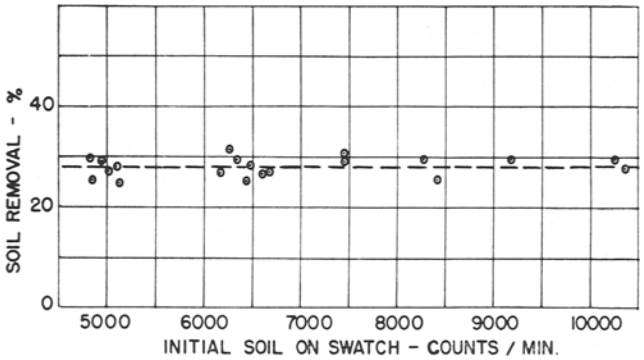

Fig. 8. Soil removal values for single swatches, showing effect of initial soil level.

Precision and Reproducibility of Wash Test Results

The following distinctions are made between the terms "precision" and "reproducibility" as used: the precision of test results relates to the reliability of an average detergency value for a given detergent in relation to values for other detergents, all determined with representative replicate swatches from the same soil group and all stated in terms of a parallel determination with a standard reference detergent. Reproducibility refers to the extent of variation in detergency values obtained with a given detergent or group of detergents with different soil groups; the individual values are always stated in terms of an equivalent value for the standard reference detergent with the same soil group.

Soil Removal Evaluations. Although a considerable quantity of data have been accumulated, the frequent modifications that have been made in soiling and wash methods complicate any attempt at accurate estimates of precision and reproducibility. However on occasion fairly large groups of swatches have been washed with a single detergent, providing data on the precision to be expected. In Table I results are given for four such groups, involving several detergents with a range of soil removal values. The standard deviations as tabulated are stated in terms of the percentage of soil removal and relate to individual swatches. Confidence limits at the 95% level for averages of six swatches are given in terms of the percentage of soil removal and also as the percentage of standard reference detergent, based on a soil removal value of 30% for the reference detergent. These data indicate a decrease in precision with an increase in soil removal level. This effect might be due to other variables, such as differences in the soil groups used in the different tests, or variation in washing action over a period of time. However the higher removal values have tended to scatter more than the lower values so long as washing action was constant. Any variations in washing action however tend to affect the lower values more than the high ones. It will be noted that these estimates of confidence limits take no account of uncertainties in removal value for the standard reference detergent. This is justified so long as comparison is limited to soil removal values obtained with a single soil group and based on the same value for the reference detergent.

TABLE I

Precision of Soil Removal Tests, Using Miniature Washer and Carbon-Nujol Soil

Detergent	No. of Swatches	Average Soil Removal	Standard Deviation[a]	95% Confidence Limits for average of 6 swatches[b]	
				As % Removal	As % Ref. Det.
		%			
I	20	28.0	1.85	1.48	4.9
II	20	33.7	1.99	1.59	5.3
III	18	45.3	2.24	1.79	6.0
IV	16	53.6	2.50	2.00	6.7

[a] $s = \sqrt{\frac{\Sigma(x-\bar{x})^2}{(n-1)}}$, where n = total swatches in group.

[b] 95% limits = $\pm 1.96 \frac{s}{\sqrt{n}}$, where n = 6.

Reproducibility of relative soil removal values from one soil group to another involves additional variables, namely, the precision of the soil removal value for the reference detergent in each case, and variations in characteristics of the soil from one group to another. Data are not yet sufficient to provide accurate estimates of reproducibility, but the data in Table II provide a general indication. Table II gives all evaluations that included these three detergents over a period of three months. Detergent A is the standard reference detergent. Detergent D (alkylarylsulfonate built with sodium tripolyphosphate) and Detergent G (high titer soap) have served as secondary references. During the period minor modifications were made in the miniature wash test apparatus, accounting for part of the fluctuation in the percentage of soil removal values for the reference detergent. Stating values for the other two detergents as percentage of reference detergent tends to compensate for these variations in washing action as well as for variations in the soil. Reproducibility of the relative values for Detergent D have been appre-

TABLE II

Reproducibility of Soil Removal Tests Over a Three-Month Period, Using the Miniature Washer and Carbon-Nujol Soil

Soil Group	Detergent A —Reference	Detergent D	Detergent G
	% Soil Removal	% of Ref. Detergent	% of Ref. Detergent
1	28.0	124	176
2	35.5	120	184
3	24.0	122	182
4	29.8	118	167
5	27.9	124	188
6	34.0	120	171
Average		121.3	178
Standard deviation, s[a]		2.4	8.1

[a] $s = \sqrt{\frac{\Sigma(x-\bar{x})^2}{(n-1)}}$ where n = 6.

ciably better than for Detergent G. This may be related to a better precision at lower soil removal levels, but it also appears that variations in soil characteristics from one group to another affect the high removal values relatively more than the low ones.

Although the data in Table II indicate reasonable reproducibility of relative soil removal values in comparison with spread, in making evaluations of detergents or of variables in the wash process, reliance has not been placed on a high degree of reproducibility from one soil group to another over a period of time. Tests have been set up so as to make desired comparisons within a single soil group. Reliability is increased, of course, by making two or more independent comparisons with different soil groups.

Whiteness Retention Values. Whiteness retention values as determined in the current procedure would necessarily show poorer precision than the soil removal values. Only three whiteness retention replicates are run in an evaluation, and counting precision is poorer as was pointed out in the section on radioactivity measurements. On the other hand, spread in whiteness retention values for the various detergents is greater than the spread in soil removal values. Consequently precision of whiteness retention values may be poorer and still show up significant differences in detergents.

The degree of scattering of redeposition values as determined for individual swatches has been indicated in Figure 1, showing results with several soil groups. Taking 15 of these redeposition values obtained with a single soil group and correcting to the standard soil loading of 10,000 counts per min. in the detergent solution gives an average redeposition of 330 counts per min., with a standard deviation of 30.8 counts per min. Taking this standard deviation and assuming three replicate determinations provides a rough estimate of ± 35 counts per min. for the 95% level confidence limits. This would be equal to about 11% when converted to whiteness retention as percentage of reference detergents. As the spread between detergents having good and poor whiteness retention properties may amount to 300%, this precision should be reasonably adequate. Whiteness retentions by the current method have not been run over a sufficient period of time to give accurate information on the long term reproducibility of values, but the scatter of values for a single soil group appears to be about the same as for different soil groups, indicating that reproducibility of values should be of the same order as the precision indicated above.

Reference Series of Detergents

To facilitate the evaluation of variations in the radioactive tracer tests for soil removal and whiteness retention and to provide comparisons between the tracer and conventional type of tests, a reference series of detergents was set up. This series of detergents, listed in Table III, includes different types of active agents, alone and in combination with various builders. It was designed to cover a range of detergency values and to bring out the effects of various materials. The compositions do not necessarily represent practical washing formulations. Materials were of commercial grade. A large sample of each was set aside, and all test evaluations were made with portions of the same sample.

TABLE III

Reference Series of Detergents Used in Comparison of Test Methods

Detergent	Composition
A	100% Alkylarylsulfonate (40% active agent)
B	50% A, 50% Soda Ash
C	95% A, 5% Sodium Carboxymethyl Cellulose (CMC)
D	50% A, 50% Sodium Tripolyphosphate (STP)
E	48% A, 50% STP, 2% CMC
F	50% A, 50% Sodium Metasilicate (Anhyd.)
G	100% High Titer Soap (92% active agent)
H	50% G, 50% Soda Ash
I	50% G, 50% Sodium Metasilicate (Anhyd.)
J	100% Nonionic (Polyoxyethylene-Polyoxypropylene Type)
K	50% J, 50% STP
L	20% J, 39% STP, 39% Modified Soda, 2% CMC

Comparison of Soil Removal Results with Carbon-Oil and with Dry Carbon Soils

Soil removal evaluations have been run with most of the reference series of detergents listed in Table III, using both the dry carbon and the oily carbon soils, both applied by the rubbing procedure described previously. These tests were run with type 1 washer (Figure 4), using 300 ml. of detergent solution, at 0.25% in demineralized water. Washing was for 5 min. at 60°C. Results with the two types of soil are compared in the chart, Figure 9. It is apparent that there is considerable difference in spread among detergents, the oily carbon showing the greater spread in soil removal. Otherwise correlation is excellent; both soils give the same relative rating of detergents.

It cannot be assumed that the difference in spread of removal values with the two soils is due entirely or even largely to the presence of mineral oil in the one case. During the development of these procedures it has been observed that various factors in the soiling process can affect the spread between detergents. One important factor is the extent of abrasion of the

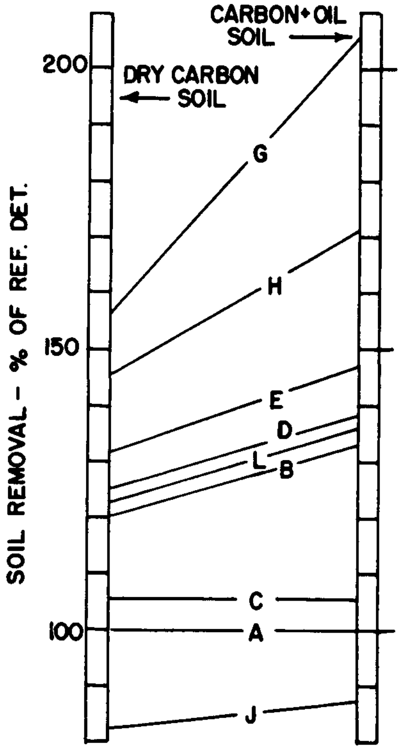

FIG. 9. Comparison of soil removal evaluations with dry carbon and oily carbon soils. Detergent compositions given in Table III.

cloth surface during the soiling process. The greater the abrasion generally, the less the spread. With increase in abrasion, through use of rough, dry soiling plates, a point can be reached where little difference is observed in soil removal by different detergents. Since different soil plates were used in preparing the two types of soil, degrees of abrasion would be different, and probably greater with the dry soiling plate. This may account for a large part of the difference in spread.

Comparison of Different Types of Wash Test Apparatus

Figure 10 compares the soil removal results obtained with the two types of wash test apparatus, type 1 being the open washer (Figure 4) having a low cloth to solution ratio, and type 2 being the closed, miniature washer (Figures 5 and 6) having high cloth to solution ratio. Differences are apparent in the rating of the various detergents by these two types of washers. The most pronounced difference is in the rating of Detergent L, nonionic built with phosphate, modified soda, and CMC. The type 1 washer rates it as decidedly less effective than built soap (H) and about equal to the alkylaryl built with phosphate (D) whereas the type 2 (miniature) washer rates Detergent L as equal to H and distinctly better than D. Detergent B, alkylaryl built with soda ash, is rated lower in relation to the other detergents by the type 2 washer than by the type 1. Detergent H, high titer soap built with soda ash, also is rated somewhat lower, relatively, by the type 2 washer.

Although the most obvious difference between the two washers is in the cloth to solution ratios, there are other differences in action that may have more important bearing on the relative rating of detergents. The type 1 washer is open, and washing is performed under the solution level. Consequently sudsing tendencies of detergents would not be likely to affect soil removals. On the other hand, the miniature washer is closed, washing is performed in the suds as well as in solution, and the presence of suds could have a cushioning effect on the movement of the ring assembly holding the soiled swatches. Detergent L produces relatively little suds in comparison with the anionic materials, and the lack of cushioning effect may account for the relatively better performance of the built nonionic in the miniature washer. On the other hand, the nonionic alone (J), which has slight sudsing action, performed slightly better in the type 1 washer than in the type 2 whereas the reverse might have been expected if the cushioning effect of suds in the miniature washer were an important factor. Some further investigation of the effects of washing action on relative performance of detergents would be desirable.

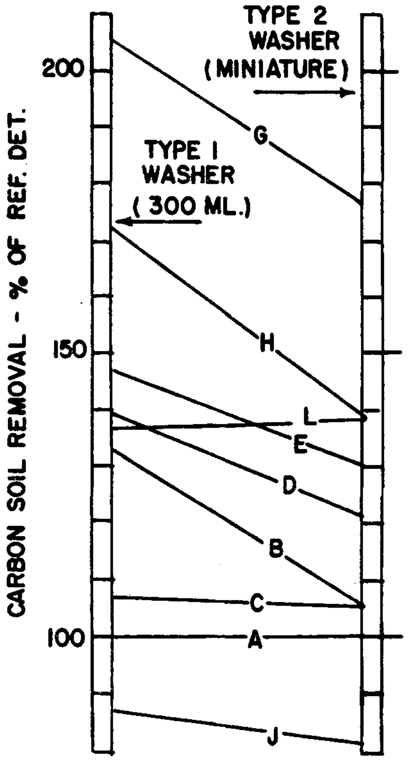

Fig. 10. Comparison of soil removal evaluations with different types of laboratory washers. Detergent compositions given in Table III.

Comparison of Tracer and Conventional Test Method Results

Using the reference series of detergents listed in Table III, determinations of soil removal and whiteness retention have been made with the tracer methods and with the conventional test methods currently in use. With each test method at least two independent evaluations were made with each detergent, and detergency values given are averages for two or more evaluations. The tracer evaluations were run with oily carbon soil, using the miniature (type 2) wash test apparatus. The conventional soil removal evaluations were run with a water-bound type of carbon soil (based on Aqua Blak B) and a Launder-Ometer wash apparatus. Soil removals were determined by measuring turbidities of used detergent solutions. Conventional whiteness retention tests were run in the Launder-Ometer with detergent solutions containing a standard quantity of suspended carbon (Aqua Blak B). Pick-up of carbon by initially clean swatches was determined with a Hunter reflectometer. These conventional tests have been thoroughly standardized over a period of years, and details of the procedures have been described elsewhere (6).

Soil Removal Comparison. Soil removal values by the two methods (tracer and conventional) are compared in Figure 11. Conditions were the same with the two methods except for the different types of wash machines and a difference in washing times, 5 min. in tracer tests and 10 min. in the conventional ones. In both cases, soil removal values have been stated as percentages of the standard reference detergent (A). It is apparent from the chart that there is little overall correlation in the evaluation of these detergents. However when the results are inspected in relation to the compositions of the detergents, some order becomes apparent. In Figure 11 an attempt has been made to bring this out by showing some of the detergents in solid lines and some in dotted lines. The solid lines include anionics (soap and alkylarylsulfonate) and the anionics plus alkaline builders. With this group of detergents correlation with the two methods is relatively good. The other group of detergents, shown as dotted lines, contain either CMC or nonionic, or both. It is apparent that the two methods give this group of detergents entirely different soil removal ratings, both in relation to each other and in relation to the other group of detergents. The most striking reversal in results is with Detergent J, the unbuilt nonionic, which is rated as decidedly the best by the conventional test, but poorest (in soil removal) by the tracer test. It will be noted in the next section that Detergent J is rated as best in whiteness retention by both test methods. All of the group of non-correlating detergents shown as dotted lines have good whiteness retention characteristics, and it might be reasoned from this that soil redeposition effects enter into soil removal evaluations as made by the conventional test. It has been demonstrated however that soil redeposition effects are not likely to have any significant effect on soil removal values as given by the conventional test in use here (6). Further, from the nature of the tests involved, soil redeposition effects alone could not account for the extreme reversal in soil removal evaluations for Detergent J by the two methods. The high titer soap, G, which also has good whiteness retention properties, shows a relatively lower soil removal value, in comparison with other detergents, in the conventional test than in the tracer method.

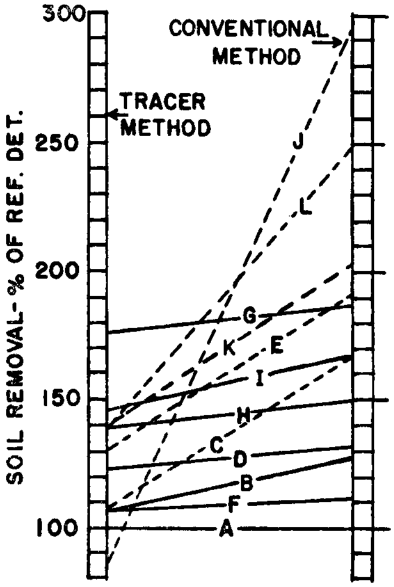

FIG. 11. Comparison of soil removal evaluations with the tracer method (radioactive soil) and the conventional laboratory procedure, using swatches heavily loaded with carbon soil. Detergent compositions given in Table III.

It would appear that some property or properties (as for example dispersive or protective colloid effects) of certain detergent components which make for good whiteness retention also make for very effective removal of the particular type of soil used in the conventional test procedure, but not of the type of soil used in the tracer method. These differences in action of detergents may be related primarily to the method of soil application, degree of soil-loading on the cloth, or nature and particle size distribution of soil particles.

Although different types of wash test apparatus were used in the tracer and conventional tests, the large differences in relative evaluations of detergents are due primarily to differences in the test soils, rather than to differences in washing action. As indicated in the previous section (comparison of different types of wash test apparatus), some reversals may take place with variation of washing conditions; however sufficient wash trials have been made with the radiocarbon soil in the Launder-Ometer and with the conventional type of soil in the miniature washer to determine that the general evaluation of detergents is much more a function of the type of soil used than of the particular washing action employed.

No particular attempt is being made in this paper to demonstrate the degree of correlation between the laboratory evaluations and practical wash results in the field. It is hoped that this will be the subject of a future report. However some general observations in terms of field performance might be made. The nonionic, Detergent J, is not a highly effective washing agent when used alone. This would be indicated by the tracer results while the conventional test results could be misleading on this point. It might be noted that the nonionic J is an extreme example of non-correlation of the test methods, shown for that reason. Other nonionics of the same type show much higher soil removal by the tracer evaluation and lower removal (than J) by the conventional method. Although nonionic J might not be effective in soil removal when used alone, a great deal of practical experience has shown that when the nonionic is properly built to give a composition such as L, the practical washing performance is very good. This would be indicated by the tracer evaluations, which rate it as about equal to built high titer soap. The distinctly superior rating of Detergent L by the conventional method perhaps is not so realistic in terms of soil removal. Any over-all practical performance evaluation, of course, takes into account whiteness retention, hard water tolerance, and other factors. The difficulty of separating the effects of these factors in actual wash operations complicates any attempt to correlate laboratory soil removal results with field performance.

Whiteness Retention Comparison. Whiteness retention values for the reference series of detergents as given by the tracer and conventional test methods are compared in Figure 12. A tendency toward correlation between the relative results with the two test methods is more apparent than in the case of soil removal values. With the exception of Detergent A, the alkylarylsulfonate, and G, the high titer soap, the detergents are rated in the same order, qualitatively, by the two methods. However, in relation to these two detergents (A and G), ratings by the two methods differ significantly. The conventional procedure rates the whiteness retention of high titer soap (G) below the built nonionics (K and L) whereas the tracer method rates the unbuilt soap as better than the built nonionics. The conventional method rates the built soaps (I and H) below the alkylarylsulfonate in whiteness retention whereas the reverse is true with the tracer method. In general the conventional method appears to give lower ratings to the alkaline anionic detergents (G, E, I, H, F, D, and B) in relation to the other detergents than does the tracer method.

There were several pronounced differences in the test conditions involved in the tracer and conventional whiteness retention procedures that could enter into relative ratings of detergents. Soil loading in the detergent was much higher with the conventional test and amount of soil deposited on the cloth much greater. The conventional tests were run for a sufficient time (30 min.) so that essentially equilibrium conditions were reached. In the tracer test procedure the system probably does not reach an equilibrium condition. Further, the carbons used in the tests were of different types. The conventional procedure used a colloidal carbon having spherical particles of very small size within a relatively narrow range (6). The tracer evaluations used a carbon having irregular shaped particles of larger average size and greater range of sizes.

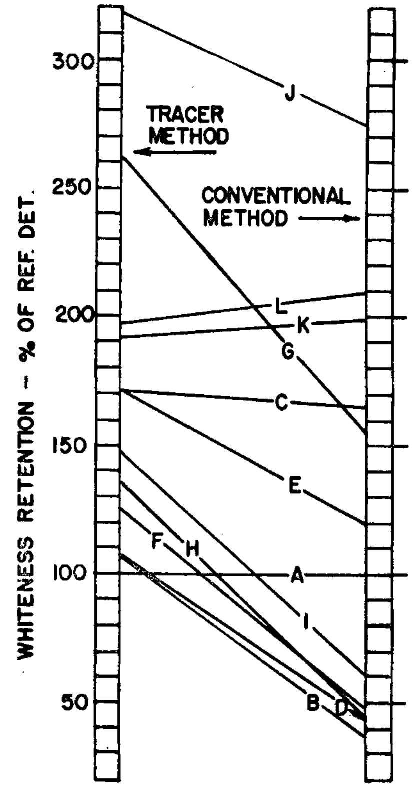

Fig. 12. Comparison of whiteness retention evaluations with the tracer method and the conventional laboratory procedure. Detergent compositions given in Table III.

It appears now that the type of carbon used in the whiteness retention test has an important bearing on the relative rating of detergents. Some trials have been made in which Aquadag carbon was used in the conventional test procedure in place of the Aqua Blak B normally used. The Aquadag being a colloidal graphite and having larger particles than the Aqua Blak B probably is more similar to the radiocarbon black used in this work. With this substitution of carbons it was found that the conventional whiteness retention procedure rated built soap (I) as better than the alkylarylsulfonate, and it also appears to rate the unbuilt soap (G) relatively higher on the scale. Values for all the reference series of detergents have not been determined with the conventional method using the different carbon black, but it appears that correlation between the conventional and tracer results would be better.

Discussion

Because of the great variety of natural soils and wide variation of soiling levels found in practice, any laboratory test based on a single standard soil has limited significance in terms of practical performance. Reliable estimates of general performance based on laboratory evaluations require the use of a variety of test soils, involving different soil materials and different methods of application. There is no "typical" natural soil, and it seems highly improbable to us that any single soil or soil mixture with a single method of application can provide an over-all laboratory evaluation. Because of these apparent difficulties involved in valid laboratory detergency evaluations, there has been a tendency in some quarters to rely almost entirely on practical large scale wash evaluations using natural soils, with little reliance on laboratory tests. The final evaluation of a detergent must be based on extensive practical washing trials, but such practical wash tests are not suitable for preliminary evaluations and screening tests because of the work and time involved. There is definite need for laboratory evaluations, and it is believed that the use of radioactive soils in conjunction with the more conventional types will permit studies of a greater variety of soil systems, with closer approach to natural soils, resulting in more reliable laboratory evaluations of performance.

More extensive correlation with field performance will be required, but it appears that the particular type of rubbed carbon soil described gives results free of some of the anomalies that have been observed in laboratory evaluations using the conventional carbon-soiled swatches. We do not propose at the present stage of development that detergency tests using radioactive soil should replace the more conventional laboratory evaluations. In these laboratories the tracer evaluations, employing rubbed carbon and other radioactive soils, are being used to supplement the more conventional procedures, providing additional information on which to base an estimate of over-all performance of a detergent. In addition to this application to performance testing, the tracer evaluations also are providing basic new information on the detergency process, which in time should aid in the better understanding of mechanisms involved.

Summary

As an approach to the problem of providing for more adequate laboratory evaluations of laundry detergents, test methods have been developed employing radioactive carbon-black soil on cloth. The radioactive carbon, either in dry form or combined with a small amount of mineral oil, is rubbed into the surface of the cloth in a reproducible manner. A machine designed for the purpose is described.

Two new types of wash test apparatus designed for use with small discs of cloth soiled with the radioactive material are described. One machine is of a miniature type employing a cloth to solution ratio within the range employed in practical washing operations. Provision is made for evaluating whiteness retentions from measurements of soil redeposition on clean swatches. Comparison of soil removal values obtained with the two washers for a variety of different types of detergents indicates that type of washing action may have a significant effect on relative ratings.

With the soiling conditions employed in the tests, it has been determined that the initial soil level on a swatch may vary over a considerable range without affecting significantly soil removal values. Estimates of precision and reproducibility of soil removal and whiteness retention determinations indicate that they are adequate in terms of differences being measured.

Soil removal evaluations have been made with a number of different types of detergents using dry carbon soil, and a carbon-mineral oil combination. The two soils were found to give the same relative ratings of the detergents.

Using a series of 12 detergents representing different types, soil removal and whiteness retention values determined with the tracer methods have been compared with values obtained with conventional laboratory test methods. Soil removal evaluations differ considerably with the two methods, and noncorrelating results can be related to the general types of detergent compositions involved. The tracer method appears to give evaluations free of some anomalies that have been recognized in the conventional laboratory tests.

It is believed that the use of radioactive soils in laboratory evaluations will permit studies with soil types approaching natural soils more closely than have the soils used in conventional methods. Use of tracer methods in conjunction with conventional tests should provide for more reliable laboratory evaluations of detergency.

REFERENCES

1. Chemical Week, *75*, 64 (1954).
2. Harris, J. C., and Kamp, R. E., Metal Finishing, *48*, 75 (1950).
3. Hensley, J. W., Iron Age. *170*, 151 (1952); also Plating, *40*, 366 (1953).
4. Lambert, J. M., Roecker, J. H., Pescatore, G., and Stigman, S., Nucleonics, *12*, 40 (1954).
5. Ridenour, G. M., Sanitation, *4*, 61 (1952).
6. Vaughn, T. H., and Suter, H. R., J. Am. Oil Chemists' Soc., *27*, 249 (1950).

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Synthetic Detergents from Animal Fats. IV.[1] Sodium 9,10-Dichlorooctadecyl Sulfates[2]

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SULFATED hydrogenated tallow alcohols (sodium tetradecyl, hexadecyl, and octadecyl sulfates) are good detergents and surface-active agents, with some disadvantage because of limited solubility in water at room temperature. Sulfated tallow alcohols (mainly sodium tetradecyl, hexadecyl, octadecyl, and oleyl sulfates) are likewise good detergents and surface-active agents, adequately soluble because of the presence of sodium oleyl sulfate. Retention of unsaturation appears desirable but may be difficult, depending upon the reduction and sulfation methods selected (7).

Acting upon a suggestion of John C. Cowan, Northern Utilization Research Branch, we have found that chlorinated tallow alcohol sulfates (sodium tetradecyl, hexadecyl, octadecyl, and 9,10-dichlorooctadecyl sulfates) can be prepared by the addition of chlorine to the unsaturated constituents of tallow alcohols (mainly oleyl alcohol) and sulfation of the chlorinated tallow alcohols with chlorosulfonic acid. This method has the advantage that it does not require the use of a special sulfating agent to avoid reactions involving the double bond; and the sulfated chlorinated tallow alcohols are adequately soluble at room temperature.

The present paper is concerned with preparation of sodium 9,10-dichlorooctadecyl sulfates from oleyl and elaidyl alcohols, and the chlorination and sulfation of tallow alcohol. The products have been compared and evaluated in terms of solubility, surface and interfacial tension, calcium stability, wetting properties, stability to hydrolysis, foam height, and detergency.

Sodium 9,10-Dichlorooctadecyl Sulfates

9-Octadecenols. Oleyl alcohol (I no. 92.5, theoretical value 94.5) and elaidyl alcohol (I no. 94.7, m.p. 36.1-37.0°) were prepared from a commercial oleyl alcohol as described in previous publications (5, 7).

9,10-Dichlorooctadecanols. Chlorination was carried out according to a method for the chlorination of unsaturated alcohols described to us by H. M. Teeter (6), Northern Utilization Research Branch, modified by use of a lower reaction temperature and lower solvent ratio.

A slow stream of chlorine was introduced into a stirred solution of 100 g. of purified oleyl alcohol in 300 ml. of dichloromethane, cooled in a dry ice-carbon tetrachloride bath maintained at —45°. Chlorine was passed in at such a rate that the reaction temperature remained in the range —13° to —23° throughout 4.5 hours. Completion of reaction was indicated by the development of a yellow-green color in the solution and a fall in reaction temperature as a result of no further heat of reaction. Solvent and excess chlorine were removed at reduced pressure in a stream of nitrogen, finally being heated on the steam bath to remove the last trace of solvent. 9,10-Dichlorooctadecanol was obtained as a colorless oil, yield 97%, m.p. 12°, n_D^{20} 1.4760, d_4^{20} 0.9898, molecular refractivity 96.71 (theoretical value 96.58), I no. 0.3, 19.95% Cl (calculated for $C_{18}H_{36}Cl_2O$, 20.90% Cl; calculated with correction for saturated impurities in the oleyl alcohol, 20.45% Cl).

Elaidyl alcohol chlorinated in the same manner gave a different racemic mixture, a 9,10-dichlorooctadecanol, a white solid, m.p. 31°, yield 94%, n_D^{20} 1.4757, d_4^{20} 0.9946, molecular refractivity 96.19, I no. 0.3, 20.59% Cl.

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[1] I, II, and III in this series are references (5), (4), and (7), respectively.

[2] Presented at the meeting of the American Oil Chemists' Society in Minneapolis, October 1954.

[3] A laboratory of the Eastern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture.