A Triply Labeled Particulate Soil for Detergency Studies

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Abstract

A kaolinite type of clay made radioactive by neutron irradiation (Spinks Bandy Black), described in an earlier report, has undergone extensive testing to determine its suitability as a particulate component of an artificial radioactive soil. The other components of the soil are labeled with ^{14}C and tritium. The incorporation of the radioactive clay into an established soil required the development of a reproducible padding procedure and the development of suitable analytical methods for the clay, as well as modification of the existing method for ^{14}C and tritium in the presence of the radioactive clay. A problem arose when it was noticed that, after the padding step, the specific activity of the clay adhering to the fabric was higher than the starting clay. This was traced to the fact that Spinks Bandy Black is not only a mixture of varying particle sizes, but of changing chemical composition with varying particle size. Thus, one could not readily convert radioactivity to weight. The problem has been resolved by resorting to chemical analysis for SiO_2 and Al_2O_3 of a few representative swatches from each padding run to give the weight of clay per swatch and thus the specific activity. Chemical and radiochemical analyses of the swatches after laundering have demonstrated that further disproportionation of the clay is minor. A large Terg-O-tometer washing study was made under a variety of conditions to determine the precision of the method for all three labeled components of the soil. It was found from sets of four replicates that the precision for clay detergency is ±2.5%; for the polar fatty soil detergency (^{14}C) is ±2.3%; and for the nonpolar fatty soil detergency (tritium) is ±3.5%. Redeposition of the clay in the presence of a built detergent is usually less than 1%.

Introduction

In a recent report (1) the preparation of a radioactive clay (Spinks Bandy Black, H. C. Spinks Co., Paris, Tenn.) for use as the particulate component of a synthetic soil was described. The distinctive feature of this clay was that it was made radioactive by neutron irradiation so that one avoided the drastic treatment required to fix the radiotracer into the clay matrix. Solid clay particles in the micron size range are reasonably transparent to thermal and fast neutrons and it was anticipated that the clay would have a near uniform specific activity, basis weight, across the particle size distribution.

The major problem with preparing a radioactive particulate soil in this manner appeared to be the production of radioactive nuclides not firmly fixed in the particles so that they might be readily dissolved, extracted, or ion exchanged by the built detergent. The presence of such labile nuclides was established early in this work and a procedure was devised which reduced them to an innocuous concentration (1). This consisted essentially of washing the clay with sodium tripolyphosphate which appeared to render the clay immune to further radio-

nuclide extraction by fully built detergents containing either anionic or nonionic surfactants.

Because the clay emitted both beta and gamma radiation, some consideration was given to the possibility of adapting the analytical method used for the analysis of ^{14}C and tritium labeled fatty soil to the clay (2–4). This method, liquid scintillation counting of the wash water (4), involves beta ray spectrometry to separate ^{14}C from tritium. The beta radiation emitted by the clay particles have a broad range of energies which overlap the ^{14}C and tritium spectra and so would cause some interference. However, the clay also emits harder beta radiation so that one could readily set up the liquid scintillation spectrometer to count these radiations independent of ^{14}C and ^{3}H interference, although the converse is not true. However, for reasons advanced below, this approach was not taken and all analysis for clay was based on gamma ray counting.

In order to consider the radioactive Bandy Black as the particulate component in the labeled fatty sebum, two techniques had to be developed. First, a reproducible method for padding all fabrics of interest was required. Besides reproducibility, firm adherence of the clay to the fabric was desirable, so that the deposited clay would not be easily removed by simple agitation in water. Second, it was required that the analytical methods for the three labeled fractions be compatible with automated sample and data processing for large numbers of samples.

Experimental Procedures

Padding Study

Materials used were the following: cotton, Indianhead, style 405; nylon 66, 100% spun, style 354A; dacron, 100% spun, style 754 AW; dacron/cotton (d/c) shirting, 65/35, style 7406; and permanent press d/c (p-p), style 7406 WRL. All fabrics were obtained from Testfabrics, Inc., New York, and were desized, scoured, etc., by the supplier.

Since the clay was to be applied to 4 in. square swatches, it was necessary to seal the fabric edges to avoid ravels. The cotton swatches were edge-sewn with a zig-zag stitch. The other fabrics were cut and heat-fused on the edges by Testfabrics, Inc. After the edges were sewn, cotton swatches were scoured five times with sodium tripolyphosphate (STPP) prior to padding; the other fabrics were used without further treatment.

To be acceptable, any method of padding had to meet three criteria: (a) About 4–6 mg of clay had to go onto each 4 × 4 in. swatch (approx. 15% of the total soil). (b) Not more than 10% of the clay could be removed in a 10 min wash in hot water of the hardnesses used in detergency studies; and (c) Built detergents had to remove a sufficient amount of clay to permit discrimination between detergent formulations.

Although other workers have used rubbing-in and air soiling techniques for applying particulate soils (5), these methods were not considered due to the difficulties inherent in handling dry radioactive dusts. All clay padding was done from slurries.

All clay analyses in the padding section were done by gamma ray counting of swatches, usually a set

TABLE I

Removal of Clay From Cotton in a Blank Wash

Method of clay application	Per cent clay removed in blank wash[a]
Pipet from benzene slurry	81
Pipet from water slurry	78
Tumbling in 1 gal jar with vanes[b]	46
Wrist-action shaker, 500 ml flask[b]	22
Box shaker, 1 gal jar[b]	
1 hr in slurry, approx. 50 ppm hardness	16
2 hr in slurry, approx. 50 ppm hardness	12
2 hr in slurry, 1000 ppm hardness	9
Terg-O-tometer,[c] 2 hr, 1000 ppm hardness	9

[a] Blank washing conditions: four swatches in 500 ml of water, 150 ppm hardness (calculated as CaCO₃, Ca/Mg = 60/40) at 120 F, 100 rpm for 10 min. No detergent present.
[b] Clay concentration was 600 mg/liter, at 100 F.
[c] Clay concentration was 600 mg/liter, at 120 F.

TABLE II

Effect of Rinse Water Hardness on Retention and on Washing Blank[a]

Rinse		Blank wash, per cent loss hardness of wash, ppm		
Water hardness, ppm	Retained clay, mg/swatch	50	150	300
50	10.49	11.1	9.2	7.9
150	10.39	14.5	9.2	8.7
300	12.22	16.8	10.3	9.8

[a] Cotton swatches, 12/liter, padded from 400 mg clay/liter of 1000 ppm hardness water at 120 F. The average amount of clay deposited in the padding step was 17.9 mg/swatch.

of four and converting the counts to weight by using the specific activity of the starting clay. As we shall see later this is precise, but may not be accurate.

Several methods of applying the clay were investigated including direct pipetting of benzene and water slurries onto the cloth, tumbling the cloth in a water slurry, shaking in a water slurry on a wrist-action shaker and on a reciprocating box shaker and agitating the cloth in a water slurry in a Terg-O-tometer. All of the tumbling and shaking methods included a rinse to remove loosely bound clay particles. The swatches were air dried and soiled with 26 mg of fatty soil (2). Then the swatches were given a blank wash in the Terg-O-tometer without detergent. Table I summarizes the preliminary results for the various systems using cotton as the substrate.

Table I shows that the clay is firmly attached to the fabric by the action of the Terg-O-tometer, as well as the box shaker, so subsequent investigative work was done using the Terg-O-tometer because of its greater convenience.

Varying the concentration of clay in the padding slurry was found to be effective in controlling the amount of clay deposited. For cotton, the amount of clay deposited during the padding and the amount of clay retained after rinsing were smooth functions of the starting clay concentration over a range that includes the amounts needed for this work. These curves are shown in Figure 1.

Preliminary experiments using tap water of about 50 ppm hardness for padding gave erratic results. With the hardness increased to 1000 ppm, duplicate paddings agreed within ±5%. Since 10% clay removal in a blank wash would be a substantial fraction of the amount removed by detergents, the effects of varying the hardness of the padding rinse and the blank wash were also investigated. Increasing the hardness of the padding rinse water to 300 ppm caused a substantial increase in the amount of clay
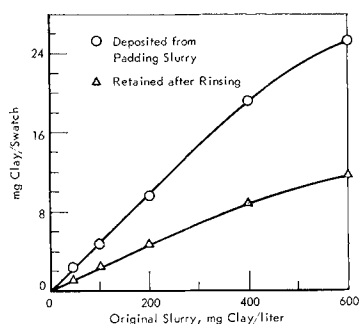
retained. An intermediate hardness, 150 ppm, showed the same retention as with a 50 ppm rinse. Next, these swatches were soiled with the fatty soil and some swatches from each rinse hardness were given a blank wash in 50, 150 and 300 ppm hardness water. These results are shown in Table II.

The fraction of clay removed appears to depend on the hardness of the padding rinse and the hardness of the blank wash. Rinsing the swatches in water of 300 ppm hardness left more clay on the swatch that could be readily removed in a blank wash in softer water. Therefore, all rinsing was done in water of 50 ppm hardness to minimize the washing blanks.

The effects shown in Table II are presumably due to the ability of the divalent calcium and magnesium cations to act as a bridge between the surface of the cotton and the basal plane of the kaolinite crystal, both anionic in character. Thus, increasing the hardness of the water increases the concentration of the cations on the cotton surface and increases the number of clay particles held on the surface. Then, during the padding rinse and the blank wash (which is essentially on additional rinse step) new equilibria are established between the cations on fabric surface and those in solution. If the conditions favor removal of cations from the surface (low hardness of wash water) into the water relatively more clay is removed as shown in Table II. Thus, the amount of clay removed when a 50 ppm rinse is followed by a 300 ppm blank wash is lower than that removed when a 300 ppm rinse is followed by a 50 ppm blank wash.

Variations between different varieties of cotton were demonstrated when two lots of cotton, scoured at different times were padded together in the same beaker. The swatches designated Lot B exhibited a much greater affinity for the clay during padding and rinsing at two different concentrations. These results are shown in Table III.

Table III shows the need for preparing each batch of swatches at one time to ensure a uniform padding. Furthermore, it suggests the need for analyzing the padded swatches for clay content before use.

The tagged clay has been pretreated to remove activity which is in soluble form or which can be removed by ion exchange in a built detergent solution (1). The pretreatment with STPP removes some of the organic material on the clay, so batches of clay treated at different times may deposit differently. This was demonstrated by padding cotton swatches with clay from two different batches. These results are shown in Table IV.

While the differences are not large, Table IV shows the need for preparing large batches of clay to minimize padding variations.

Nylon, dacron, dacron/cotton (d/c) and permanent press dacron cotton (p-p) were all successfully padded with clay by this technique. In each case, the amount of clay deposited and retained was a function of the clay concentration in the padding slurry, al-

FIG. 1. Effect of clay concentration on the padding of cotton.

TABLE III
Effect of Fabric Variations on Padding of Cotton

| Clay | Padding slurry, mg clay/liter[a] | | | |
| | 200 | | 400 | |
	Fabric A	Fabric B	Fabric A	Fabric B
Deposited during padding, mg/swatch	8.6	11.2	16.6	20.3
Retained after rinsing, mg/swatch	4.1	6.3	10.0	13.4

[a] Six swatches of each fabric were in each beaker. They were padded for 2 hr at 120 F in water of 1000 ppm hardness and rinsed for 30 min.

TABLE IV
Variation in Padding Due to Different Batches of Clay

| Clay | Padding slurry, mg clay/liter[a] | | | |
| | 100 | | 200 | |
	Clay 1	Clay 2	Clay 1	Clay 2
Deposited during padding, mg/swatch	4.9	5.4	9.7	10.9
Retained after rinsing, mg/swatch	2.3	2.8	4.5	6.4

[a] Data for Clay 1 taken from Figure 1. Cotton was padded for 2 hr at 120 F in water of 1000 ppm hardness and rinsed for 30 min.

though the characteristics for each fabric were different.

The following padding conditions were found to yield satisfactory results: 12 swatches, 4 in. square, in 1 liter of slurry containing 1000 ppm hardness (calculated as $CaCO_3$, Ca/Mg = 60/40), at 120 F) agitated for 2 hr at 100 rpm followed by a rinse in 1 liter of water of 50 ppm hardness at 120 F, agitated for 30 min at 100 rpm. These conditions were adopted as standard except that not all the fabrics required a full 2 hr for the padding. Reference to "standard" padding conditions later in this report refers to the padding and rinsing conditions described above. The padding results for the various fabrics are summarized in Table V.

Table V illustrates that one may control the concentration of clay on the fabric by varying the clay content of the padding slurry.

Large-Scale Padding

To prepare large quantities of swatches for routine use in detergency testing, the conditions found suitable for exploratory work were applied directly on a larger scale. The padding and rinsing were done in a Philco Twin-A-Matic washing machine. A steel-mesh basket, coated with Kel-F, was designed to fit underneath the agitator to allow the operator to remove the swatches without reaching into the radioactive slurry. The temperature is maintained with a knife-blade heater controlled by a variable transformer. A schematic of the basket and agitator is shown in Figure 2. The first swatches padded showed a clay relative standard deviation of 4.3%. When the drain pump was operated with the effluent being returned to the padding tub, the relative standard deviation for the load was reduced to 2.6%. Therefore, the pump is regularly used to assist in the circulation of the slurry. Approximately 500 swatches are padded in 40 liters of slurry of 1000 ppm hardness at 120 F. The appropriate clay concentration is chosen from the data in Table V to yield approximately 4.5 mg of clay per swatch. After rinsing, the swatches are air-dried and stored until needed. This procedure is very similar to that described by Rutkowski (6).

The uniformity of padding was determined by counting 50 vials of four swatches each for each fabric. The relative standard deviation for each fabric is shown in Table VI. These results show that the agitation in the washing machine is quite adequate.

Limited experience indicates that the reproducibility between loads is better than ±10%. However, for a new batch of clay or fabric the proper slurry concentration must be determined by Terg-O-tometer experiments as shown in Figure 1.

Analytical Method Development

Since the clay emits both beta and gamma radiation from several nuclides, the option was open to

use either type of radiation for analysis. ^{14}C and tritium, the labels for the fatty sebum, are pure beta emitters and are routinely determined in the wash water by liquid scintillation counting (4). It seemed reasonable, therefore, to take advantage of the existing method and try to adapt it to the radioactive clay analysis. A few runs were, therefore, made by suspending known weights of clay in a liquid scintillation gel, Triton X-100/toluene/water (5.7:11.3:5 v/v/v). The results were quite erratic and this was attributed to the varying beta ray self absorption by particles of different size. Therefore, the beta ray analysis for clay was abandoned for these reasons: (a) Self absorption of beta rays originating from solids varies with particle size resulting in reduced counting efficiency with larger particles. (b) Liquid scintillation counting of radioactive fatty soil on fabric is accurate and precise because the soil is dissolved by the counting solution, which is not the case with clay. (c) Because of the uncertainties in padding hundreds of swatches from a large clay slurry (see section on padding), it was found desirable to determine the clay on all the swatches before washing. This could only be done by gamma ray counting which is nondestructive. (d) Gamma ray counting is insensitive to the physical state of the fabric or clay (i.e., density, moisture, particle size), it is free of interference from beta emitters and requires only the simplest development to devise an analytical method.

For these reasons we decided to retain the existing method, liquid scintillation counting (4), for the analysis of the fatty soil (i.e., ^{14}C and ^3H) and NaI crystal scintillation counting for the clay. In this method four swatches of a fabric (charge to a Tert-O-tometer beaker) were folded into a 1¼ diameter × 2⅛ in. plastic vial, placed in a well of a
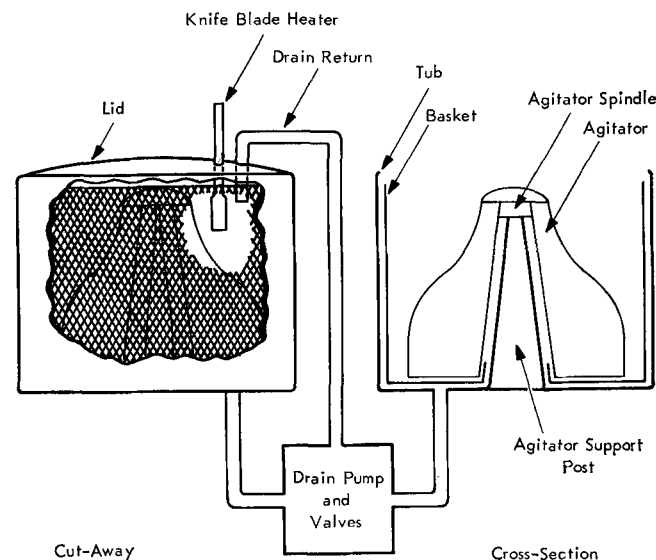

FIG. 2. Diagram of washing machine with baskets in place.

TABLE V
Padding of Various Fabrics

Fabric	Clay in slurry, mg/liter	Padding Clay deposited, mg/swatch	Rinsing Clay retained mg/swatch	Loss in blank wash, %
Cotton	200	9.7	4.5	9
	400	19.3	8.7	9
Nylon	50	3.9	3.9	<1
	100	7.8	7.8	1
Dacron	50	3.2	2.8	<1
	100	6.0	4.9	1
D/C	100	4.1	3.7	3
	200	7.8	6.8	3
P-P	100	3.8	3.2	3
	200	6.5	5.3	3

3 × 3 in. NaI detector, counted on a scaler-printer assembly, (Baird-Atomic Model 530-A Scaler-Spectrometer-Printer) inverted and counted again. The purpose of the inversion was to correct for uneven distribution of the clay on the folded fabric. Rarely did the two counts differ by more than 5%. The clay was counted in the gamma ray energy range of 0.32–1.8 MeV, where the bulk of radioactivity was located. Background from the detector was 250 cpm in a 4 in. lead shield. On those occasions when samples of clay had to be counted directly, two techniques were used. The first was to disperse the clay in a gelled 0.5% solution of Carbopol-934 (B. F. Goodrich Chemical Co., Cleveland, Ohio) in the same volume of water in a similar plastic vial as that occupied by the four folded swatches. This was to avoid errors due to differences in geometry. In the second, the clay was placed on the bottom of a plastic vial and counted. By previously obtaining a conversion factor, counting clay in the bottom position and in the dispersed position, we could intercompare radioactivity from a variety of samples. Furthermore, a standard sample of clay (gelled) was counted periodically to obtain decay corrections. Therefore, all count rates reported here have been corrected for geometry and decay.

Before discussing problems arising from clay analysis, it is appropriate to discuss the modification to the method for measuring ^{14}C and tritium in the wash water. As stated above, the beta activity of the clay overlapped that of ^{14}C, so a correction had to be obtained. This was done by suspending known weights of clay in the gelled liquid scintillator (4) used for the analysis of wash water samples. The radioactivity of the clay was measured in the ^{14}C energy channel, the tritium energy channel, and a third energy channel which contained only counts from the clay. The ratios of counts between the ^{14}C and clay channel and the ^3H and clay channel were calculated and are shown in Table VII. The correction factors were entered into the computer programs written for the analysis of fatty sebum detergency (3).

The earlier arguments against the beta ray analysis of clay also apply to the correction described above. However, by controlling the specific activities of the

TABLE VI
Uniformity of Padding Within a Machine Load

Fabric	RSD, %[a]
Cotton	2.6
Nylon	3.3
Dacron	2.7
D/C	2.0
P-P	3.3

[a] Relative standard deviation of a single determination, based on 50 samples for each fabric.

TABLE VII
Correction Factor for Clay Counts

Clay, mg	Net cpm ^3H	^{14}C	Clay	Ratio (correction factor) ^3H/clay	^{14}C/clay
0.23	332	334	82	4.05	4.07
0.46	651	660	165	3.95	4.00
1.15	1570	1706	422	3.72	4.04
Average				3.91	4.04

clay, the ^{14}C labeled soil ingredients and tritium labeled soil ingredients inaccuracies in the clay analysis were minimized. Thus, at 5 mg of clay per swatch and four swatches per beaker, the maximum amount of clay which can appear in the water is 20 mg. Since we take a 5/600 aliquot of the wash water for counting in the liquid scintillation spectrometer, the maximum amount of clay which can be present in the water sample is 0.16 mg. If the beta ray specific activity of the clay in its channel is ~400 cpm/mg, the total interference would be 4 × 400 × .16 = 256 counts in the tritium and ^{14}C channels. An error, due to self absorption of 25% would cause a variation of ±70 cpm, but the specific activities of the ^{14}C and tritium fractions are adjusted to give several thousand cpm for each, after a wash. Thus, a large error in the clay analysis would cause a minor error in ^{14}C and ^3H.

Following the development of the padding procedure, a careful study was made to determine whether we could account for all the radioactivity introduced into the system. To this end, some padding runs were made in the Terg-O-tometer wherein the padding slurries and rinsing slurries were filtered, after the soiling step. The filter cakes and the filtrate were taken for analysis. Several filters were tested and the results for cotton are shown in Table VIII.

The radiochemical closure is very good which was true for all the fabrics. However, a most disquieting fact is shown in the last column, namely, that the clay on the fabric has a different specific activity than that of the starting clay. Since one relies on the specific activity to convert observed counts to weight, this evidence of selective deposition and change in specific activity suggested that the Spinks Bandy Black has the unfortunate property of having a different chemical composition at different particle sizes. It had been observed earlier that the clay left in the slurry was coarser than the starting clay. Analysis of the various fractions of clay were then made by the Inorganic Analysis Section (Si gravimetrically and Al colorimetrically). The results are compared with a pure kaolinite in Table IX.

It is immediately clear that Bandy Black is a heavily contaminated kaolinite. It has a high silica content which seems to be concentrated in the coarser particles, i.e., the residue from the padding step. This bears out the contention of nonhomogeneity in composition across the particle size range. Assuming that free silica is a major contaminant, this would explain the observation that the residual clay from the padding step has a lower specific activity than the starting clay because silica tends to have fewer contaminants than kaolinite.

This finding complicated the analytical procedure because one must determine not only the activity, but the specific activity of the clay on the fabric after padding, rather than rely on the original specific activity of the clay. This must be done on the fabric rather than in the slurry for the simple reason that

TABLE VIII
Radioactivity Balance During Cotton Soiling

Clay	mg	Total activity, cpm		Specific activity cpm/mg
Added	410	3.26×10^5		794
On filters[a]	193	1.21×10^5		629
On filtrate	8[b]	0.05×10^5	$= 3.16 \times 10^5 = 97\%$	629[b]
On fabric	209[c]	1.90×10^5		909

[a] Filters from padding and rinsing steps. Reduced by ashing with H_2SO_4. Counting the ash and converting the ash weight back to clay weight.
[b] Calculated assuming this had the same specific activity as that on the filters.
[c] By difference.

it is very difficult to get a representative sample of slurry from 40 liters in a washing machine.

Before resorting to the direct chemical analysis of the fabric, it was hoped that, inasmuch as the segregation of the clay during padding shows some particle size discrimination, presegregation of the clay would avoid the problem. Accordingly, several 6 g batches of a new preparation of radioactive clay were wet screened by settling in distilled water in a separatory funnel. The fraction settling in 5 min was discarded, the fraction unsettled after 64 hr was also discarded. The data, (Table X) showed clearly the change in specific activity with particle size.

This clay was then used to soil some fabrics in a Terg-O-tometer and the specific activity of the residual clay in both padding and rinsing solution was determined after filtration and sulfate ashing. The sulfate ash weight was converted back to the original clay weight by a factor obtained by ashing a known weight of Bandy Black. The results are shown in Table XI.

Table XI shows no improvement in presegregation of the clay. The extent of the difference between the specific activity of the starting clay and that left in the fabric is controlled by the fraction of the starting clay which adheres to the fabric. Thus, for Dacron, most of the clay went in, hence the minor change (1767 vs. 1682) while for P-P only a small amount entered the fabric, thus the large change (2459 vs. 1682). Two conclusions are derived from Table XI. First, presegregation does not eliminate changes in specific activity during the padding step. This may be due to the crude segregation technique used or to the fact that differential deposition is not entirely controlled by particle size. Second, not obvious in Table XI, is the fact that the sulfate ash method of converting back to clay weight is not precise because different silica and alumina contents yield ashes having different ratios of ash to clay. It would be more desirable to have a more specific analytical method.

This can be done by analysis for Si and Al because Table IX showed that, regardless of the SiO_2 and Al_2O_3 concentrations the sum was 86% of the original clay weight. This, of course, is a strongly damped system because if the SiO_2 content goes down, the Al_2O_3 content necessarily goes up and the sum shows little change. However, it does provide a mechanism to measure more accurately the weight of clay in the various media during padding and washing. Therefore, we proceeded to pad, rinse and wash some fabrics and to analyze the various solutions for clay via the determination of Si and Al by either wet chemical analysis or neutron activation analysis. The additional purpose of this experiment was to determine whether additional segregation occurred during the washing step which would further complicate the analysis. It was clear from Table XI that the specific

TABLE IX
Analysis of Clay and Clay Fractions

Sample	SiO_2, %	Al_2O_3, %	$Al_2O_3 + SiO_2$, %
Pure kaolinite[a]	46.5	39.5	86.0
Original Bandy Black	61.0	24.5	85.5
Radioactive Bandy Black	62.3	23.6	85.9
Padding residue	69.2	16.8	86.0
Clay on fabric	55.9	30.1	86.0

[a] Pure kaolinite may be written as $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$.

activities of the clay on the different padded fabrics would be different, but if no additional segregation occurred, then measuring the total gamma ray activity before and after washing would be sufficient to determine the detergency. The two fabrics used in this experiment, cotton and perma-press, were those showing the greatest difference in Table XI.

After the soiling operation, the precipitates from padding and rinse water were isolated by filtration through a 0.45 μ Millipore filter. These were analyzed for SiO_2 and Al_2O_3 and converted back to clay weight. The difference between starting clay weight and that on the filter was the amount retained by the fabrics. The fabrics were then counted, washed and counted again. The wash water was filtered, counted, and the SiO_2 and Al_2O_3 content of the insolubles again obtained which give the weight of the clay in the precipitate. Thus, one could compare the specific activity of the clay on the fabric with the deterged clay. The results are shown in Table XII.

Table XII shows that only a modest change, 5–7%, in specific activity occurs during the washing process which suggests that one can obtain reasonable values for detergency by comparing the total gamma ray activity in the wash water with that on the unwashed padded swatches. This finding, while made with presegregated clay, was also found with the original radioactive Bandy Black. While it may be desirable to determine the specific activity of the clay in the fabric via analysis for SiO_2 and Al_2O_3, it is not required. Once it has been established that there is only a minor change in specific activity after washing, then only the total activity on the swatch set (4) before washing and after washing is needed.

The reduction in specific activity between the before and after washing may be due to analytical uncertainties in the SiO_2 and Al_2O_3 analysis or it may be real. In any case, this change in specific activity results in a negative error of a few per cent in detergency values. While this may be acceptable from a laundering viewpoint because the data are normally expressed on a comparative basis, it is not analytically ideal. We intend to exercise better control over the specific activity of the clay either by a better segregation method before irradiation or by a change in the type of clay used.

Precision Study

Having assured ourselves that specific activity changes during washing were minor, we were in a position to make a large scale study of detergency

TABLE X
Change in Specific Activity With Particle Size

Sample	Wt %	Specific activity, cpm/mg
Original	100	1600
Settled in 5 min	29.4	1110
Settled in 64 hr	66.6	1677
Fines	4.0	>3000

TABLE XI
Padding With a Presegregated Clay

Fabric	Specific activity, cpm/mg[a]		
	Clay in padding slurry	Clay in rinsing slurry	Clay on fabric[b]
Cotton	1590	1942	1437
Dacron	683	968	1767
D/C	1442	1650	2097
P-P	1237	1614	2459

[a] Starting clay, 1682 cpm/mg.
[b] By calculation.

precision using the triply labeled soil. Clay padding was done as described above. After gamma counting swatch sets (four to a set), the fabrics were then padded with the fatty sebum as reported previously (4).

The swatches are suspended in a hood and 1 ml of a benzene solution of the sebum is pipetted onto each swatch. The pipetting is done by a Brewer Automatic Pipettor (distributed by Baltimore Biological Laboratory, Inc., Baltimore, Md.) which has had the variable speed control replaced with a constant speed motor of 10 rpm. The solution is spread over the swatch by rapidly moving the tip of the delivery tube (1/8 in. Teflon tubing) across the face of the swatch. Minor variations in the distribution of the sebum over the swatch have been found not to affect the detergency values. After the benzene has evaporated the swatches are aged overnight. Swatches may be stored at room temperature for 15 days without affecting detergency values (4). The precision of the pipettor is 1.2%, relative standard deviation, for a single sample.

Five fabrics were prepared and laundering in a Terg-O-tometer was done under a variety of conditions which are set forth below. Every condition (i.e., fabric, temperature, water hardness, etc.), was run in quadruplicate, i.e., four beakers per set for the washes and duplicates for the blank washes. Into each Terg-O-tometer beaker was placed one unpadded swatch for clay redeposition values. Clay detergency was obtained by gamma ray counting the swatches after laundering, fatty sebum detergency was obtained by beta ray counting the wash water. While one could also obtain clay detergency by gamma counting the wash water, which is probably more convenient, this was not done because the count rate of an aliquot of wash water would usually be lower than the count rate of the laundered swatches, thus requiring more counting time.

The detergent used had the following composition: active matter (NEODOL 25-9), 0.1 g/liter; sodium silicate, 0.05 g/liter; sodium tripolyphosphate, 0.4 g/liter; sodium sulfate, 0.30 g/liter; carboxymethylcellulose 0.005 g/liter; water, 50 and 300 ppm expressed as $CaCO_3$ (Ca/Mg = 60/40); Tergotometer, 10 min, 100 rpm, 60 F, 120 F, 4 swatches/beaker plus one unpadded swatch; fabrics, Testfabrics Inc., 4 × 4 in., cotton, nylon, dacron, d/c, p-p; and soil, 15.4 mg³H labeled soil and 12.6 mg¹⁴C labeled soil, per swatch (2).

The clay, Spinks Bandy Black, was used at rate of 4-5 mg/swatch for cotton, nylon and p-p, 6-7 mg/swatch for dacron and 2-3 for d/c.

The results are in Tables XIII and XIV which demonstrate that good precision is obtained by this method. The precision expressed in Tables XIII and XIV are those calculated by the normal method for repetitive analyses. It is true that the error includes errors due to both counting statistics and experimental variations. The error contribution from counting was kept small simply by counting all samples for long enough periods because this error decreases with increasing total counts. Therefore, the observed standard deviations are controlled almost entirely by the experimental variations in washing. The large relative standard deviations for the clay blank washes is due to the fact that little clay was removed by the water hence the count rate before and after washing was similar; the detergency value was the difference between two large numbers.

The blank washes show a significantly greater clay removal than was found with swatches padded in the Terg-O-tometer (see Table I). The Terg-O-tometer was operated at 100 strokes/min and the agitator had a rotation of about 270°, while the washing machine was operated at its fixed speed of 60 strokes/min at about 135° rotation. This lower agitation rate in the washing machine probably causes less flexing of the fabric resulting in less penetration of clay particles into the threads.

It is very interesting to note that, for the fatty components, blank washes remove a significant amount from cotton and virtually none from nylon. Upon adding a detergent, nylon is virtually washed clean while cotton is much less affected.

Clay detergency values are reasonably precise averaging about ±2.5% relative standard deviation, an entirely acceptable value. The surprisingly low redeposition values, <1%, indicate that this is a problem of no concern in laundering performance, although it is of major concern in dry cleaning. Higher temperature washing tends to derge more of the clay than ambient temperature washing, but here again the pure synthetics, nylon and Dacron, show the largest detergency ~85-90%.

The blank values are the amounts of clay and sebum removed in the absence of surfactant and builders and thus measure the effect of agitation, temperature and water hardness upon soil removal. Future work with this technique will allow the separation of the effects of the various builders from the surfactant effects in the removal of clay. The blank values for clay removal compared to the built detergent clearly demonstrate the importance of a built detergent. Clay detergency, however, is not only due to the solubilization of the fatty binder, but also to a direct interaction with the clay (7). Thus, redeposition values without detergent are much higher than with detergent. One should note, however, that the amount of redeposited clay is low with blank washes because the amount of detergency is low. It would be in-

TABLE XII
Effect of Washing on Specific Activity of Clay

Fabric	Clay used for soiling, mg	Clay in padding and rinse water, mg	Clay retained by fabric, mg	Soiled fabric, cpm	Clay on fabric before washing, cpm/mg	Clay in wash water, mg	Deterged clay, cpm	Clay on fabric after washing, cpm/mg
Cotton	196.8	146.7	50.1	77868	1554	18	25592	1422
P-P	193.4	129.8	63.6	137228	2157	35	71926	2055

TABLE XIII

Precision of Detergency Studies With Triply Labeled Soil at 60 F

Fabric	Detergent	Hardness, ppm	Detergency, %			Clay[a] redeposition
			^{3}H Fraction	^{14}C Fraction	Clay	
Cotton	No[b]	50	11.5 ± 0.1[d]	9.4 ± 0.1	15 ± 2.5	1.0
Cotton	Yes[c]	50	57 ± 2.9	56 ± 2.5	43 ± 1.2	0.9
Nylon	No	50	0.5 ± 0.1	0.9 ± 0.3	6.4 ± 0.5	28.0
Nylon	Yes	50	85 ± 3.2	89 ± 1.5	94 ± 0.9	0.7
Dacron	No	50	1.0 ± 0	1.8 ± 0	6 ± 0.4	11.0
Dacron	Yes	50	51 ± 1.1	82 ± 1.0	76 ± 0.9	0.3
D/C	No	50	2.6 ± 0.5	3.0 ± 0.8	7 ± 1.7	4
D/C	Yes	50	59 ± 1.2	68 ± 0.4	66 ± 1.2	0.5
P-P	No	50	2.1 ± 0.1	3.2 ± 0.2	4 ± 0.2	11
P-P	Yes	50	59 ± 1.8	69 ± 2.2	67 ± 5.0	0.1
Cotton	No	300	8.8 ± 1.0	7.3 ± 0.6	11 ± 0.6	3
Cotton	Yes	300	46 ± 1.7	40 ± 0.7	40 ± 0.4	0.7
Nylon	No	300	0.3 ± 0	0.7 ± 0.1	7 ± 0	26
Nylon	Yes	300	64 ± 2.0	73 ± 2.2	82 ± 2.9	0.8
Dacron	No	300	0.9 ± 0.3	1.6 ± 0.2	6 ± .02	13
Dacron	Yes	300	43 ± 2.4	58 ± 2.6	66 ± 3.3	0.2
D/C	No	300	1.8 ± 0	2.1 ± 0.1	7 ± 0.5	7
D/C	Yes	300	32 ± 2.0	36 ± 2.8	52 ± 1.6	0.5
P-P	No	300	1.6 ± 0	2.6 ± 0.2	5 ± 0.6	13
P-P	Yes	300	42 ± 1.7	48 ± 1.9	47 ± 3.4	0.3

[a] Basis clay in wash water.
[b] No builders or surfactant.
[c] Built detergent with NEODOL 25–9, quadruplicate runs.
[d] Absolute standard deviation, one sigma.

teresting to measure the effect of surfactant and builders on redeposition when larger (i.e., 10–20 mg) amounts of clay are in the wash water.

Now that this technique has been developed, it will be applied on a large scale to determine the effects of various parameters in detergency. Such studies generate enormous amounts of samples and data, so that automation of sample handling and data processing is a necessary part of these programs. Liquid scintillation counting is, of course, completely automatic, but crystal scintillation counting for clay is not. To this end, we intend to replace our manual system with an automatic gamma counter (Nuclear-Chicago Co., Des Plaines, Ill), which will process 100 samples unattended.

It is obvious that the large disproportionation of clay during the padding operation and the small disproportionation during the washing step should be eliminated. To this end we are studying a number of methods of preparing a clay of constant specific activity over its particle size range.

The foregoing method has several significant advantages as a means of measuring detergency. First, it entails the use of a mixed fatty plus particulate soil with provisions for analysis of each component.

Second, since it is an accurate measure of the mass of material deterged, it expresses true detergency rather than appearance. This is of importance in any attempt to study detergency mechanisms. Third, the high precision of the method permits one to more accurately determine the effect of different parameters some of which may be rather subtle second order effects. Fourth, the high precision sharply reduces the number of replicates required to reach a desired confidence limit. Fifth, it permits one to follow soil removal on a component-by-component basis if desired. Finally, it is well suited to redeposition measurements of the various sebum components.

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[Received April 30, 1969]

TABLE XIV

Precision of Detergency Studies With Triply Labeled Soil at 120 F

Fabric	Detergent	Hardness, ppm	Detergency, %			Clay[a] redeposition
			^{3}H Fraction	^{14}C Fraction	Clay	
Cotton	No[b]	50	18.8 ± 0.2[d]	16.1 ± 0.3	8.5 ± 1.7	3.0
Cotton	Yes[c]	50	78 ± 2.3	79 ± 1.0	53 ± 1.5	0.5
Nylon	No	50	0.6 ± 0.1	0.9 ± 0.1	8 ± 3	23.0
Nylon	Yes	50	83 ± 3.1	88 ± 2.0	95 ± 3.5	0.1
Dacron	No	50	3.1 ± 0.6	3.9 ± 0.8	6 ± 7	16.0
Dacron	Yes	50	21 ± 1.6	85 ± 1.0	88 ± 0.3	0.6
D/C	No	50	3.4 ± 0.5	3.8 ± 0.9	8.4 ± 0.9	6.0
D/C	Yes	50	62 ± 1.2	81 ± 0.7	76 ± 0.8	0.7
P-P	No	50	5.2 ± 0.5	5.3 ± 0.2	4.8 ± 1.7	15
P-P	Yes	50	63 ± 1.2	84 ± 1.0	82 ± 1.0	0.1
Cotton	No	300	11.7 ± 1.8	10.3 ± 1.7	12 ± 3.9	3
Cotton	Yes	300	69 ± 2.7	60 ± 2.4	47 ± 0.5	0.8
Nylon	No	300	0.4 ± 0.1	0.6 ± 0.2	6 ± 0.3	33
Nylon	Yes	300	43 ± 1.7	69 ± 1.2	91 ± 2.6	0.5
Dacron	No	300	2.4 ± 0.3	3.1 ± 0.4	4 ± 2.3	21
Dacron	Yes	300	22 ± 0.5	71 ± 1.5	84 ± 0.7	1.0
D/C	No	300	1.9 ± 0.2	2.4 ± 0.4	7 ± 0.6	13
D/C	Yes	300	44 ± 2.0	59 ± 1.3	68 ± 0.8	0.4
P-P	No	300	3.3 ± 0.3	3.9 ± 0.4	4 ± 0.4	9
P-P	Yes	300	46 ± 1.6	61 ± 1.3	66 ± 2.3	0.4

[a] Basis clay in wash water.
[b] No builders or surfactant.
[c] Built detergent with NEODOL 25–9, quadruplicate runs.
[d] Absolute standard deviation, one sigma.