Source of variation	Shake flask		Semicontinuous	
	Variance	Degrees of freedom	Variance	Degrees of freedom
Lab-to-lab	.1928	14	.2045	10
Run-to-run	.0585	66	.0425	39
Unit-to-unit	.0120	97	.0033	36
Total for single determination	.2633	31[a]	.2503	20[a]

[a] Harmonic mean.

Confidence and Tolerance Limits. Table II presents the means and limits obtained. The lower tolerance limit is that value above which 95.0% of the results of single determinations are expected to fall (*with* 95% *confidence*). For dodecene-1 derived LAS and ABS lot #3, the lower tolerance limits are derived from the individual variances since the variance of these materials was found to be significantly smaller and greater, respectively, than the variance for the other materials. The tolerance limits for the other materials are derived from a pooled variance weighted by the degrees of freedom for each surfactant.

Soil Redeposition Versus Deposition Tests in Evaluation of Laundry Detergents

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Abstract

Whiteness retention results obtained with a soil "deposition" type test, in which soil material as such is added to the detergent bath, are found to be in contradiction to those obtained with soil "redeposition" tests, in which clean and soiled cloth are washed together. A carbon soil deposition test shows polyvinyl alcohol (PVA) and polyvinylpyrrolidone (PVP) to be superior to sodium carboxymethyl cellulose (CMC), and a polyethylene glycol (PEG) equal to CMC in improving whiteness retention results with a built anionic detergent, with pronounced synergistic effects for PVA-CMC and PEG-CMC combination. In contrast, the redeposition tests, employing either carbon black or tagged clay soil, show only the CMC to be effective, the nonionic polymers being ineffective alone and in combinations with CMC. Further, in evaluating the effect of tripolyphosphate builder with an alkylbenzene sulfonate, the deposition and redeposition tests give quite contradictory results. The observed contradictions cast considerable doubt on the validity of the usual carbon soil deposition tests, and emphasize the need for further study of whiteness retention test methods.

Introduction

IN CONSIDERING the performance of a laundry detergent, we tend to think primarily in terms of its ability to remove soil. The reverse phenomenon of soil redeposition, however, can be equally important. It has been suggested that, in home laundering, poor performance of a detergent may be due more often to excessive soil redeposition, or poor whiteness retention, than to inadequate soil removal (1). The need for soil redeposition measurements in connection with laundry detergency evaluations has been generally recognized, and the literature on the subject is fairly extensive. The approaches to this problem, and test methods developed by various investigators, have been well covered in reviews and bibliographies (2–5).

Perhaps the obvious approach to a soil redeposition test is to simulate practice, washing clean cloth along with soiled, and determining soil redeposition on the clean cloth, usually by reflectance measurement. This is a true "redeposition" type test in that soil is washed from cloth and redeposited. In such a test, however, the amount of soil redeposited depends on the amount of available soil in the wash liquor, which in turn depends on the soil-removing ability of the detergent. This complicates the comparison of soil redeposition results for two detergents of widely different soil removal abilities. Further, in such tests simulating practice, the soil redeposited in one wash is likely to be too slight for accurate determinations. Time-consuming multiple-wash tests often are required in order to build up the redeposited soil so as to bring out differences among detergents. In order to bypass these complications, most detergency workers have turned to "deposition" type tests, in which the soil material is added as such to the detergent bath (generally as aqueous carbon black dispersion) and soil pick-up by clean cloth determined. This approach permits accurate control of the soil loading in the detergent bath, and if the total soil loading is high in comparison to that deposited, the free soil loading in the bath is always essentially constant. The heavy soil loading results in a high, readily measured soil deposition. Because of these experimental advantages, deposition-type tests generally have been preferred over redeposition types, and most published work has been based on the former. In the absence of contradictory evidence, it has been generally assumed that deposition and redeposition type measurements give essentially equivalent results, at least on a qualitative basis (4).

Along with others concerned with detergency testing, our laboratories developed a whiteness retention test based on carbon soil deposition (6) and employed it for a number of years for basic studies and routine evaluations. Concurrently, we developed detergency test methods employing various radioactive tagged soils (7,8). With the use of these soils, it was found to be convenient to determine both soil removal and redeposition in a single test. The extreme sensitivity of the radiotracer method permitted accurate measurements of redeposited soil after a single wash. Also, it was found to be feasible to correct soil redeposition results in such a way as to compensate for differences in soil removal, permitting what we consider to be reasonably valid whiteness retention comparisons at different soil removal levels.

During the course of many evaluations with a tagged clay soil, it was observed that whiteness retention values often contradicted those given by the

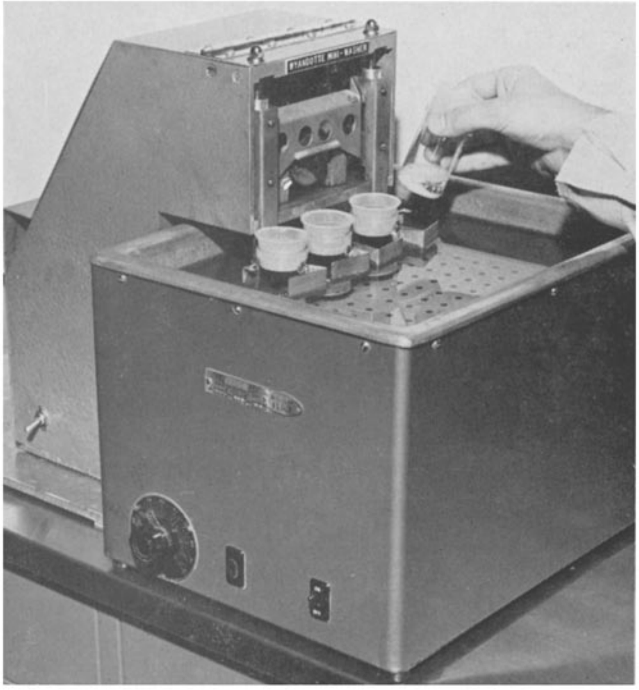

FIG. 1. Washing machine used in redeposition tests.

carbon soil deposition test. These contradictions were especially apparent when certain polymeric materials were evaluated as whiteness retention additives. Contradictions also were apparent in tests showing the effects of alkaline builders on whiteness retention. It was realized, of course, that the observed contradictions might be due to the different soils, rather than the different test methods. Consequently, as a check, data were obtained also with a carbon soil redeposition test, using cloth soiled with the same carbon as that used in the deposition test. In all cases in which such comparisons have been made, the carbon soil redeposition test results have tended to verify the tagged clay soil redeposition results, contradicting the carbon soil deposition test results. The purpose of this report is to present a few examples of these contradictions, and to raise the question as to whether the soil deposition type test necessarily yields basically valid whiteness retention evaluations.

Test Procedures and Materials

In all test procedures, the fabric was bleached, unfinished Indian Head cotton muslin. Demineralized water was used for preparation of solutions and for rinsing. All washing was performed at 60C (140F), with detergents at a total concentration of 0.25% (w/v).

Tagged Clay Soil Redeposition

Preparation of the tagged clay soil has been described in detail in a previous publication (8). Briefly, tagging of the montmorillonite type clay is done by exchange through treatment with radiocalcium chloride solution, and the tag fixed by firing to 1000C. The tagged clay is ground with water and washed to remove any loose calcium-45. After drying, it is then ground for a prolonged period with base stock lubricating oil. The resulting dispersion is diluted with dispersol and applied to cloth discs by pipet. The dispersol is allowed to evaporate before the soil is used. Soiling level is on the order of 0.5 mg of clay per square inch.

The soil as prepared is high in oil (10 parts oil to 1 part clay), which we consider to be desirable for removal measurements. When a nonoily soil is desired, batches of soiled discs are extracted with chloroform (this removes a negligible amount of tagged clay). To eliminate any possible effects of the oil, nonoily clay soil was used for the present work. Very similar results have been obtained with oily clay soil.

Washing was done with the Mini-Washer shown in Figure 1, a machine designed primarily for use with radioactive soils. The four small glass wash vessels are shaken vertically in a constant temperature bath, normally at 900 cycles/min with a ¼ in. stroke. Two cloth discs, one soiled and one clean, are washed in each vessel in 7 ml of solution along with 10 stainless steel balls. With 5-min wash periods, soil removal level has been found to be comparable to that obtained with a home washing machine using the normal wash cycle. Solution to cloth ratio is about 20:1, which is fairly close to ratios employed in practice. Washed discs were hand-rinsed in three portions of water.

Radioactivity measurements were performed with automatic counting equipment, employing an end-window gas-flow counter. For counting, cloth discs were mounted on cardboard discs coated with rubber cement. The aluminum sample holders supplied with the Nuclear-Chicago Model C110B automatic sample changer have been modified to accept 1.5 in. discs.

From the percent soil removal, as determined from initial and final counts on each soiled disc, the soil loading of the detergent bath was determined. Soil redeposition, as indicated by counts per minute on the initially clean disc, was corrected to an arbitary standard soil level in the solution, assuming redeposition to be a linear function of soil in the bath. From the corrected soil redeposition values, whiteness retention values (inversely proportional to soil redeposition) were calculated as percent of a reference detergent. Details of the calculation and experimental justification for this method of correcting soil redeposition for differences in soil removal by different detergents have been given in a previous publication (8).

Carbon Soil Redeposition

The Mini-Washer was employed in these tests, and the procedure was the same as that with tagged clay soil, except that the soil discs were cut from conventional carbon-soiled swatches. Also, two 10 min washes were used, with fresh soiled discs each time, in order to build up the soil redeposition level. The soiled cloth was the same as that used in our carbon soil removal test (6), prepared by a padding procedure using an aqueous dispersion of Aquablak B. The soil loading is relatively heavy, reflectance of the soiled cloth being about 12%.

Reflectance measurements (on the initially clean discs) were made with a Photovolt model 660 meter, using a green filter and four thicknesses of fabric. In the tests involving the addition of small percentages of whiteness retention promoters to the same basic detergent composition, soil removals did not vary significantly, and no corrections were required for differences in soil loading in the detergent baths. Whiteness retentions as percent of reference detergent were calculated from reflectances as read. In the measurements with varying ratios of surfactant and builder, removals varied considerably and apparent whiteness retentions were not comparable. In this case, corrections were made on the assumption that loss in whiteness due to redeposited soil would be proportional to soil loading in the bath. Soil loading was estimated from transmittancy measurements on the used detergent solutions, and measured losses in whiteness adjusted to a reference soil level by multiplying by the ratio of transmittancies. The corrected losses in whiteness were converted to reflectance values, and percent whiteness retentions calculated as in the other tests. While the validity of this method of correction for differences in soil removal has not been established experimentally, it represents an improvement over the use of uncorrected reflectances, and, we believe, serves for qualitative comparisons involving large differences.

Carbon Soil Deposition

The procedure employed in these tests was a modification of one described previously (6), the principal modification being the use of a Terg-O-Tometer instead of a Launderometer. Detergent solutions were prepared with diluted suspension of Aquablak B so as to contain 0.5 g of carbon black per liter. Ten clean Indian Head swatches (2.5 × 3.5 in.) were agitated for 10 min at 60 cycles/min in one liter of carbon-loaded detergent solution, rinsed for 5 min at room temperature, and oven-dried. Reflectances were measured with a Hunter reflectometer with green filter, using ten thicknesses of fabric. Results were stated as percentage of the reference detergent by taking the ratio of reflectances times 100.

For comparison, a few carbon deposition type tests were run with the Mini-Washer, although this is not one of our standardized procedures. In this case, a reduced amount of Aquablak B suspension was used so as to give the equivalent of 0.1 g of carbon per liter of detergent solution. Two clean Indian Head discs were washed for 10 min in 7 ml of carbon-loaded detergent solution, and rinsed in three portions of water at room temperature. Reflectances were measured with the Photovolt model 660 meter, using a green filter and four thicknesses of fabric.

Detergent Test Materials

The "built ABS" detergent used in this work was one of our standard reference compositions, intended to represent a typical household product minus whiteness retention additives. Composition is as follows:

	Parts by Weight
Alkylbenzene sulfonate (ABS), 100% active basis	20
Sodium tripolyphosphate (STP)	45
Soda ash	3
Sodium metasilicate, anhydrous basis	5
Sodium sulfate	20
Water	6

The sodium carboxymethyl cellulose (CMC) was Carbose D (Wyandotte Chemicals Corporation); the polyvinyl alcohol (PVA) was Elvanol grade 51-05 (E. I. duPont de Nemours & Company); the polyvinylpyrrolidone (PVP) was Antara K30 (General Aniline & Film Corporation); and the polyethylene glycol (PEG) was Carbowax 6000 (Union Carbide Corporation).

Test Results and Discussion

Whiteness Retention Additives

Various investigators (9,10) have demonstrated that a number of polymeric materials are equal or superior to CMC when employed as whitness retention additives, and some exhibit distinct synergistic effects when employed in combination with CMC. So far as we have been able to determine, all these observations have been based on deposition type tests of one kind or another. From among many additive types that have been proposed, we have selected three well-known examples for comparison of results by the deposition and redeposition type tests. In all tests, total detergent concentration was constant at 0.25%, and total additive concentration was held constant at 1%, (active agent basis) of the detergent formulation. Whiteness retention values for all three tests have been stated as percent of the detergent (built ABS) without additive.

In Figure 2 are shown whiteness retention results for CMC, PVA, and varying combinations of the two. The carbon deposition test, in agreement with findings of other investigators, shows PVA alone to be distinctly more effective than CMC, and combinations of the two exhibit pronounced synergism, with a 50:50 combination of CMC and PVA giving very superior results. In complete contrast, both carbon and clay redeposition tests show PVA alone to have a some-

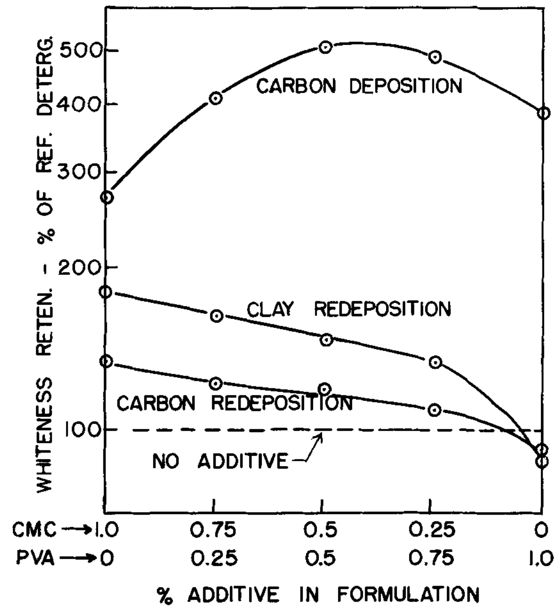

FIG. 2. Comparison of test results, CMC and PVA with built alkylbenzene sulfonate detergent.

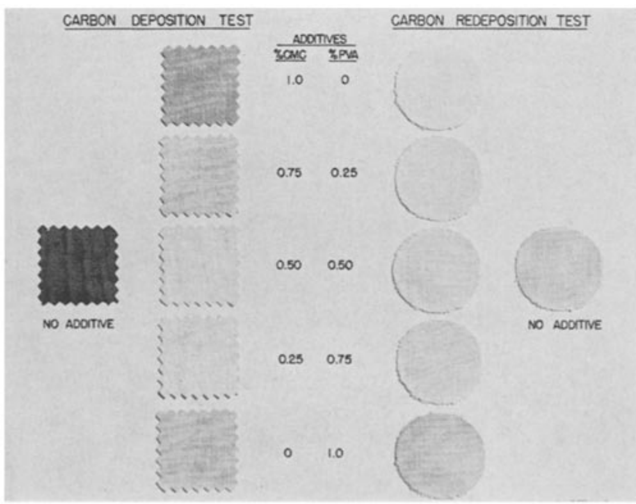

FIG. 3. Cotton test swatches, carbon soil deposition and redeposition tests.

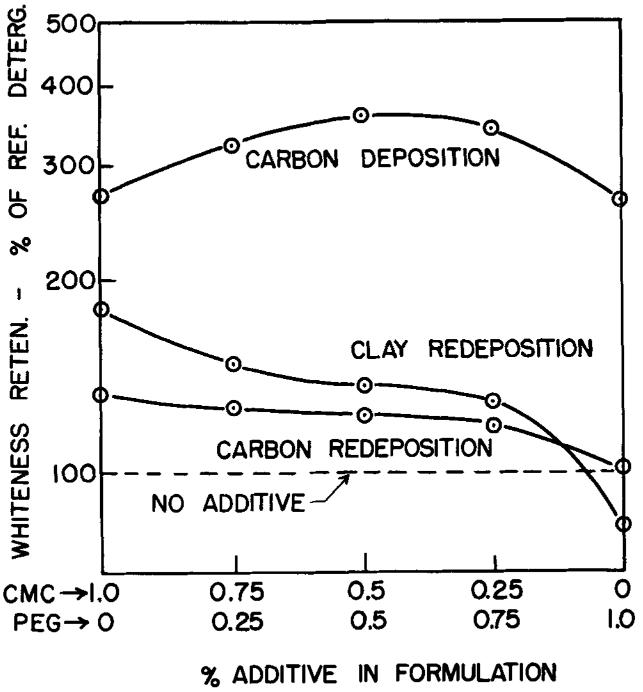

FIG. 4. Comparison of test results, CMC and PEG with built alkylbenzene sulfonate detergent.

what detrimental effect on whiteness retention, with no indication of a beneficial effect in combination with CMC. The two redeposition tests agree extremely well considering the difference in soils and methods of measurement. As an illustration of what the plotted data represent in terms of appearance, a photograph of the carbon soil test swatches is shown in Figure 3 (the deposition test swatches were trimmed to a smaller size to provide a better photograph).

Test results for CMC and polyethylene glycol (PEG) are given in Figure 4. In this case, the carbon soil deposition test would indicate that CMC and PEG used alone are about equivalent, and again the two show synergistic action, with superior results for a 50:50 combination. These indications again are contradicted by results of the two redeposition type tests, which are in good agreement with each other qualitatively. They indicate that substitution of PEG for CMC is detrimental, while PEG alone as an additive is ineffective by the carbon redeposition test and detrimental by the tagged clay redeposition test.

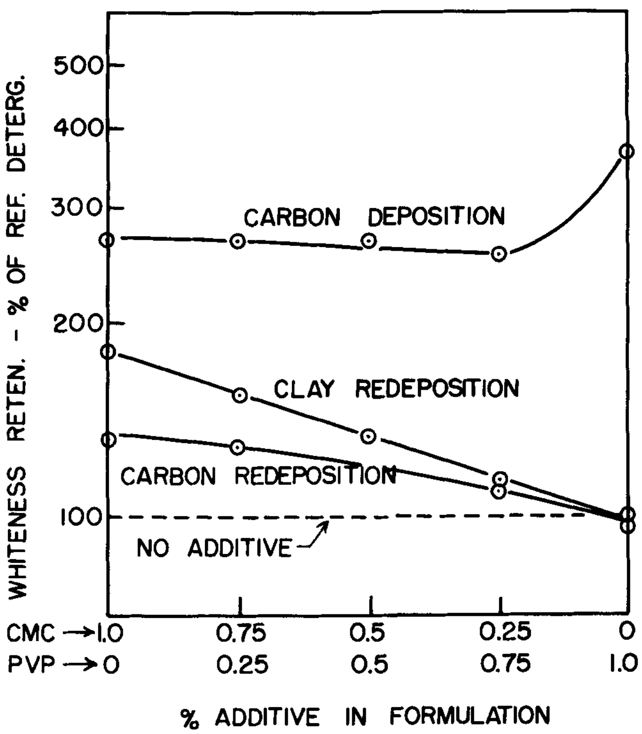

FIG. 5. Comparison of test results, CMC and PVP with built alkylbenzene sulfonate detergent.

In Figure 5, the carbon soil deposition data show PVP to be superior to CMC and about equal to PVA when used alone as an additive; however, there is no indication of synergism with CMC. The two redeposition tests, again in good agreement with each other, show PVP to be ineffective when used alone or in combination with CMC.

Admittedly, the test conditions employed in the deposition and redeposition tests were quite different in terms of soil loading, solution to cloth ratio, and nature of agitation. It seemed unlikely that these factors could account for the observed contradictions. However, in order to minimize these effects insofar as possible, a few carbon soil deposition tests were run with the Mini-Washer, with test conditions as nearly as feasible the same as those employed in the redeposition tests. Carbon loading in the detergent solution was reduced to one-fifth that used in the regular deposition test, which resulted in a reflectance level (for built ABS without additive) about the same as that obtained in the carbon soil redeposition test. Results for CMC and PVA by this test, in comparison with those by the regular (Terg-O-Tometer) carbon deposition test are compared in the table below.

Comparison of Carbon Soil Deposition Tests

Additive to Built ABS		Whiteness retention As % of built ABS without additive	
% CMC	% PVA	Terg-O-Tometer	Mini-Washer
1.0	0	270	120
0.75	0.25	410	151
0.50	0.50	510	153
0.25	0.75	487	147
0	1.0	381	139

Although spread in results with the Mini-Washer was much reduced in comparison with those with the Terg-O-Tometer, due presumably to the much reduced carbon loading and difference in washing actions, results with the two procedures were qualitatively similar, both showing PVA to be more effective than CMC, with significant synergism between the two.

Effect of Alkaline Builders

Information in the literature regarding the effects of alkaline builders on soil redeposition has been quite contradictory. This has been due to differences in test methods, soil materials, surfactants involved, water hardness, and other factors. It is a commonly held belief now, however, that, in soft water, all the commonly used alkaline builders, including the phosphates and silicates, tend to increase soil redeposition (11). This belief appears to be based almost entirely on the results of deposition type tests.

We have observed, however, that even in distilled water, redeposition type tests may indicate that builders have beneficial effects on whiteness retention, while deposition tests indicate detrimental effects. An example of such a contradiction is given in Figure 6, showing the effect of sodium tripolyphosphate

(STP) in combination with an alkylbenzene sulfonate (ABS). The carbon deposition test shows the pronounced adverse effect of STP on whiteness retention as commonly reported in the literature. The two redeposition tests, however, indicate that substitution of STP for part of the ABS results in distinctly improved whiteness retention. We believe that the redeposition test results are more in accord with practical observations—certainly a 50:50 combination of a commercial ABS and STP will give better overall wash results than the ABS without alkaline builder, which would not be the case if soil redeposition for the combination were as severe as indicated by the deposition test results.

Our soil redeposition studies with various soil types and detergent systems indicate that builders may have either beneficial or adverse effects on whiteness retention, depending on soil type, builders, surfactant type, water hardness and other factors. Generalized statements without the benefit of numerous qualifications probably have little practical significance.

General Discussion

The mechanisms involved in soil redeposition and the functioning of antiredeposition agents and other detergent components undoubtedly are complex and not yet well understood. On the basis of the present limited work, we are not in a position to suggest with any great confidence an explanation for the rather dramatic contradictions in the results of soil deposition and redeposition type tests as illustrated here. There are several apparent factors that may be involved. One of these could be the differing modes of operation of different types of polymeric materials. It is fairly generally accepted now that the action of CMC is due largely to its adsorption by the fabric, and perhaps also by the soil, resulting in a decreased attraction between the two. Recent studies with radiotracers in particular tend to substantiate this view (12,13). Nonionic polymers such as PVA, on the other hand, may act primarily at the soil-solution interface (14). Stillo and Kolat (15) propose that the function of nonionic additives is steric in nature. These authors also point out that valid evaluation of the effectiveness of antiredeposition agents is quite difficult, and that the unrealistic conditions employed in carbon deposition tests may result in an exaggeration of the effect of an antiredeposition agent whose major action is on the soil. Unfortunately, the best published studies on soil redeposition and effects of additives have been based on carbon soil deposition measurements. We believe that some of these earlier data and resulting theories should be reconsidered on the basis of more realistic soil redeposition measurements.

In considering possible explanations for the contradictions in results by the two types of tests, we had thought that a time factor might be involved, due to the differing dynamic conditions. In the redeposition test, in which soiled and clean cloth are washed together, soil removal and redeposition might occur during a very brief time interval, not providing sufficient time for nonionic additives to be effective through some protective colloid or soil stabilizing action. On the other hand, in a deposition type test in which soil is added to the detergent bath containing nonionic additive, there might be sufficient time for such soil stabilizing action to take place. We have found, however, in some preliminary tests, that when a detergent solution is preloaded with soil by

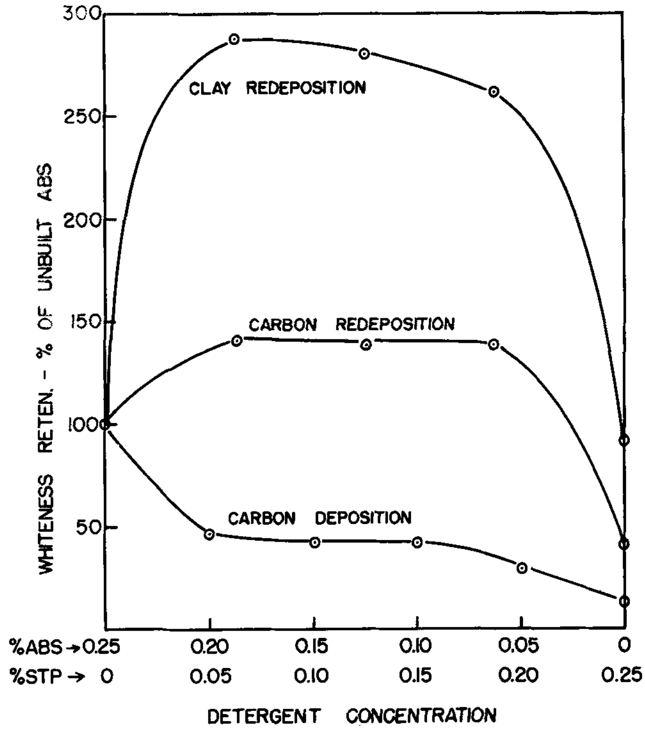

FIG. 6. Comparison of test results, effect of sodium tripolyphosphate with alkylbenzene sulfonate.

washing cloth soiled with either carbon or clay and then used for washing clean cloth alone (as in a deposition test), results are qualitatively the same as in tests in which soiled and clean cloth are washed together. This seems to eliminate as an explanation the differences in dynamic conditions or time factors.

Our results so far indicate that there is a difference in the nature or behavior of soil washed from cloth, and soil added directly to the detergent bath, such that certain nonionic polymers are effective in reducing the deposition of the latter, but ineffective in reducing redeposition of the former. This difference might relate to particle size distribution, degree of agglomeration, or materials adsorbed on the soil particles in the two cases. Further study of these and other variables is needed, and it would appear that a fresh approach to the problem of whiteness retention evaluation is indicated, employing test methods more realistic than the usual carbon soil deposition measurements.

ACKNOWLEDGEMENT

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