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Evaluation of Hand Dishwashing Formulations[1]

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THERE IS CURRENTLY much interest in the development of hand dishwashing formulations. A prerequisite of any development program is a method of evaluation. This paper is concerned with evaluation of soil removal and sudsing characteristics of hand dishwashing detergent formulations. Its purpose is to present a practical method of evaluating these characteristics and to illustrate the use of this method in the formulation of hand dishwashing detergents.

The object of dishwashing, and therefore the detergents used in dishwashing, is to get dishes clean. In formulating a hand dishwashing detergent to aid in accomplishing this objective, there are many well recognized considerations besides the primary one of removing soil. One of the most important of these secondary characteristics is sudsing. While the functional value of suds varies widely with different types of detergents, the psychological importance in the minds of the general public is an established factor which it is not practical to ignore.

Evaluation of foaming properties too often involves methods and conditions not closely related to actual use situations. While such methods often yield interesting and sometimes useful information, it is very difficult or impossible to interpret this information in terms of over-all field performance to be expected of a detergent.

Other properties of detergent chemicals which are known to have some relationship to performance characteristics are surface tension, interfacial tension, adsorption, micelle formation, spreading coefficient, film strength, pH, molecular structure, ionization, ionic character, and solubility of reaction products. From a practical point of view however it is very difficult to assign the relative importance of each of these properties to the actual performance obtained. Therefore ultimate evaluation should be made by a test method which measures the cumulative effect of all these properties.

In choosing an evaluation method, uniform procedures for soiling the test surface, curing the soil, washing the test pieces, and measurement of the properties being tested are essential. We believe that these procedures, as well as selection of test surfaces, soils, water hardness, and temperatures, must be related, as closely as practical, to use conditions if the test results are to be of maximum significance.

The method to be presented involves actual manual washing of soiled china dinner plates under uniform conditions. Evaluation of the test detergent is based on the number of plates which can be washed before the solution is exhausted to arbitrary, predetermined limits. These limits are based on the ability of the solution to remove and retain soil and to maintain a foam layer.

The findings presented in this paper touch briefly on several phases of detergent formulation evaluation. It is our intent only to illustrate the application of this method to the development of detergent formulations. The results themselves are of significance only when interpreted within the confines of the particular test conditions used.

Materials

The following materials were used in carrying out the test:

1. restaurant quality china, 9-in. dinner plates free from scratches and other defects.
2. fatty soil with titer of 42.2°C. This was prepared by mixing 90 parts by weight of Swift's edible grade tallow with 10 parts of Mazola corn oil and 0.5 parts fluorescent dye. The fluorescent dye tracer used is Calcoflour RWP obtained from Calco Division, American Cyanamid Company, Bound Brook, N. J.
3. ultraviolet ray lamp and viewing box.
4. rubber-covered or stainless steel 1-in. mesh wire screen to lay between dishes.
5. round dishpan 10 in. in diameter at base.
6. ring stand and funnel arrangement (see Photo 1)—funnel with 7/16-in. inside diameter, straight, short stem with 650-milliliter capacity (Corning No. 6120, Code No. 400380) and placed 26 in. above bottom of dishpan to generate foam.
7. weighted tampico utility brush (Utility Brush No. 509, Flour City Brush Company, 1501 Fourth avenue S., Minneapolis, Minn.) with lead weight to total 3¾ lbs. Handle was cut off the brush to make it more convenient to use.
8. dish rack.
9. clock with sweep second hand.
10. water bath to maintain a temperature of 70°C
11. beaker, pipettes, thermometers, etc.

Method

Preparation of test pieces. The test plates were washed thoroughly to remove all visible soil, using a domestic dishwashing machine, alkaline detergent sold under the name "Electrasol" (manufactured by Economics Laboratory Inc., St. Paul, Minn.), and hot water, and were dried in an oven at a temperature of 80 to 85°C. (A domestic dishwashing machine equipped with a heating element was found to be suitable for washing and drying the test pieces.)

Soiling test pieces. The plates were soiled while still warm (80°C.) to facilitate even distribution of soil. Five milliliters of the fat soil (maintained at

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70°C. in a constant temperature bath) were added to each plate and distributed evenly over the entire depressed center of the plates by a rolling motion of the plate. The soiled plates were placed in a special rack to keep the plates level and separated while they "cured" at room temperature (20 to 25°C.) for 18 to 24 hrs. before use.

Preparation of washing solution. The washing solution was prepared by spreading a weighed amount of the detergent to be tested on the bottom of the dishpan, leaving the weighing dish in the bottom of the pan. (Alternatively one could dissolve the weighed sample in 500 ml. of water at 50°C.) To dissolve detergent and generate foam 3 liters of water (50° ± ½°C.) were poured through a funnel supported by a ring stand, allowing stream to strike the bottom of the pan near its outer edge. The dishpan was rotated through 2 complete 360° turns while adding the water. (No attempt was made to maintain water temperature in the dishpan after the test run was started.) Without delay the weighing dish was removed, and the soiled dishes were washed by the method described below. Well water of 216 to 220 p.p.m. hardness, as $CaCO_3$, was used for washing and rinsing throughout entire studies.

Washing the test pieces. At zero time a soiled plate was placed, right side up, in the dishpan containing the washing solution.

At 55 seconds after zero time a second soiled plate was placed beneath the first one, placing a stiff stainless steel or rubber-covered 1-in. mesh screen between them to keep the two test pieces from touching each other.

At 60 seconds after zero time, with the first plate completely immersed in the washing solution, the plate was washed by brushing the front of the plate 5 times with a rotary motion in one direction and 5 times in the reverse direction. The plate was inverted, and this brushing procedure repeated on the back side. In order to provide uniform brushing action a weighted utility brush was used; no extra force was used other than to provide the rotary motion. The entire brushing procedure was timed so that the operation was completed in 22 to 25 seconds, thus allowing about 1 second for each complete rotation of the brush. The brush was presoaked in 60°C. tap water for 30 minutes before using.

The test plate was then rinsed for a total of 5 seconds under cold running water and placed in a dish rack to drain and dry. Cold water rather than hot was used for rinsing in order to minimize the effect of rinsing and give a more specific measure of detergency.

At 1 minute and 55 seconds after zero time the third test plate was placed under the second one.

At 2 minutes after zero time, the washing, rinsing, and draining of the second plate was started, following the same procedure as for the first. Soaking, washing, rinsing, and draining of test plates on the same time schedule were continued until the endpoints for suds and detergency were reached.

Judging the endpoints. Two endpoints were observed and recorded. The "suds endpoint" is arbitrarily chosen as the point at which a thin layer of suds is visible over approximately one-half the surface of the solution. The number of plates washed before this condition is reached is recorded as the suds endpoint.

The "detergency endpoint" was determined by examining and grading the washed test plates in an ultraviolet light box (see Photo 1). An arbitrary grading system was used, with a scale from (—) to (++++) representing no soil to various increasing degrees of soil residue. The fluorescent tracer in the soil made the detection of traces of soil more easily discernible. The grading system is based on the following scale: the symbol (—) represents a clean plate; (+) denotes plates having traces of soil detectable under ultraviolet light but not detectable under ordinary light; (++) denotes definite soil residue easily detectable under ultraviolet but discernible only with difficulty under ordinary light, in other words, satisfactory under ordinary light; (+++) denotes plates which have heavy residue under ultraviolet light and residue which can be detected without difficulty in ordinary light; (++++) denotes plates which have very heavy residue under ultraviolet light and which have objectionable residue under ordinary light.

The detergency endpoint is the total number of plates with a rating of (++), (+), and (—). Occasionally a "skip" may occur, *i.e.*, a plate with a (+++) rating interspersed between two (++) plates. Regardless of this occurrence the total number of plates with (++) or better is counted and recorded as the endpoint.

Redeposition of soil on plates is easily detected under the ultraviolet light since redeposited soil will show up as a film or islands of fat on areas which originally had no soil (see Photo 2). The ability of a detergent to prevent redeposition is an important formulation consideration and was taken into account in the grading of the washed plates.

Discussion of Method

Only one variety of soil was used in the data being reported. Preliminary studies made on a variety of soils indicated that the fatty constituents were chiefly responsible for exhausting the two properties of detergent solutions under investigation, namely, detergency and foaming. Even among fatty soils however there are significant differences in deleterious effect on the detergent solution. Our choice of this particular soil is therefore an arbitrary one and definitely limits the interpretation which can be put upon the results. For some purposes the use of other fats or soils may be desirable.

The washing operation was carried out in a manner closely approximating that commonly used in hand dishwashing although certain minor changes were made to facilitate standardization of the procedure.

The suds endpoint used was chosen with two considerations in mind. First, it was felt that it represents a condition where the ordinary user would consider the solution exhausted. Second, it was in a region of rapidly changing slope on the suds deterioration curve. Therefore it could be determined with a greater degree of sensitivity than other suds levels.

Three methods of estimating the soil residue on washed plates were investigated: visual observation under ordinary light, visual observation of fluorescent soil tracer under ultraviolet light, and radioautographs of radioactive isotope-tagged soil. Relative evaluation of different formulations was essentially the same for these three methods. The sensitivity to soil residue is quite different however with radioautograph being most sensitive and visual observation under ordinary light least sensitive. The ultraviolet light observation technique was used in compiling the data because of its relatively high degree of sensitivity and ease of use.

(For tests in which radioautographs were made, a small portion of the tallow in the test soil was replaced by iodinated tallow formed by reaction of tallow with I^{131}. This we found to be a very satisfactory way of tagging fatty soils without significantly altering their properties as soil for comparative studies.)

Results

Table I, showing the reliability of results, is based on nine replicate runs. While this is a small number of tests on which to base a statistical evaluation of the method, it does indicate good reproducibility by a single operator. Several different laboratories, using a method very similar to this, were able to classify four liquid detergents in the same order although the exact values obtained were not identical. The data shown in Table I suggest that duplicate tests will probably establish the difference between a poor, mediocre, and good detergent though a larger number of replicate runs will be required to establish finer differences.

TABLE I
Reproducibility of Results
(for a single operator)

Test	Detergency Endpoint		Suds Endpoint	
	No. plates washed	Deviation from mean	No. plates washed	Deviation from mean
1	18	−0.3	19	−1.7
2	19	0.7	21	0.3
3	20	1.7	22	1.3
4	20	1.7	20	−0.7
5	17	−0.7	17	−3.7
6	18	−0.3	20	−0.7
7	19	0.7	21	0.3
8	16	−2.3	22	1.3
9	18	−0.3	24	3.3
	18.3	Arithmetic Mean	20.7	
	1.0	Average Deviation	1.5	
	1.3	Standard Deviation	2.0	
	17.4–19.2	— 95% Confidence Interval —	19.3–22.1	

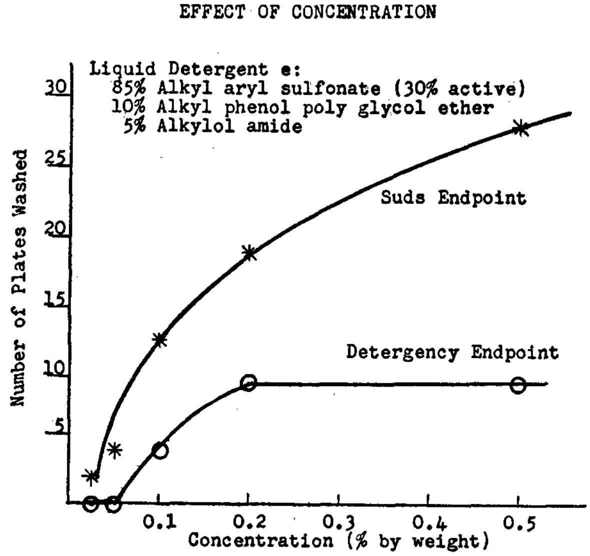

FIG. 1.

The effect of detergent concentration on the suds and detergency endpoints for one liquid detergent formulation is illustrated in Figure 1. The leveling-off of the detergency curve in this case was caused by redeposition of soil from the fat layer on the surface of the solution, as evidenced by appearance of soil on the originally unsoiled rim of the plates. All liquid detergent formulations tested exhibited a higher suds endpoint than detergency endpoint. This point is further illustrated by Figures 2 and 3. Note in Figure 1 that this difference in endpoints tends to become greater at higher concentrations.

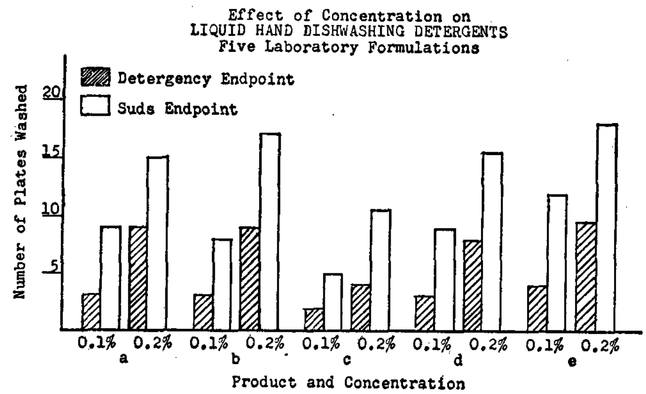

FIG. 2.

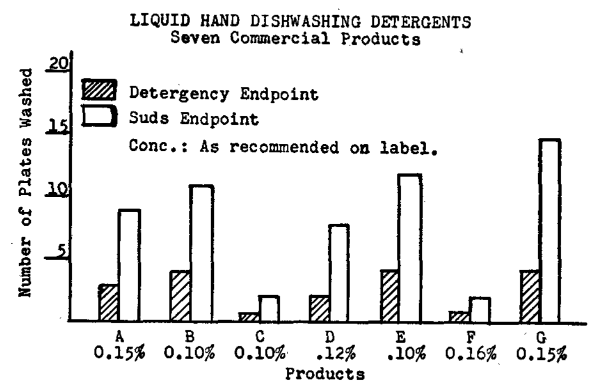

FIG. 3.

Ideally the detergency of a formula should slightly exceed its suds stability at the use concentration if the suds are to be used as an indication of solution exhaustion. Solid detergent formulations seem to approach more nearly this ideal situation than do liquid formulations.

Six commercial solid (powdered, flaked, and beaded) detergent formulations were tested at 0.75% concentration. (This higher evaluation concentration was used because it corresponds closely to recommended use concentration for these detergents and because it gives results in the same range as liquid detergents at 0.2% concentration.) Results are shown in Figure 4. These solid detergent formulations demonstrated a better balance between detergency and suds endpoints than did the liquids.

This difference in characteristics between the two types of products is undoubtedly due in part to the absence of alkylolamides in most of the dry formulations and the absence of significant amounts of inorganic builders in the liquid detergents. The

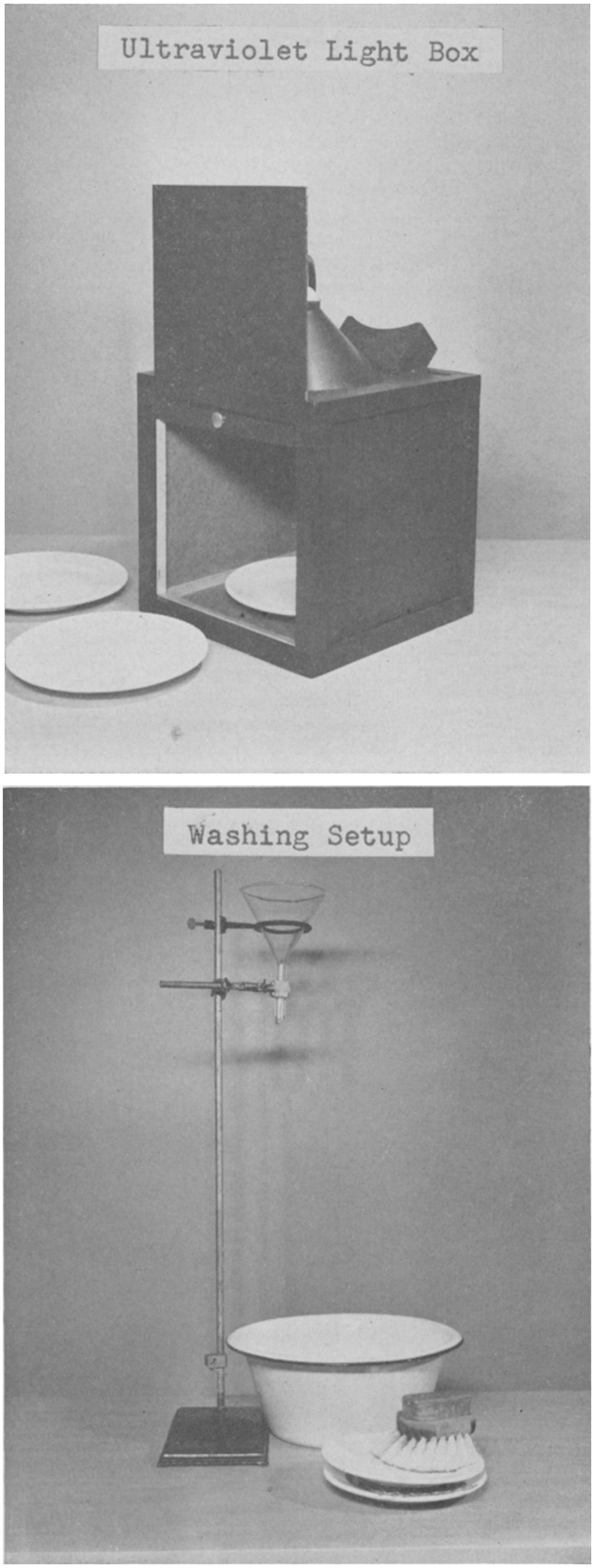

PHOTO 1.

alkylolamides, often referred to as foam stabilizers or foam boosters, are chiefly responsible for the better foaming characteristics of many liquid detergents.

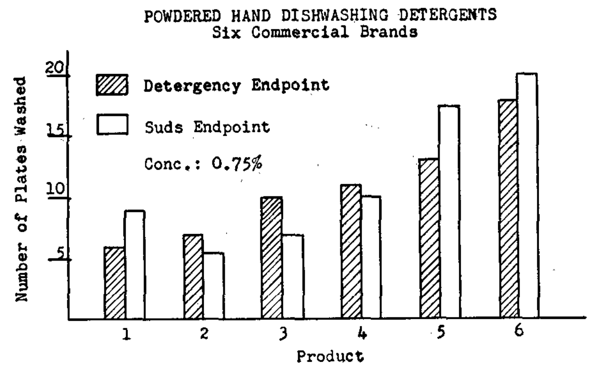

FIG. 4.

Differences in the performance of the commercial products tested can be attributed in part to differences in active organic content and in part to other formulation variations. Test concentrations shown are based on the products as sold and not on the active detergent content.

The economy resulting from the synergistic effect of three commonly used liquid detergent ingredients is presented in Table II. Although the alkylolamide is superior to the three-component formulation on a weight basis, the formulation is roughly three times as efficient on a use-cost basis. Relative costs in Table II are based on an index value of 1 for the formulation. Two values are calculated, using the approximate limits of the raw-material costs range.

An indication of the sensitivity to formulation existing in a three-component system is given in Table III. By varying the proportions of any of the ingredients in amounts totaling only 5% of the composi-

TABLE II
Synergism in Liquid Dishwashing Detergent Formulations

Material tested [a] and (¢/lb. cost)	No. plates washed to reach endpoints		Relative cost [b] per plate washed at prices shown
	Detergency	Suds	
A (7–12¢)	2	8	2.9 – 3.5
B (26–30¢)	6	8	3.6 – 2.9
C (44–48¢)	12	>18	3.1 – 2.3
I (10.75–15.6¢)	9	18	1 – 1

[a] Each test at 0.2% concentration.
[b] Relative cost based on detergency endpoint.
A = 30% Active alkyl aryl sulfonate slurry.
B = 99% Active alkyl phenol poly glycol ether.
C = 99% Active alkylol amide.
I = Mixture of 85% A, 10% B, 5% C.

TABLE III
Effect of Formula Variations on Performance and Relative Cost

Formula tested [a] and (¢/lb. cost)	No. plates washed to reach endpoints		Relative cost [b] per plate washed at prices shown
	Detergency	Suds	
I (10.75–15.6¢) 85% A, 10% B, 5% C	4	9	1 – 1
II (11.65–16.5¢) 85% A, 5% B, 10% C	2.5	>8	1.7 – 1.7
III (9.8–14.7¢) 90% A, 5% B, 5% C	2	>7	1.8 – 1.9

[a] Each test at 0.1% concentration.
[b] Relative cost based on detergency endpoint.
A = 30% Active alkyl aryl sulfonate slurry (7–12¢/lb.).
B = 99% Active alkyl phenol poly glycol ether (26–30¢/lb.).
C = 99% Active alkylol amide (44–48¢/lb.).

tion, relative costs are changed to the extent of 70% to 90%.

Tables IV, V, and VI illustrate the effects that different materials having the same general chemical structure can have on a given formulation. All of the alkyl aryl sulfonates used in compiling the data shown in Table IV were commercial products of the so-called sodium dodecyl benzene sulfonate type sold for detergent purposes. The alkyl phenol polyethylene glycol ethers tested were also represented commercially as being equivalent, but they gave significant differences in performance of the formulation. In this particular formulation, different commercial alkylolamides also gave different results, as is shown in Table VI.

It can be readily seen from the foregoing data that investigation of the formulation possibilities, even in a given three-component system, are very extensive and have been only touched upon in this paper. We believe that the method developed does facilitate a systematic evaluation of these possibilities and can be of assistance in finding optimum combinations of detergent materials.

TABLE IV
Alkyl Aryl Sulfonate Surfactants from Different Sources
Effect on Performance in Same Formula [a]

Alkyl aryl sulfonate	Number of plates washed to reach endpoints	
	Detergency	Suds
1a	2	8
1b	2	8
1c	4	9
2a	2	6
2b	2	6

[a] Formula used:
85% Alkyl aryl sulfonate (30% active).
10% Alkyl phenol poly glycol ether (99% active).
5% Alkylol amide (99% active).
Each test at 0.1% concentration.

TABLE V
Poly Ethylene Glycol Nonionic Surfactants from Different Sources
Effect on Performance in Same Formula [a]

Nonionic	Number of plates washed to reach endpoints	
	Detergency	Suds
8	4	11
9	2	9
6b	3	11
10	3	>8
7b	2	8
11	4	9

[a] Formula used:
85% Alkyl aryl sulfonate (30% active).
10% Alkyl phenol poly glycol ether (99% active).
5% Alkylol amide (99% active).
Each test at 0.1% concentration.

TABLE VI
Alkylol Amide Surfactants from Different Sources
Effect on Performance in Same Formula [a]

Alkylol amide	Number of plates washed to reach endpoints	
	Detergency	Suds
3	9	15
4	7	17
5	3	11
6a	8	16
7a	9	18

[a] Formula used:
85% Alkyl aryl sulfonate (30% active).
10% Alkyl phenol poly glycol ether (99% active).
5% Alkylol amide (99% active).
Each test at 0.2% concentration.

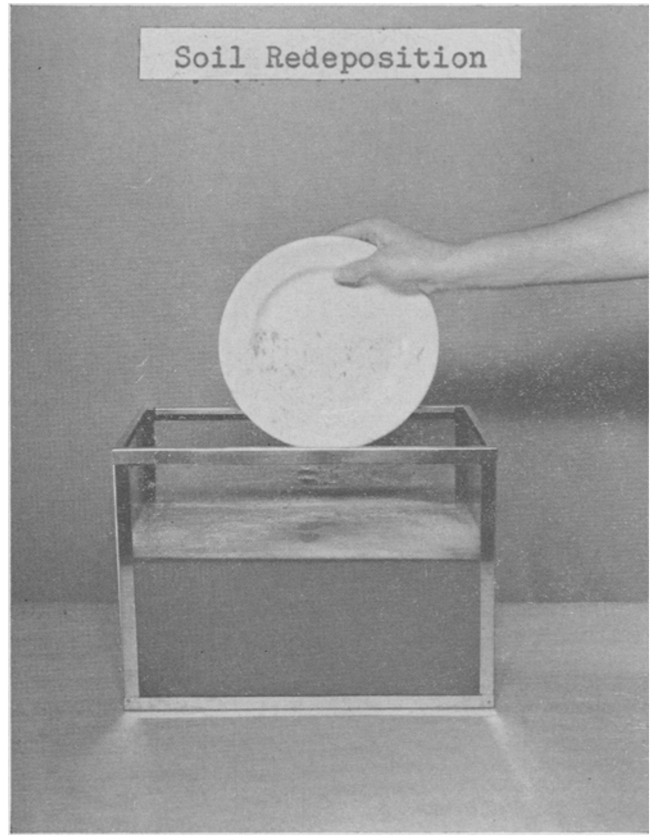

PHOTO 2.

Summary

The primary objective of a hand dishwashing detergent is to assist in getting dishes clean. Of the many secondary considerations, foaming is one of the most important.

A method closely simulating actual use-conditions was developed to evaluate hand dishwashing formulations on the basis of soil residue left on the dishes and stability of foam in the dishpan. Endpoints for suds and detergency were selected to represent what would ordinarily be considered the limit of satisfactory dishwashing conditions. Observation of the suds endpoint is made visually. Detection of the detergency endpoint is aided by the use of a fluorescent dye tracer in the soil and an ultraviolet light viewing box.

This method was then used to study several proprietary and experimental detergent formulations. The suds endpoint for the liquid detergents studied was invariably much higher than the detergency endpoint. This tendency appears to increase with solution concentration. The solid detergents tested exhibited a more balanced relationship between these two characteristics.

A three-component system consisting of alkyl aryl sulfonate, alkyl phenol polyethylene glycol ether, and alkylolamide was studied. The economic synergism of these components is demonstrated, and differences resulting from formulation changes and sources of materials are shown.

It is believed that the method, with appropriate modifications, is useful for evaluation and development of hand dishwashing detergents.

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