# Soil Removal by Dishwashing Detergents[1]

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MUCH HAS BEEN WRITTEN in the literature about methods of testing the efficiency of heavy duty household washing machine detergents. At one extreme are the totally artificial tests. These employ the Launderometer, Tergotometer, or Determeter and synthetic soils including the more recent "tagged" radioactive material. At the other extreme are the so-called "practical" tests. Here large panels of participants test the detergents by washing naturally soiled clothes in their home washers. From such a wide range of tests a manufacturer or compounder can select one which will fit his individual needs or budget and be reasonably sure of obtaining answers to his questions.

Unfortunately such a choice of tests is not possible in the case of the light duty detergents, which are used primarily for washing dishes in the home. This situation is unexpected, especially since the light duty field was the first to be invaded by the syndets. Upon closer examination of the problem this apparent lack of testing procedure is not too startling. When the syndets began to make inroads in the soap field, competition was not keen and competitive performance figures were not necessary. However now that syndets comprise a major share of the detergent business, better methods for choice of active ingredients are necessary so that the individual manufacturer may determine if a certain product can be produced and marketed economically. True, the ultimate test of any product is still in the hands of the consumer, but such large-scale testing is frequently out of the realm of possibility for many concerns, from the standpoint of both time and expense.

Most of the laboratory tests encountered in the literature for the testing of dishwashing detergents are of a manual type, wherein an artificial greasy type of soil is spread on a series of plates and then a sufficient number of these plates are washed until the foam in the dishpan disappears. Although such a test is a semi-practical approach, reproducibility depends on such factors as even distribution of soil on the plate and, more significantly, the ability of two operators to handle the dishes in the same manner.

Several tests have been developed to determine the performance of detergents on hard surfaces by using the Launderometer as the testing device. These evaluations deal primarily with commercial applications and do not include many of the constituents of the soils found in kitchens. Again the ratings are made by visual observations of the test pieces, and small formula variations are not susceptible to accurate measurement.

In practical use a detergent must clean a surface completely in order to be a satisfactory product. Laboratory rating of raw materials or formula variations precludes such end-results. Methods have been proposed for testing dishwashing detergents (6, 7), using soiled microscope slides and determining the efficiency by measuring the amount of light transmitted through the slides before and after soiling and after washing. A simple formula based on Lambert's and Beer's Law was used to determine soil removal:

$$R = \frac{\log Iw - \log Is}{\log Ic - \log Is} \times 100$$

R = percentage of soil removed by washing
Iw = transmitted light through washed slides
Is = transmitted light through soiled slides
Ic = transmitted light through clean slides

### Experimental

*Washing Machine.* Mann and Ruchhoft (6) had developed a special washing machine which consisted essentially of a reciprocating circular holder that supported slides on end at an angle of 20° to the tangent of the circumference. The movement of these slides through the water produced the mechanical work; and since oscillations, time, and water temperature could be accurately controlled, this phase of detergent efficiency could be kept constant, a condition not possible in manual dishwashing tests.

A plastic model was designed in our laboratory to adapt the Tergotometer for this type of evaluation. The details of construction are shown in Figure 1. Initial testing proved the design to be correct, and subsequently brass units were prepared to permit use at elevated temperatures in the event that mechanical dishwashing detergents were to be evaluated. A photograph of the brass unit in position on the Tergotometer agitator is shown in Figure 2. It should be mentioned that, in the construction of brass holders, care should be taken to eliminate as much excess weight as possible to prevent fluctuations in the oscillations when two or more units are used simultaneously.

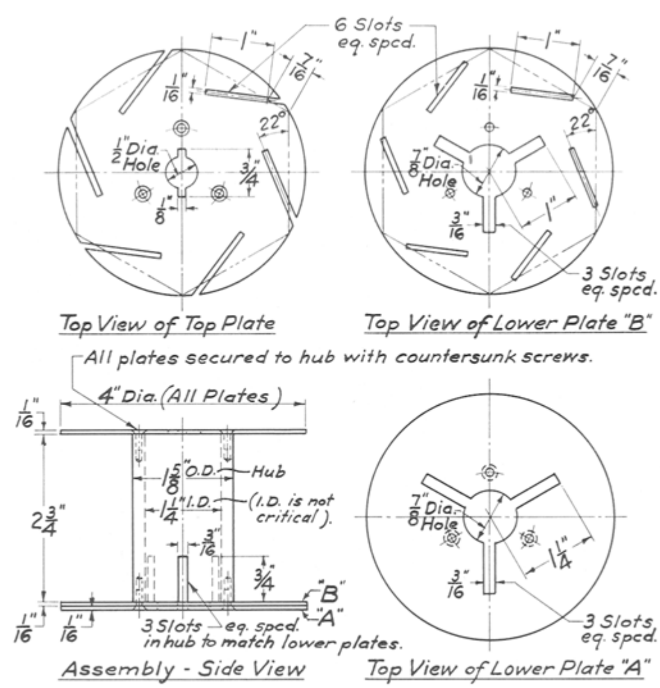


FIG. 1. Microscope slide dishwashing test unit.
Material: Any material which will withstand detergents at 200°F.

*Soil.* The soil used by the U. S. Department of Health was one developed by Hucker (9). An attempt to use this soil in the present test was not successful because of separation of

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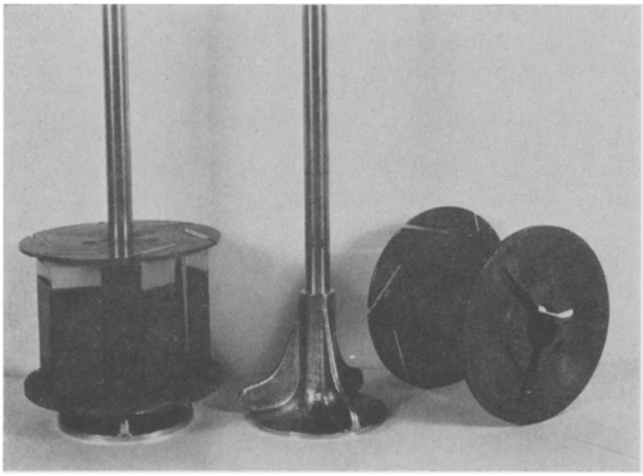

FIG. 2

the oily and water-soluble portions, resulting in spotty deposition. At this point it was deemed advisable to use two separate soils, a water-based protein-carbohydrate soil and a greasy soil as in the York Test (5). In addition to uniformity of deposition such a soil system has the advantage of distinguishing the performance characteristics of detergent formulations, permitting a better choice of ingredients for the particular performance desired.

Experimentation with various constituents resulted in the following soils and soiling procedures:

**Protein-carbohydrate Soil**

a) *Ingredients:*

| | |
|---|---|
| flour (Pillsbury's All-Purpose) | 30 g. |
| powdered egg yolk | 30 g. |
| evaporated milk | 40 ml. |
| Higgins India ink (No. 4417) | 10 ml. |
| $NH_4OH$ (concentrated) | 4 ml. |
| distilled water | 530 ml. |

b) *Mixing Steps*

Place the egg yolk and the flour in an Osterizer type of blender; mix for a few seconds. Add 200–300 ml. of water and mix for 15 seconds. Dilute the milk to 100 cc. and add to the flour and egg. Add the ink; rinse ink and milk into the flour, etc., using the remaining water from the 530 ml. Add the $NH_4OH$, and mix for about 1 min. Transfer soil to a 1-liter separatory funnel. Allow to stand for 5 min. Drain off 20 ml. and discard. Drain into the staining dishes an amount sufficient to cover slides to the frosted ends.

**Greasy Soil**

a) *Ingredients:*

| | |
|---|---|
| lard (Luer-Quality Pure Lard) | 35 g. |
| oleomargarine (Sun Valley) | 35 g. |
| peanut butter (Skippy Homogenized) | 35 g. |
| carbon black | 1 g. |
| $CCl_4$ | 535 ml. |

b) *Mixing Steps*

Weigh lard, oleo, and peanut butter (in order) into a 400-ml. beaker. Melt slowly in a hot water bath, and mix with a stirring rod. Add 100 ml. of $CCl_4$ and stir. Transfer to an Osterizer type of blender and mix for 15 seconds. Add the carbon black and mix for 15 seconds. Wash all soil from beaker into the blender with the remaining $CCl_4$. Mix for about 1 min. Transfer to a 1-liter separatory funnel and allow to stand for five min. Drain off 20 ml. and discard. Drain into the staining dish an amount sufficient to cover glass slides to frosted ends.

**Cleaning of Slides**

a) Place slides in a Coplin staining rack and soak in a detergent solution for about one-half hour, agitating slides several times during this period. Remove rack with slides and rinse with distilled water. Allow to drain. Place rack and slides in chromic acid cleaning solution for about 15 min. Remove and rinse in three changes of distilled water. Allow slides to air-dry.

**Soiling of Slides** (Figure 3)

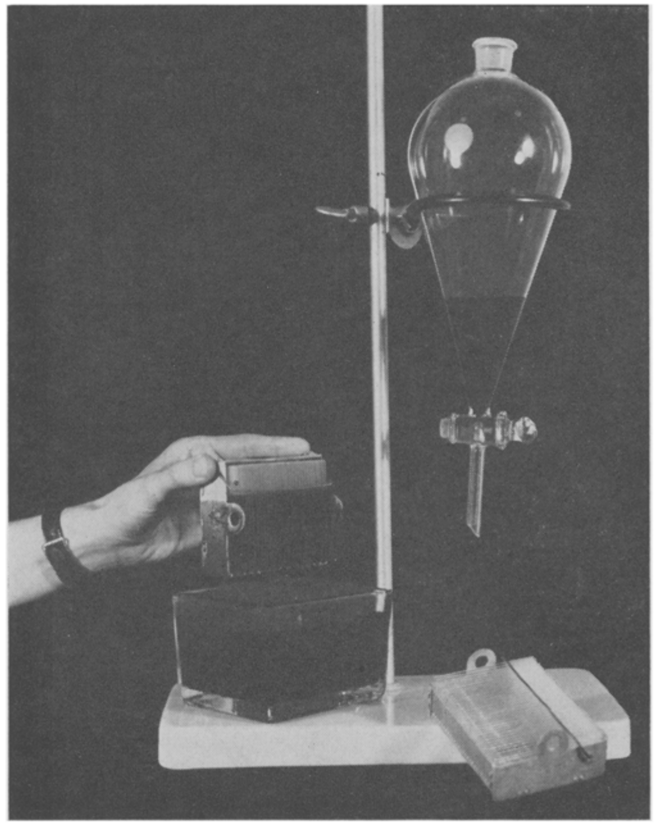

FIG. 3

a) Place slides in the staining rack so that all of the frosted ends are at the top.
b) Drain soil from separatory funnel into staining dish. Dip slides into the appropriate soil by slowly lowering the slides into the solution (frosted end up) until all of the clear portion is covered. After 5 seconds slowly remove slides from soil and drain for 15 seconds. Repeat twice (a total of three dips). Allow slides to drain in a vertical position for 10 min. Place slides in a constant temperature oven, maintaining the vertical position throughout the baking period. Bake slides for 2 hrs. (greasy at 150°C. and the protein-carbohydrate at 60°C.). After baking, permit slides to cool to room temperature and measure transmission.

**Washing Procedure**

The following procedure was evolved for the most satisfactory results in evaluation of light duty detergents:

*Tergotometer Set-up* (Figure 2):

a) Place dishwashing unit on Tergotometer agitator.
b) Place one set (3) of each type of soiled slides in slots of the dishwashing unit, alternating them so that no two adjacent slides have the same type of soil.
c) Place a rubber band around the unit (as near to the top of the slides as possible) to keep them in place during washing.

*Washing Operation:*

a) Wash the slides in 1,200 ml. of detergent solution for 5 min. at 120°F., 90 CPM.
b) Remove the agitator and empty the beaker.
c) Replace agitator in an empty beaker.
d) Run for 10 cycles to throw off excess detergent.
e) Remove agitator and replace in a beaker containing 1,200 ml. of tap water at 120°F.
f) Run for 2 min.
g) Remove agitator and replace in an empty beaker.
h) Run for about a minute to throw off excess water.

*Drying Operation:*

Permit slides to air-dry before making transmission measurements.

**Transmission Measurement:**

The data presented in this paper were obtained by using a Photovolt Lumetron to measure the light transmission. The light source was a 100-watt G. E. Mazda projection lamp. Two ground glass filters were inserted in the filter holder, and no reduction plates were used. A special holder, shown in Figure 4, was made to hold the slides in the sample compartment. An overhead view in Figure 5 shows the position of the slide-holder in the sample compartment of the Lumetron. Measurements were made on each soil separately, using the three slides from each run to obtain the transmission reading. The soil removal was calculated by means of the formula shown elsewhere.

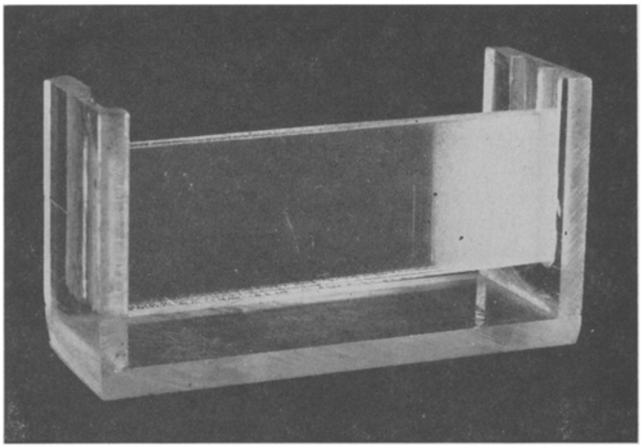

FIG. 4

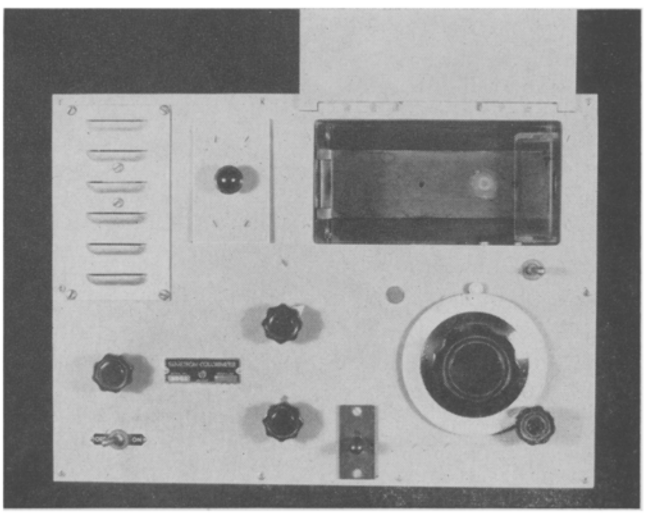

FIG. 5

## Results and Discussion

Initially the detergents were evaluated at 0.3% concentration; however a consumer research revealed this to be too high, and subsequent tests were conducted at 0.1–0.2%. Those who would disagree on this choice of testing concentration may choose any figure they desire; however the baking time and temperature may have to be altered to control the soil removal range. Early testing also revealed that the soils could not be stored but had to be used the same day they were prepared as shown by the detergency figures in Table I.

TABLE I
Effect of Age on Soil Removal

| | % Soil Removal | |
|---|---|---|
| | P–C | Greasy |
| Fresh soil | 82.0 ± 0.0 | 62.8 ± 0.5 |
| 24-hr.-old soil | 63.8 ± 0.4 | 36.8 ± 0.8 |
| Detergent concentration 0.1% | Water hardness 150 p.p.m. as $CaCO_3$ | |

In actual use the rating of a dishwashing detergent by a housewife is either a "go" or a "no go" situation; degrees of effectiveness are not important. However a satisfactory laboratory testing procedure is one in which there is a sufficiently wide range of results obtainable in order to distinguish small differences between various products and minor formula variations. The soils should be neither too easy nor too difficult to remove. The results in Table II show the range obtained with the current testing method.

TABLE II
Range of Soil Removals

| | % Soil Removal | |
|---|---|---|
| | P–C | Greasy |
| Detergent A | 51.0 | 57.8 |
| Detergent B | 50.5 | 53.2 |
| Detergent C | 43.3 | 58.6 |
| Detergent D | 47.8 | 58.0 |
| Detergent E | 91.6 | 79.8 |
| Detergent F | 90.3 | 82.8 |
| Detergent concentration 0.1% | Water hardness 150 p.p.m. as $CaCO_3$ | |

Another criterion of an acceptable evaluation test is the degree of reproducibility, especially in the order of rating, that exists from one time to another. The results shown in Table III were obtained by using identical samples on two different days and employing freshly soiled slides in each case.

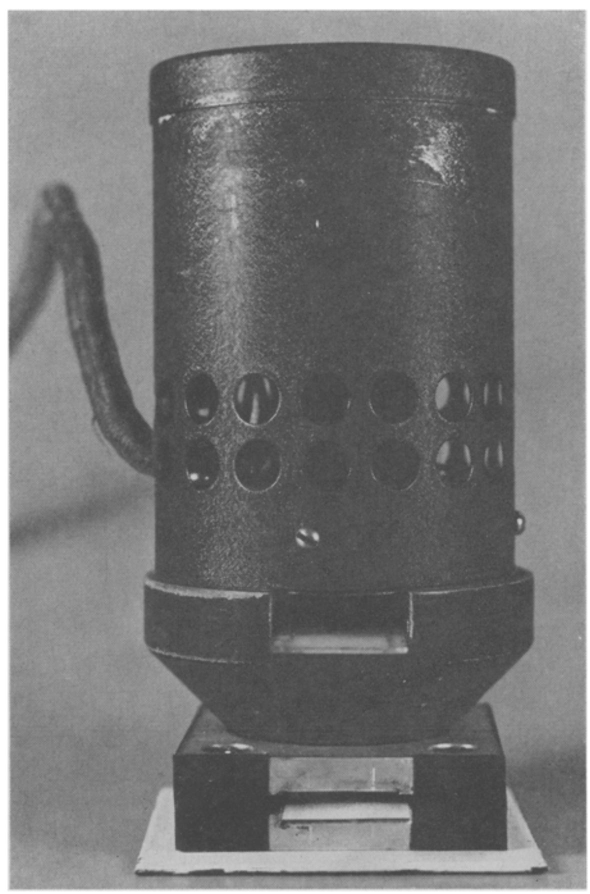

FIG. 6

TABLE III
Reproducibility of Results

| | % Soil Removed | | | |
|---|---|---|---|---|
| | Test A | | Test B | |
| | P–C | Greasy | P–C | Greasy |
| Syndet No. 1 | 88.8 ± 1.6 | 76.5 ± 2.3 | 88.7 ± 1.0 | 70.0 ± 1.2 |
| Syndet No. 2 | 55.4 ± 2.2 | 72.4 ± 2.9 | 54.3 ± 0.7 | 68.6 ± 0.4 |
| Syndet No. 3 | 58.1 ± 0.3 | 70.4 ± 3.0 | 54.0 ± 0.0 | 65.7 ± 2.8 |
| Syndet No. 4 | 52.4 ± 1.8 | 67.5 ± 5.3 | 46.2 ± 1.5 | 62.9 ± 3.5 |

Detergent concentration 0.1% Water hardness 150 p.p.m. as $CaCO_3$

Tests have also been conducted, using a photovolt Reflectometer 610B with the scanning unit 610Y for measuring the amount of light transmitted through the slides. This resulted in performance ratings identical to those obtained by the Lumetron, indicating that methods of measurements other than the Lumetron can be used satisfactorily. Measurements were made in this case on single slides, using the arrangements shown in Figure 6. In order to provide diffused light a ground glass filter was inserted in the scanning unit in place of the usual tristimulus filter. The hole in the bottom of the holder permits the light to pass through the slide and then be reflected back to the photocell. Although the current tests were made by using a porcelainized metal plate of approximately 76% MgO reflectance, the slide-holder may be placed on any arbitrary reflective surface without altering the detergency values. Details of the construction of the slide holder are shown in Figure 7.

Preliminary investigations have been undertaken to adapt the washing unit on the Tergotometer and the transmission measurement equipment to accommodate both ceramic and metal slides in order to evaluate dishwashing effectiveness on substrates other than glass. The use of such solid surfaces eliminates the necessity of a reflecting surface under the 610Y scanning unit.

A comparison of the results of this testing technique with those obtained by using a manual "suds-endpoint" test has indicated good correlation in the order of rating of various detergent formulations as shown in Table IV. In this instance the protein-carbohydrate and greasy soil removals were averaged and compared with estimated soil removals in the manual test. Of special significance is the wide spread between water alone and the detergent solutions in the slide technique, and the rather narrow one in the case of the manual test. Further the slide technique indicates a noticeable difference between Detergents B and C while in the manual test they would be considered identical. In order to compare the foaming characteristics of these detergents, a beater test employing the soil developed by Weeks, Harris, and Brown (1) was used. This test gave the same order of rating as the manual "suds-endpoint" method and was accomplished in a much shorter period of time.

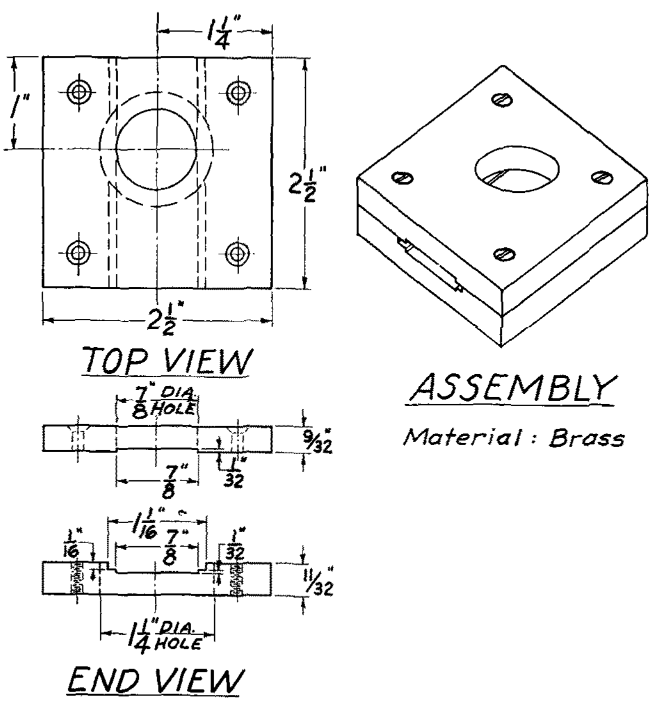


FIG. 7. Microscope slide holder for transmittance measurements.

TABLE IV
Comparison with a "Suds-endpoint" Test

| | % Soil Removed | | | | Foam Stability | |
|---|---|---|---|---|---|---|
| | Slide Technique | | | Manual Test | Beater Test | Manual Test |
| | P–C | Greasy | Av. | | Soil Loads | Plates |
| Formula A | 40.5 | 65.6 | 53.1 | 69 | 10 | 12 |
| Formula B | 65.9 | 69.8 | 67.9 | 85 | 2 | 5 |
| Formula C | 70.8 | 84.6 | 77.7 | 84 | 5 | 7 |
| Water | 1.2 | 7.5 | 4.4 | 60 | 0 | 0 |

## Summary

A new technique for the evaluation of dishwashing detergent efficiency in terms of percentages of soil removed has been developed by the adaptation of conventional detergency laboratory equipment. The soils used are synthetic, containing ingredients encountered in home and restaurant dishwashing (egg, grease, milk, flour, etc.). The substrates to be cleaned can be varied to meet the needs of any particular test: glass, pottery, or metal. The test has been shown to be reproducible and provides a sufficiently large range of removal percentages so that minor dishwashing detergent formula variations can be measured. A correlation between this new technique and a more cumbersome and time-consuming, semi-practical manual plate washing method has been demonstrated.

## Acknowledgment

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REFERENCES

1. Weeks, L. E., Harris, J. C., and Brown, E. L., J. Am. Oil Chemists' Soc., *31*, 254–257 (1954).
2. Sanders, H. L., and Knaggs, E. A., Soap and Sanitary Chemicals, *29*, 6, 45–48, 93 (1953).
3. Fineman, M. N., Soap and Sanitary Chemicals, *29* (2), 46–49; (3) 50–53, 114 (1953).
4. Fineman, M. N., J. Colloid Sci., *8*, 288-99 (1953).
5. Machlis, S., and Michaels, E. B. Soap and Sanitary Chemicals, *24* (9), 42–44 (1948).
6. Mann, E. H., and Ruchhoft, C. C., U. S. Public Health Reports, *61*, 877–887 (1946).
7. Norris, F. I., and Ruchhoft, C. C., U. S. Public Health Reports, *63*, 97–104 (1948).
8. Harris, J. C., Soap and Sanitary Chemicals, *28* (12), 45–47, 101 (1952); *29* (1), 42–44, 77 (1953).
9. Hucker, G. J., Progress Report on Detergent Evaluations Investigations, April 1, 1942–March 1, 1943, N. Y. Agr. Exp. Sta., Geneva, N. Y.
10. Staff Article, Soap and Chemical Specialties, *31* (5), 54.

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