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A Comparison of Two Methods for Testing Detergents[1]

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ALTHOUGH the laboratory testing of detergency has been a controversial subject since its beginning, it attained relatively little importance until the advent of synthetic detergents in commercial quantities. The very early work on the laboratory determination of detergency was restricted to a measurement of factors, such as surface tensions or interfacial tensions between oil and aqueous solutions, which are related to detergency only indirectly (1). The next approach to the indirect measurement of detergency was the determination of deflocculating power by ascertaining the suspension of a finely divided solid such as graphite by soap solutions. Chapin (2), Snell (3), and others (4) pioneered in this work.

Modern detergency studies using an artificially soiled fabric and a standardized washing technique began about 1929 with the work of many investigators, including Rhodes and Brainerd (5) and Hill (6). The first studies employing artificially soiled fabrics depended upon visual observation to "measure" the soil removal by washing in soap solutions. The visual method was soon supplanted by measurement of the degree of whiteness with a reflectance photometer. The next step in the evolution of laboratory detergency tests was the estimation of soil removal by measuring the light transmission of the wash liquors. Vaughn and co-workers were pioneers in this field (7). Because of its simplicity and time-saving characteristics the latter method has met with increasing favor by detergent laboratories. There has arisen among detergent technologists some disagreement concerning the equivalence of the last two methods for the laboratory determination of detergency.

The purpose of this paper is to present data, obtained in two different ways, to show the detergency of three types of detergents and to show the extent of correlation between these data. A further objective of the present discussion is to demonstrate and describe some of the limitations of the method employing light transmissions of the soil-containing wash liquors. An extension of the above objectives is to devise an experiment to demonstrate quickly the applicability of the light transmission method to any particular detergent system.

Experimental

Standard Soiled Fabric. As emphasized in a previous paper, the character and method of preparation of the soiled fabric is one of the most influential factors in measuring detergency. All of the tests described were made with a soiled cotton fabric, prepared as previously described (8). The fabric employed in the soiling operation was a bleached, unfinished cotton print cloth, 39-inch, 80/80 count (9). Since this fabric was unfinished, no desizing operation was necessary prior to soiling.

Measurement of Detergency by Light Reflectance of Soiled and Washed Fabrics. The test procedure for evaluating the detergency by light reflectance measurement was as follows: A solution of the detergent system under study was prepared at the desired concentration in soft water (45-50 p.p.m.). Five hundred milliliters of this solution was placed in one of the stainless steel beakers of the Baker Terg-O-Tometer (10). The solutions were brought to 120°F. ± 2°F. at which temperature the tests were conducted. The agitators were started (75 ± 3 cycles per minute) and a soiled swatch, 4" x 4", and an unsoiled swatch of the same size were introduced into each beaker. After introduction of the swatches the agitators were permitted to run for 10 minutes. The swatches were removed, squeezed lightly by hand, and rinsed twice in 500 ml. of water each time with 3 minutes of agitation in the Terg-O-Tometer. The cloth was finally passed through a washing machine wringer and dried in an oven at 180-190°F. The reflectance of the soiled fabric was measured before and after washing with a Hunter Reflectometer.

The soil removal is calculated by the following formula:

$$\text{Soil Removal} = \frac{R_w - R_s}{R_u - R_s} \times 100$$

Where R_w = Reflectance of the washed fabric
R_s = Reflectance of the soiled fabric
R_u = Reflectance of the unsoiled, unwashed fabric.

For the purpose of illustrating the effect of concentration on detergency in Figures 1, 2, 3, and 4 the soil removal at 0.1% concentration was arbitrarily assigned the value of 100 on the Relative Detergency Scale. Relative Detergency, as shown on the graphs, is the ratio of the soil removal at a given concentration to the soil removal at 0.1% concentration multiplied by 100.

The tenacity of the soil on this artificially soiled fabric and the mechanical action of the Terg-O-Tometer are indicated by the change in light reflectance upon washing in the absence of a detergent. The soiled fabric used in these tests showed an initial reflectance of approximately 10% and a final reflectance of approximately 17% after washing in soft water without detergent.

In Figures 1, 2, 3, and 4 the average deviation (of four determinations) is shown as the radii of the circles.

Measurement of Detergency by Light Transmission of Wash Liquors. In measuring detergency by determination of the transmission of light by the wash liquors, the same procedure was followed through the

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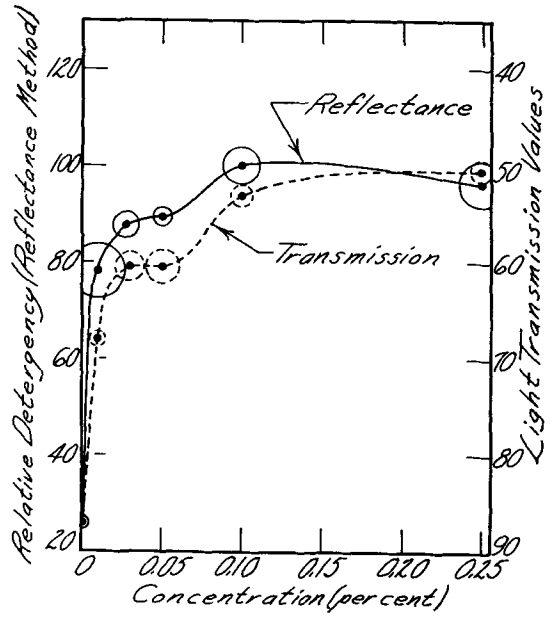

FIG. 1. Detergency as measured by reflectance and light transmission methods (non-ionic detergent).

washing operations as in experiments using light reflectance described in the preceding section. In fact, for all the work presented in this paper the same experiments were the source of both types of data (reflectance and transmission).

Immediately after the agitators were stopped, a 100-ml. sample was withdrawn from each beaker. The sample was freed of lint by centrifuging for 15 seconds in a small (Adams) laboratory centrifuge equipped with 15-ml. tubes. A sample of the original detergent system (without soil) was placed in a 13.06-mm. cuvette in the Coleman Universal Spectrophotometer, Model 14, using a wavelength of 5250A; and the scale was adjusted to 100% light transmission. The centrifuged sample of wash liquor was placed in a cuvette and its light transmission was read. This light transmission over the range employed will be shown to be proportional to the soil content of the liquor, except in the presence of certain detergent systems, and can be used as a direct measure of soil removal.

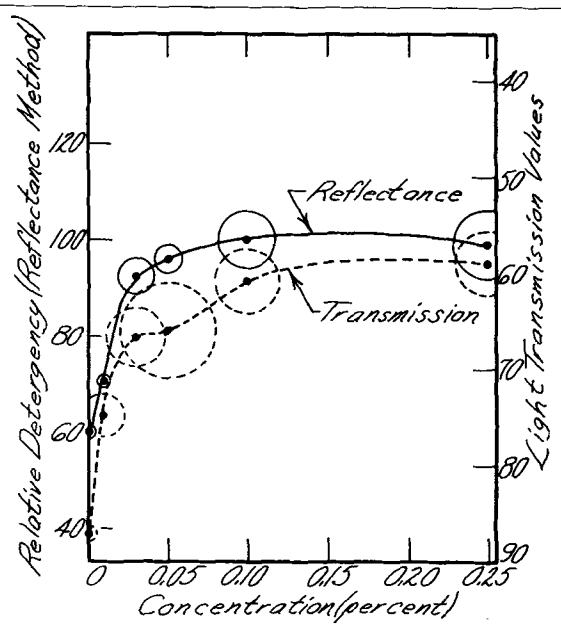

FIG. 2. Detergency as measured by reflectance and light transmission methods (anionic detergent).

In Figures 1, 2, 3, and 4 the average deviation (of four determinations) is shown as the radii of the circles.

Measurement of Light Transmission by Artificially Prepared Wash Liquors. The transmission of light by water containing dispersed soil (Figure 5) was determined as follows: A stock soil dispersion was prepared containing 8.33 g. Black Dispersion No. 10 (11) and 12 g. Shell Virgo 38P (12) diluted to one liter with distilled water. Although this dispersion was quite stable, it was shaken vigorously each time before use. Dilutions of this stock solution were made to contain 0.5 ml. (10.17 mg.), 1.0 ml. (20.33 mg.),

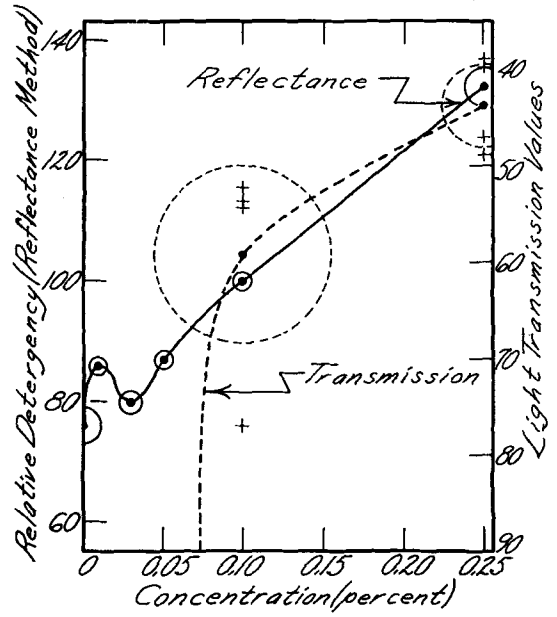

FIG. 3. Detergency as measured by reflectance and light transmission methods (tallow soap).

2.0 ml. (40.66 mg.), 3.0 ml. (60.99 mg.) and 5.0 ml. (101.65 mg.) in 1 liter of dispersed soil. (The actual soil content in milligrams is given in parentheses.) Similar dilutions of each of the two soil components were made. The light transmissions of these products were measured relative to distilled water, taken as 100%.

In the figures the average deviation (of four determinations) is shown as the radii of the circles.

Discussion

Comparison of Detergency Data. In Figure 1 the relative effect of concentration on the detergency of a non-ionic detergent, a polyoxyethylene derivative of mixed fatty and resin acids, is shown as measured by both the light reflectance of the soiled and washed fabrics and by the light transmission of the wash liquors. The soil removal, measured by the light reflectance method at 0.1% concentration, is taken as 100. A remarkable parallel exists in the data obtained by the two methods. Any conclusions drawn from one set of data would be equally evident from the other.

In Figure 2 the effect of concentration on the detergency of an anionic detergent, oleylmethyl tauride sodium sulfonate, is presented graphically as meas-

ured by both the light reflectance of the soiled and washed fabrics and by the light transmission of the wash liquors. Again, good agreement exists between the two sets of data.

A third detergent, tallow soap, was tested to show the effect of concentration on the detergency as measured by both the light reflectance of the soiled and washed fabrics and by the light transmission of the wash liquors. The data shown in Figure 3 indicate that the determination of the detergency of tallow soap by measurement of the light transmission of wash liquors is much less precise than by the measurement of the light reflectance of soiled and washed fabrics. The data obtained by the former method in

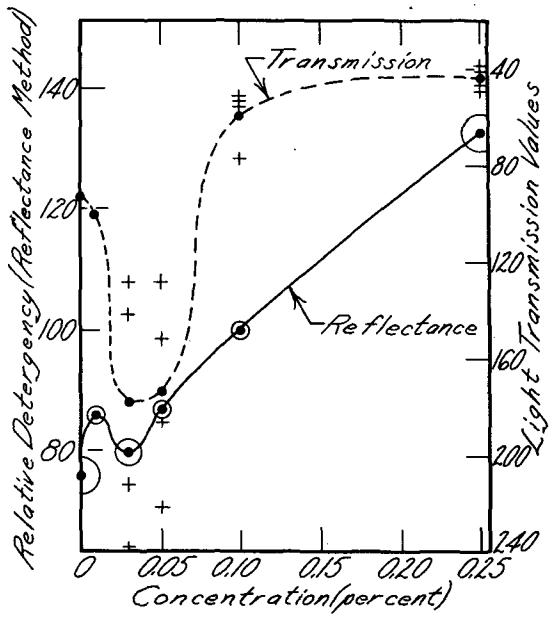

FIG. 4. Tallow soap detergency as measured by reflectance and light transmission methods (data of Fig. 3 replotted).

these tests showed poor agreement at concentrations below 0.25%. The data of Figure 3 are replotted in Figure 4 using a different scale in order to show the relative light transmissions at concentrations below 0.1%. At these low concentrations the wash liquors transmitted more light than the tallow soap solutions alone. By setting the spectrophotometer scale at 30 for the light transmission of the tallow soap solution and measuring the light transmission of the wash liquor, it was possible to obtain an indication of the extent of this effect. For example, a reading of 60 obtained in this manner was taken to represent 200% light transmission. On Figures 3 and 4 the crosses representing the individual data points illustrate the erratic nature of these measurements on tallow soap solutions. From inspection of the curves it is quite apparent that conclusions drawn from the light transmission of the wash liquors will be contrary to those arrived at by consideration of the data from the light reflectance of the soiled and washed fabrics.

Correlation Between Soil Concentration and Light Transmission. The proportionality of light transmission to soil concentration has been reported previously (13). The data presented in Figure 5 show the extent of correlation between light transmission and the concentration of the soil and each of its components. Curve A shows the effect of the total soil concentration on the light transmission of its dis-

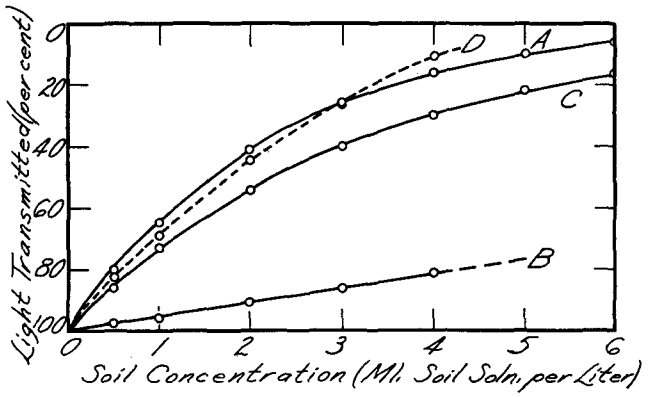

FIG. 5. Light transmitted by standard soiling liquors and components.

persion in distilled water. Curves B and C show the effect of concentration of the Shell Virgo 38P and Black Dispersion No. 10, respectively, on the light transmissions of dispersions of each of these materials in distilled water. Curve D represents the effect of concentration on the light transmitted by the soil mixture calculated from the data for the individual components. Curve D is more readily obtained by the graphic addition of Curves B and C. This shows the effects of the individual components to be essentially additive above 25% light transmission. For practical purposes the light transmission is directly proportional to the soil concentration in the range of 25 to 80% light transmission and 10 mg. (0.5 ml.) to 70 mg. (3.0 ml.) of total soil per liter.

Effect of Concentration, Time, and Detergents on the Transmission of Light by Artificially Prepared Wash Liquors. The effect of concentration and time on the transmission of light by artificially prepared wash liquors were studied for the three detergents used in the detergency tests. In Figures 6, 7, and 8 data are presented showing the effect of time and detergent concentration on the light transmission at two levels of soil concentration. In each figure the curve labeled "zero soil concentration" represents the percentage of light transmitted by the various detergent concentrations at 1, 3, and 24 hours after prepara-

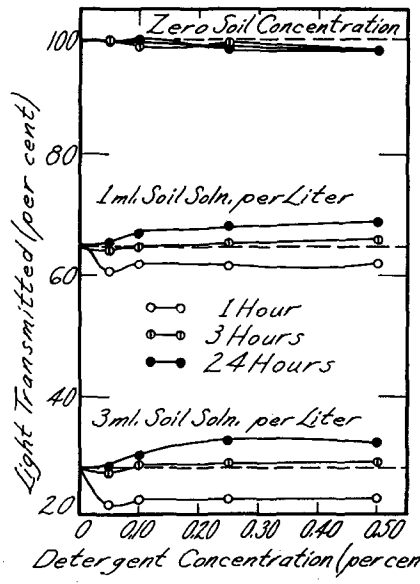

FIG. 6. Effect of concentration, soil load, and time on light transmissions of a non-ionic detergent system.

tion as compared with distilled water (100% transmission). The curves labeled "1 ml. of soil/liter" and "3 ml. of soil/liter" represent the light transmission values obtained when a detergent solution containing the indicated amount of soil was measured relative to the detergent solution alone. The dotted lines are datum lines representing the transmission values when no detergent is present. The differences between the dotted lines and the solid lines represent the change in light transmission caused by the presence of detergents. The data in Figure 6 show that this non-ionic detergent has little effect on the light transmission by the soil containing liquor and that the effect varies with time but is almost independent of detergent concentration. In Figure 7 the oleyl-

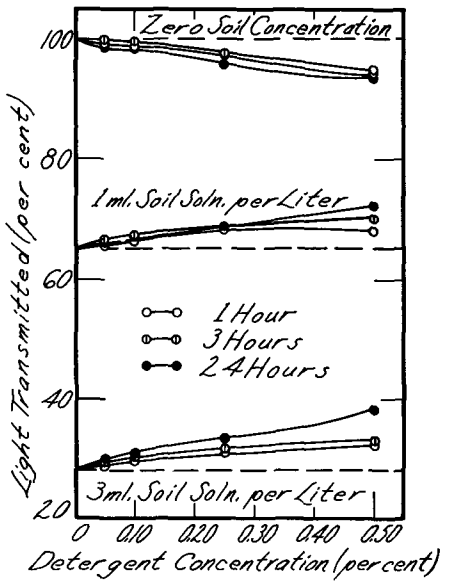

FIG. 7. Effect of concentration, soil load, and time on light transmissions of an anionic detergent system.

methyl tauride sodium sulfonate affects slightly the light transmission of the soil dispersions and the affectation varies with time. The curves in Figure 8 show the great effect of tallow soap on the light transmission of the soil containing liquor. Furthermore the effect is quite erratic at low concentrations, making it impossible to measure the soil concentration by the light transmission in the presence of tallow soap. In fact this phenomenon explains the inconsistencies in the detergency data obtained by the two methods, light reflectance and light transmission when using tallow soap.[2]

These data have suggested a relatively rapid and reliable method for determining whether a detergent system would be expected to give results determined by the light transmission of the wash liquors comparable to results obtained by the light reflectance of soiled and washed fabrics. When the light transmission of the soil suspension in the presence of detergent does not vary excessively (3% to 5%) from that of the soil suspension alone, it is concluded that the light transmission method can give data comparable to the light reflectance method.

[2] During the discussion of this paper Dr. Vaughn revealed that his laboratory has successfully used the light transmission method on soap solutions by introducing a modification, which employs the addition of non-aqueous solvents to the wash liquors.

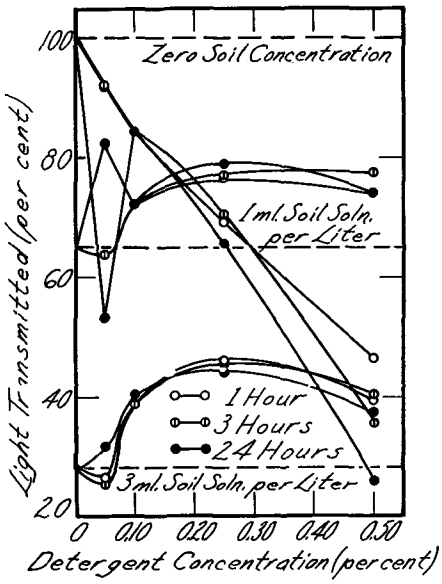

FIG. 8. Effect of concentration, soil load, and time on light transmissions of tallow soap system.

Conclusions

This work has led to the following generalized conclusions:

1. A limited correlation has been shown between a light transmission and a light reflectance method of measuring detergency.
2. A simple method is described to determine whether the light transmission procedure may be expected to give reliable results in measuring detergency.

Summary

A comparative study has been made of two common methods of measuring detergency. It has been shown that the method involving the measurement of light reflectance of soiled and washed fabrics gives results which lead to essentially the same conclusions as does the method involving the determination of the light transmission of wash liquors for a typical non-ionic detergent and a typical anionic detergent. The two methods did not give comparable results when tallow soap was used.

A simple experimental method which indicates the applicability of the method involving the measurement of light transmission of wash liquors has been devised.

Acknowledgment

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