Evaluating Detergents by a Huck Towel Method

W. B. MIHALIK and H. D. CROSS III, Colgate-Palmolive Company, Research and Development Division, Jersey City, New Jersey

Abstract

This paper describes a practical method of evaluating the performance of detergents by using huck towels soiled in plant mechanical shops and washed in a 5 gal semiautomatic washer. Detergency, redeposition and optical brightener intensity are evaluated by reflectance, yellowness, blueness and ultraviolet fluorescence measured on a Gardner Larger Area Colorimeter after six soil-wash cycles. The precision of the method is determined statistically by analysis of variance. Significant differences to a 95% confidence level that can be expected by this method are given.

Introduction

THE MAJORITY of methods used for evaluating the performance of detergents are based on their ability to remove a synthetic soil made with carbon black applied to cotton fabric in a solvent suspension of fat or oil. These methods are well summarized by Getchell (1) and Schwartz (2). The use of a synthetic soil based on carbon black has been criticized by Powe (3) and by Sanders and Lambert (4) because it does not represent the type of soil found on clothes soiled in the home. Sanders and Lambert (4) used a practical soil which was based on an average analysis of street dirt obtained from six large cities. Their method is based on washing this soil from cotton broadcloth in a Tergotometer and evaluating detergency and redeposition by reflectance. The validity of their method was substantiated because it correlated with results obtained when using a practical soil applied to huck toweling in roll form soiled in washrooms. Schwartz and Berch (5) have described a laboratory scale soil accumulation method which uses a natural soil applied to fabric swatches washed in a Tergotometer or Launderometer. Detergency and redeposition is measured by reflectance readings after six cycles with a Hunter multipurpose reflectometer.

A practical test based on individual huck towels soiled in plant mechanical shops in the Colgate-Palmolive Co. was briefly described by Vitale (6) and Vitale, Ross and Schwartz (7). In this paper additional improvements have been made on this huck towel method to reduce the number of variables which are normally inherent in a practical test of this kind. These modifications include a desizing and bleaching step which removes the starch applied to the towels by the manufacturer and which whitens the towels to a uniform maximum so that subsequent soiling and washing always produce a reduction in whiteness. These two steps also shrink the towels to their minimum size, thus eliminating shrinkage as a variable. It was also found necessary to adjust the speeds of the four Easy Whirldry washers and the speeds and temperatures of the four Whirlpool dryers so that their performance was the same throughout the washing and drying cycles. The standardization of the Gardner large area colorimeter after every four readings instead of after every ten readings was also found necessary to reduce to a minimum the instrumental variations. A statistical analysis was made of this procedure to determine the precision that could be expected to a 95% confidence level.

Experimental

Materials and Equipment

Easy Whirldry washers, 5 gal capacity, speed of agitator 76 to 77 cycle/min, made by Easy Washing Machine Division, The Murray Corp., Syracuse, N.Y.

Whirlpool automatic gas dryers, model LJD96PW10, Imperial, made by Whirlpool Corp., Benton Harbor, Mich.

Gardner Large Area Colorimeter, Manual Model, made by Gardner Laboratories, Bethesda, Md.

Huck towels, style 1211, size 12 inch x 18 inch (unprocessed), hemmed and grommeted, white, distributed by Wellington Sears, New York, N.Y.

Frigidaire automatic washer, Imperial Fabric Master, Model WI-59, 10 gal capacity.

Towel Preparation

The present huck towel method uses 20 cotton huck towels for each detergent to be evaluated. Since eight products are evaluated at one time, a total of 160 towels are necessary and 4 towels are held as original untreated towels. These 164 towels are desized in the Frigidaire automatic washer with water added at 150F, allowing to stand 20 hr overnight, the temp dropping to room temp. Desizing is done as follows: 82 Huck towels (5.4 lb); 10 gal water at 150F (initial temp); 1.0% bacterial amylolytic enzyme on wt of water; 0.05% nonionic wetting agent on wt of water.

After 20 hr of soaking, the towels are allowed to go through the "Normal" wash and rinse cycles of the automatic washer. The towels are then dried for 30 min in the Whirlpool automatic dryers at "Regular" cycle (162F).

Bleaching is done in the same Frigidaire automatic washer, as follows: 82 huck towels (5.4 lb); 10 gal of water at 150F; 0.85% Hexameta Phosphate powder on weight of water; 16 fl oz (600 ppm available chlorine) of sodium hypochlorite containing 5% available chlorine. The towels are allowed to go through the "Normal" wash and rinse cycles and then are dried in the Whirlpool automatic gas dryer at "Regular" cycle for 30 min at 162F.

The 164 towels are visually examined to determine if all towels are from the same lot. This is done by folding the towels in half and overlapping each towel by about 1 in. on a large table. The appearance of all towels should be identical: odd towels are removed and replaced. These towels are then marked and coded with permanent ink.

Towel Soiling

The towels are set up on the racks in a statistical randomized pattern at two locations in the plant shops. Pumice soap (Klex) and a scouring cleanser (Ajax) are provided for hand washing. Personnel from the pipe shop, machine shop, carpenter shop and tinsmith shop use these towels to dry their hands after washing in an adjacent sink. Previous tests indicated that these two soiling locations gave the same degree of soiling. A chain is placed through the brass grommets of the towels and locked with a padlock so that the towels cannot be removed from the rack. The soiled towels are removed daily and brought to the laboratory by a laboratory technician.

TABLE I

Reflectance of Soiled Huck Towels After Sixth Washing

Towel No.	1A 0.15%	1B 0.05%	2A 0.15%	2B 0.05%	3A 0.15%	3B 0.05%	4A 0.15%	4B 0.05%
1	.....	73.8	80.8	77.7	81.6	78.0	76.6	70.5
2	75.5	77.3	81.0	77.5	81.8	78.8	80.0	72.9
3	83.2	77.7	80.5	75.2	84.9	73.7	79.2	72.3
4	80.0	77.2	82.8	74.9	82.7	73.7	76.0	70.0
5	79.9	76.5	79.3	74.5	79.0	73.9	81.8	76.4
6	77.7	75.7	84.9	78.1	81.7	72.1	76.9	73.1
7	80.0	76.2	80.0	73.5	82.3	74.8	82.2	72.2
8	80.2	70.9	80.8	.....	78.2	75.1	80.0	76.2
9	83.7	73.8	82.1	78.7	79.5	71.7	80.9	78.1
10	82.4	70.8	80.1	75.8	77.9	72.2	77.1	70.5
11	79.9	76.5	78.5	71.4	80.6	70.2	81.1	74.3
12	81.6	72.5	79.2	72.8	78.5	79.5	81.9	73.9
13	82.0	71.5	76.7	66.8	81.1	71.6	78.1	76.5
14	80.7	70.6	84.4	72.8	75.8	71.7	72.4	74.5
15	79.1	70.1	78.8	.....	83.6	73.3	82.3	73.3
16	78.1	74.2	77.4	.....	80.6	73.3	79.9	75.8
Total	1204.0	1185.3	1287.2	969.7	1289.8	1183.6	1266.4	1180.5
Avg.	80.27	74.08	80.46	74.59	80.61	73.98	79.5	73.78

Washing and Drying

Washing is done in a 5 gal Easy Whirldry washer and drying is done in a Whirlpool automatic dryer, as follows:

Capacity of washer: 5 gal
Number of soiled towels in load: 16
Number of unsoiled towels in load: 4
Total weight of load: 1.25 lb
Ratio of load to water: 1:32
Washing time: 15 minutes
Water hardness: 150 ppm (3 Ca/2 Mg)
Washing temperature: 120F
Centrifuging time after washing: 1 minute
Number of rinsings: 2
Volume of rinse water: 5 gal
Temperature of rinse water: 100F
Time of rinsing: 2 minutes
Centrifuging time after rinsing: 1 minute
Drying time in Whirlpool dryer: 30 minutes
Temperature of Whirlpool dryer: 162F (average)
Number of soilings and washings: 6

Statistical Design

In the statistical design, two concentrations of a heavy duty powdered detergent (Fab), one realistically low (0.05% on wt of water) and one in line with package directions (0.15% on wt of water) were run in quadruplicate for a total of six soilings and washings. Soiling and washing on each replicate was done on alternate days, as follows:

Soiling and Washing Schedule

Test No.	Conc., %	Soiling	Washing
1A	0.15	Monday	Tuesday
1B	0.05	Monday	Tuesday
2A	0.15	Tuesday	Wednesday
2B	0.05	Tuesday	Wednesday
3A	0.15	Wednesday	Thursday
3B	0.05	Wednesday	Thursday
4A	0.15	Thursday	Friday
4B	0.05	Thursday	Friday

This design allowed a study of four days of the week as possible variables, as it was believed that some days gave heavier deposits of soil than other days.

Instrumentation

The Gardner Large Area Colorimeter was used to measure the color changes of the towels. This instrument is a tristimulus colorimeter which measures color on three scales. An area of 9.5 in. by 11 in. is read by the instrument, although the newer models measure an area of 12 in. by 12 in. Color is read on three large ten turn potentiometer dials—an "Rd" scale (reflectance), "a" scale (redness-greenness), "b" scale (yellowness-blueness). A special "Rb" scale is included to measure ultraviolet reflectance. To detect the contribution of optical dyes to whiteness, this instrument is equipped with a Novial Shade A ultraviolet absorbing filter which could be placed into the two incident beams of light of the tungsten lamps. With these filters in the incident beams, no ultraviolet light can reach the fabric and therefore, only nonfluorescent color is measured. The contribution of any fluorescing materials, whether caused by absorption of an optical dye or by a chemical modification of the fabric, is included in the color measured by the instrument. Since optical dyes affect the "b" scale (yellow-blue), more than the "a" scale (red-green), the removal of yellowness in the fabric produced by the optical dye is determined by the difference in the "b" scale readings with and without the Novial filter in the incident beam.

Incandescent light emitted from a tungsten lamp which has less ultraviolet than daylight is used in this instrument. Accordingly, the ultraviolet reflectance measured is smaller than that which occurs in natural daylight.

Results and Discussion

Detergency and Redeposition Evaluation

The soil which is applied to the towels in plant shops may be black, brown or yellow or a combination of these colors. A randomized distribution of towels on the racks at the soiling stations over six soil-wash cycles produces a uniform application based on the mean of 16 towels. Color measurements were made after the sixth washing on the 16 soiled towels and 4 unsoiled (redeposition) towels, as follows:

"Rd" scale—reflectance
"b" Filter In—yellow-blue values, excluding brightener effect
"b" Filter Out—yellow-blue values, including brightener effect

These three readings adequately accounted for all visible color changes in the towels. The "a" scale readings (red-green) were omitted because there were no significant changes occurring on this scale that could be measured. The "Rd" readings measured the grayness, the "b" (Filter In) readings measured the reduction in yellowness excluding the effect due to optical brightener, and the "b" Filter Out readings measured the reduction in yellowness including

TABLE II
Precision of Huck Towel Method After Sixth Washing

	Standard Error	Significant Diff. (95%)
Mean of 16 Soiled Towels		
Reflectance (Rd)	0.92	1.84
Yellow-blue values ("b" Filter Out)	0.17	0.34
Yellow-blue values ("b" Filter In)	0.11	0.22
Ultraviolet reflectance (Rb)	0.70	1.40
Mean of 4 Redeposition Towels		
Reflectance (Rd)	0.29	0.60
Yellow-blue values ("b" Filter Out)	0.18	0.37
Yellow-blue values ("b" Filter In)	0.19	0.39
Ultraviolet reflectance (Rb)	0.71	1.46

the effect due to optical brightener. The 16 soiled towels after the sixth washing showed about 25.0 reflectance units of unremoved soil, while the four redeposition towels showed about 4.0 reflectance units of redeposited soil.

Detergency efficiency is based on the decrease in grayness or increase of "Rd" values and on the reduction in yellowness or decrease in "b" (Filter In) values of the 16 soiled towels. Antiredeposition efficiency is also based on the decrease in grayness or increase in "Rd" values and on the reduction in yellowness or decrease in "b" (Filter In) values of the four redeposition towels. The efficiency of the optical brightener is based on removal of yellowness as indicated by the difference in "b" values with and without the novial filter in the light path.

A statistical analysis of the four replicates gives a standard error of the mean of 16 towels as 0.92 reflectance units (8) and to a 95% confidence level, the precision or significant difference is 1.84 reflectance units. Therefore, if the difference between two load means (16 soiled towels) exceeds 1.84 reflectance units the grayness produced by the two detergents is different, and if the difference is less than 1.84 units the grayness produced by the two detergents is the same. The significant difference of the 16 soiled towels to a 95% confidence level of "b" Filter In values was found to be 0.22 units, and "b" Filter Out values was found to be 0.34 units.

The precision that can be expected of the mean of four redeposition towels to a 95% confidence level is 0.60 for reflectance (Rd), 0.39 units for "b" Filter In values and 0.37 units for "b" Filter Out values.

Ultraviolet Reflectance Evaluation

The "Rb" scale on the Gardner Large Area Colorimeter measures the ultraviolet reflectance of the towels with a light source of two 15 watt BLB Blacklight lamps. These lamps radiate most of their energy in the near ultraviolet region of the spectrum between 320–400 mμ, and they emit ultraviolet light through a special filter glass which is part of the lamp that absorbs nearly all of the visible light. The "Rb" scale measures the intensity of ultraviolet reflectance pro-

TABLE III
Incremental Decrease in Reflectance Averages of Four Replicates

Cycle	Conc. (%)	After Soiling (Rd)	After Washing (Rd)	Soil Applied (ΔRd_1)	Soil Removed (ΔRd_2)	Soil Remaining ($\Delta Rd_1 - \Delta Rd_2$)
Orig.	.....	.....	90.0	...	...	...
1	0.15	84.9	87.7	5.1	2.8	2.3
2	0.15	82.9	85.6	4.8	2.7	2.1
3	0.15	81.1	83.8	4.5	2.7	1.8
4	0.15	80.0	82.5	3.8	2.5	1.3
5	0.15	78.9	81.4	3.6	2.5	1.1
6	0.15	77.7	80.1	3.8	2.4	1.3
Orig.	.....	.....	90.0	...	...	...
1	0.05	84.4	85.8	5.6	1.4	4.2
2	0.05	81.1	82.4	4.7	1.3	3.4
3	0.05	78.5	79.9	3.9	1.4	2.5
4	0.05	76.4	78.0	3.5	1.6	1.9
5	0.05	75.0	76.3	3.0	1.3	1.7
6	0.05	72.9	74.8	3.3	1.4	1.9

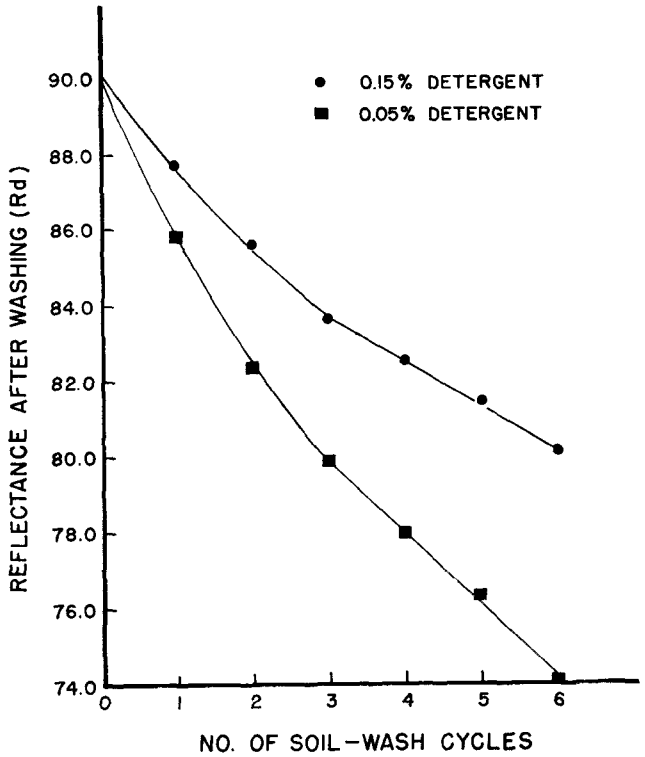

FIG. 1. Reflectance of huck towels after 6 soil-wash cycles.

duced by the optical brightener. The function of this scale is similar to that of a fluorimeter.

A statistical analysis of the four replicates gives significant differences to a 95% confidence level of 1.40 Rb units for the mean of 16 soiled towels and a value of 1.46 Rb units for the mean of four redeposition towels.

Behavior of Soil

In the Huck towel test as described, readings need only be made after the sixth washing. However, in this test, reflectance readings were made after every soiling and after every washing on the 16 towels soiled in the plant shops so that the behavior of the soil

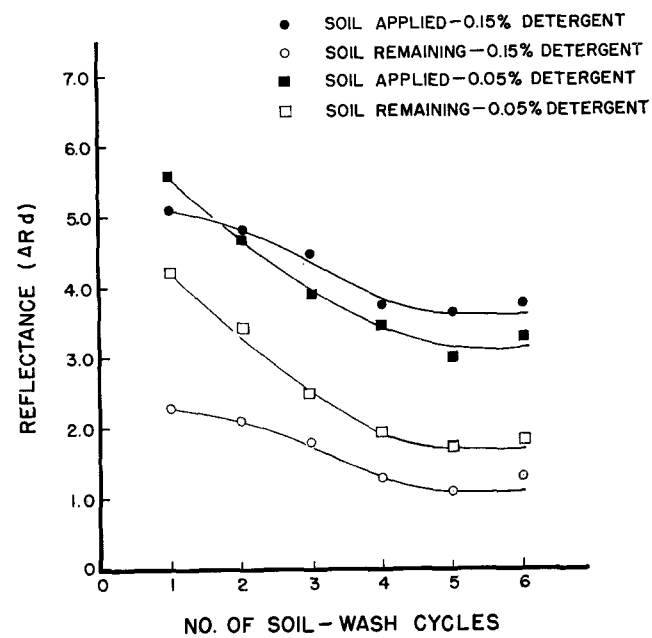

FIG. 2. Reflectance of soil applied and soil remaining after 6 soil-wash cycles.

could be determined by this procedure (Table III). Averages of the four replicates for each of the two concentrations of the detergent were plotted against the number of soil-wash cycles in Figure 1. This curve shows that the reflectance of the towels gradually decreases after each washing, indicating that some soil remains and has not been removed completely by the previous washing. The slope of this curve also shows that the soil remaining is large, and that there are definite differences between the detergency of both concentrations of the same detergent.

The incremental decrease in reflectance (ΔRd) after each soiling and washing is shown in Figure 2. The ΔRd of soil remaining on the towels and the ΔRd of soil applied after each soiling decreases in the first four cycles, then becomes constant at the fifth cycle. Apparently soil saturation occurs at the fifth cycle, at which point the soil that the towels will permanently retain and which cannot be washed out by the given concentration of detergent becomes constant. Both concentration curves are parallel to each other. The difference between the ordinates of these two curves is a constant and represents the soil removed. The saturation point occurs at the fifth cycle for both concentrations of the same detergent. This suggests that for different concentrations of the same detergent and for the same substrate (Huck towels) and for the same type of soil (mechanical shop soil), the saturation point occurs at the same cycle. Since the ΔRd's of soil applied and soil remaining become constant at the fifth cycle, the Huck towel procedure should be run at least five cycles. However, using six cycles gives greater assurance that a constant residual soil is adsorbed by the towels.

ACKNOWLEDGMENT

J. R. Trowbridge provided the design and the statistical interpretation of the results and V. S. Tarika, R. B. Handler and J. Albano performed various phases of this work.

REFERENCES

1. Getchell, N. F., Textile Res. J. *25*, 150–194 (1954).
2. Schwartz, A. M., et al., "Surface Active Agents and Detergents," Vol. II, Interscience Publishers, New York, 1958.
3. Powe, W. C., Textile Res. J., *29*, 879–884 (Nov. 1959).
4. Sanders, H. L., and J. M. Lambert, JAOCS *27*, No. 5, 153–159 (1950).
5. Schwartz, A. M., and J. Berch, Soap Chem. Specialties *39*, 78–81, 158–160 (1963).
6. Vitale, P. T., et al., JAOCS *31*, 341–344 (1954).
7. Vitale, P. T., et al., Soap Chem. Specialties *32*, 41–44, 180 (1956).
8. Youden, W. J., "Statistical Methods for Chemists," John Wiley & Sons, New York, 1951, p. 25.

[Received December 20, 1963—Accepted February 7, 1964]

A Colorimetric Method for the Determination of Parts/Million of Nonionic Surfactants

R. A. GREFF, E. A. SETZKORN and W. D. LESLIE, Analytical Research Section, Continental Oil Company, Ponca City, Oklahoma

Abstract

A method for the determination of nonionics in low concn (0–20 ppm) has been developed. This method is based on the formation of a blue complex between ammonium cobaltothiocyanate reagent and a polyethoxylated compound. This complex is extracted into benzene from a saturated salt solution and measured with a spectrophotometer at 320 mμ. The absorbance reading is compared to a standard.

The method requires only a single extraction and no preliminary concn step is necessary. It is sensitive to polyethoxylated compounds containing three or more moles of ethylene oxide. We have used this method to detect as little as 0.01 mg of nonionic in 100 ml of sample (0.1 ppm). Reaction conditions, sensitivity differences between compounds, interferences and suitability for use in biodegradation studies have been investigated. The accuracy and repeatability of this method is $\pm 3\%$ relative at 20 ppm concn.

Introduction

A REVIEW OF THE LITERATURE shows few methods for the determination of nonionics in low concn ranges. In higher concn ranges there are methods based on gravimetric, volumetric and colorimetric procedures. Shaeffer and Critchfield (11) described a gravimetric procedure using silicotungstic acid to precipitate the nonionic. They also describe a colorimetric procedure based on a molybdenum determination after precipitation with phosphomolybdic acid. Oliver and Preston (9) used phosphomolybdic acid in a gravimetric procedure. Barber, Chinnick and Lincoln (1) describe a more rapid procedure using phosphotungstic acid. Stevenson (12) developed two colorimetric methods, both based on reaction with phosphomolybdic acid. Schoenfeldt (10) developed a volumetric procedure based on reaction with ferrocyanic acid and determination of the excess reagent with standard zinc sulfate. Karabinos (7) described a phenol titration procedure for determination of ethylene oxide chain length. Ca. 3 moles of phenol are required for each 7–8 ethylene oxide units. Davis, Watman and Speel (4) used the phenol titration for determination of concn. Wurzschmitt (17) describes oxonium ion formation and the development of colored precipitates with reagents such as KI_3 and ammonium cobaltothiocyanate. Two oxonium groups appear to form for each 5.5 ethylene oxide units.

The ammonium cobaltothiocyanate reaction first described by Gnamm (5) was used as a qualitative test for polyethoxylated compounds by Wurzschmitt (17) and van der Hoeve (14,15). In 1955, Brown and Hayes (2) published a method for the quantitative determination of polyethylene glycol mono-oleate using the cobaltothiocyanate reagent of Wurzschmitt to produce a colored complex which is extracted into chloroform and determined absorptiometrically. Also in 1955, Kurata (8) published a review of methods for the analysis of nonionics in which he described a procedure using a concd ammonium cobaltothiocyanate reagent and benzene as the extraction solvent. The nonionic cobaltothiocyanate complex was extracted with benzene from a saturated salt solution. The benzene layer was dehydrated with anhydrous sodium sulfate, centrifuged, and its absorbance measured.