

Cotton Detergency

The cotton detergency of the sulfates was determined with a Terg-O-Tometer using U.S. Testing Company soiled cloth. The cleaning ability of the detergent is reported in terms of ΔR , the difference in percent reflectance between the washed cloth and the original soiled cloth. The greater the increase in percent reflectance, the more efficient is the cleaning agent.

A comparison of the relative cotton detergency of the various sulfates was made and is outlined in Table II. The thioether sulfates exhibited approximately the same cotton detergency regardless of the heteroatom sulfur position. They were also equivalent to the standard, 1-hexadecyl sulfate.

The oxyethers decreased in cotton detergency performance with increasing distance of the oxygen atom from the sulfate group and were inferior to hexadecyl-1-sulfate. It was noted above that the CMC's and the surface activities of the thioether series were not affected to nearly the same degree by the presence and position of the sulfur heteroatom as in the oxyether series. In general, the sulfates which have the lowest CMC's were found to be the most surface active and to be the most effective cotton detergents.

A plot of the change in reflectance vs. the surface activity of the surfactant shows an apparent relationship between the two. There seems to be only a certain level of surface activity needed for cotton detergency (as seen in Figure 6) because as the surface activity increases above this level, the change in reflectance does not increase. Since solubilization, wetting ability and deflocculation (10) all play major roles in cotton detergency and since the relationship of these properties to heteroatom positions has not yet been determined, a firm conclusion concerning the relationship

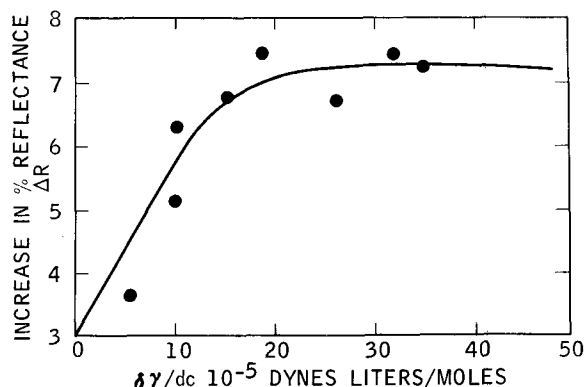


FIG. 6. Δ Reflectance vs slope of surface tension curve.

between surface activity and detergency cannot yet be drawn.

ACKNOWLEDGMENTS

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REFERENCES

- Preston, W. C., *J. Phys. Coll. Chem.* **52**, 85 (1948).
- Klevens, H. B., *JAOCS* **30**, 74 (1953).
- Williams, E. F., N. T. Woodberry, and J. K. Dixon, *J. Coll. Sci.* **12**, 452 (1957).
- Hartley, G. S., *Trans. Faraday Soc.* **37**, 130 (1941).
- Dreger, E. E., G. I. Kein, G. D. Miles, L. Shedlovsky, and J. Ross, *Ind. Eng. Chem.* **36**, No. 7, 610 (1944).
- Leermakers, J. A., and A. Weissberger, in "Organic Chemistry—An Advanced Treatise," Ed. H. Gilman, John Wiley and Sons, New York, 1943, Vol. II, p. 1720.
- Mankowich, A. M., *JAOCS* **41**, 449 (1964).
- Gibbs, J. W., "The Collected Works of J. W. Gibbs," Longmans, Green, and Co., New York, 1931, Vol. 1, p. 219.
- Gugenheim, E. A., and N. K. Adam, *Proc. Roy. Soc. (London)*, **A139**, 218 (1933).
- Stevenson, D. G., *J. Soc. Cosmet. Chem.*, **12**, 353 (1961).
- Turbak, A. F., and J. R. Livingston, Jr., *I&EC Product Res. and Dev.* **2**, 229 (1963).
- Gütte, E., 3rd Int. Congress of Surface Activity Cologne, 1960, p. 45.
- Weil, J. K., R. G. Bistline, Jr., and A. J. Stirton, *J. Phys. Chem.* **62**, 1083 (1958).

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A Laboratory Method for Testing Laundry Products for Detergency

W. G. SPANGLER, H. D. CROSS, III, and B. R. SCHAAFSMA, Colgate Palmolive Company, Jersey City, New Jersey

Abstract

A laboratory screening test for fabric detergency has been developed, which closely parallels practical laundry operations. Natural airborne particulate is used so that the argument for and against carbon soil is eliminated. The oily soil consists of synthetic sebum, thereby simulating the surface film that covers the human integument. The particulate and fatty matter are combined into an aqueous suspension and padded onto the fabric. Variables can be measured in a minimum of time because the entire procedure is carried out in the laboratory and is not dependent on a panel of subjects as is the case in most practical testing. The procedure for this test as generally employed consists of multiple washes and measures brightener build up and redeposition in addition to detergency. Precision of the method is $\pm 0.4\%$ at the 95% confidence level. Evaluations are made both visually and instrumentally.

Introduction

THE POWER TO REMOVE SOIL by a colloidal chemical process that is possessed by certain materials or systems is called detergency." (1) A laboratory test that is designed to measure this phenomenon should relate to practical testing. The most common practice today is to wash standard soiled swatches and measure the reflectance before and after washing. These reflectance data are translated into soil content or soil removal in many instances. However, the results obtained from different commercially prepared artificially soiled cloths are not always in agreement with each other (2) and interpretations must be made with perspicacity. Since a great deal of time and manpower are being used in tailoring molecules for soft detergents, the measurement of detergency takes on added importance. It is for this reason that this study was made.

The choice of soil to use for detergency measurements and the method of application have been the subject of many publications. A total review of the

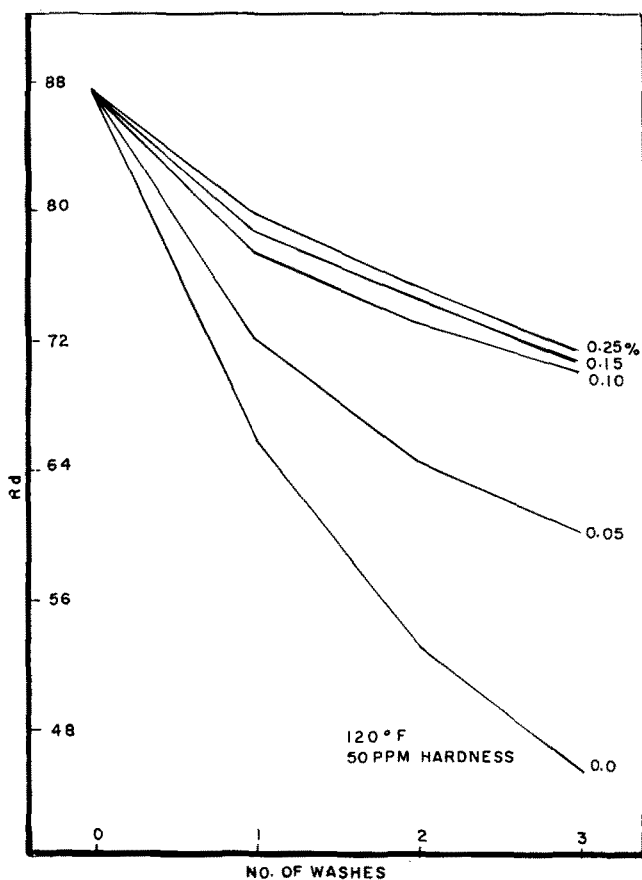


FIG. 1. Effect of concentration on detergency.

literature will not be detailed but some of the outstanding contributions will be listed. Harris (3) was one of the first to organize the testing procedures in

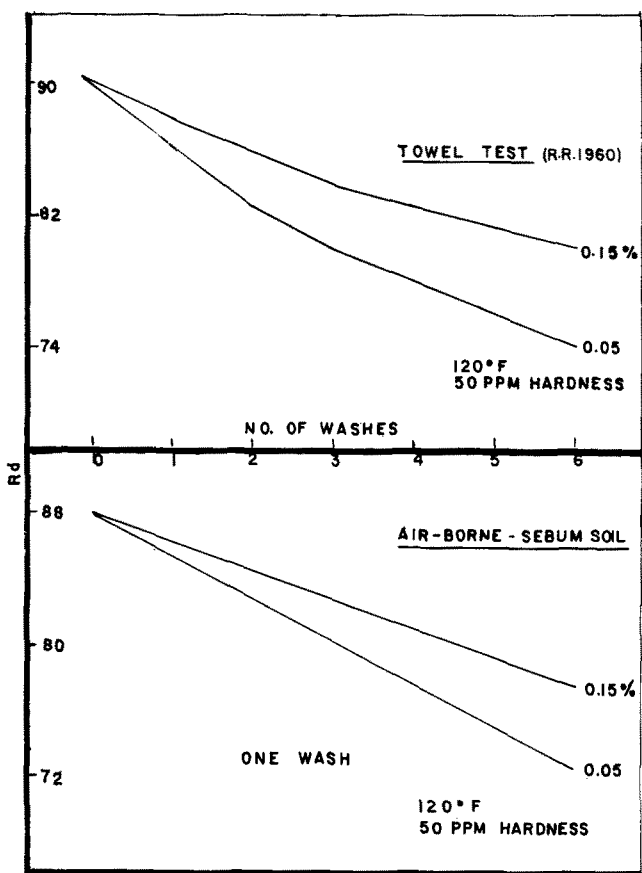


FIG. 2. Effect of concentration.

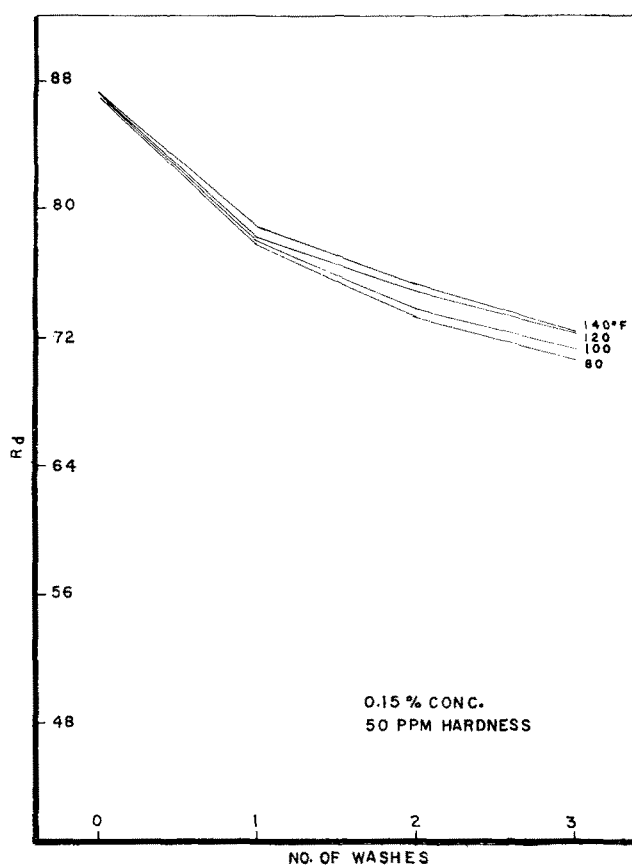


FIG. 3. Effect of temperature.

his book, *Detergency Evaluation and Testing*. The Committee of the American Association of Textile Chemists and Colorists have published some noteworthy papers, namely, Measurement of Fabric Soiling (4), Soiling of Fabrics in Contact with the Skin (5) and Soiling of Natural and Manufactured Fibers from Aqueous Systems (6). The Whirlpool Corp. has reported some interesting findings in The Fatty Acid Composition of Clothes Soil (7) and Detergency Evaluation (8).

Three excellent articles appeared in *Fette, Seifen und Anstrichmittel*, namely, Skin Fats and Their Characteristics (9), The Composition and Behavior of Clothing Soil (10) and The Causes and Prevention of Textile Soiling (11). Most recently, Schwartz and Berch (12) published an excellent laboratory procedure for predicting field performance of laundry detergents.

In practical testing, the towel test, (13) and bundle test (14) have been widely accepted. However, they are extremely costly and time-consuming and are therefore not satisfactory as screening procedures. The writers tried to use the towel test as a laboratory method by limiting the soiling procedure to laboratory technicians. This seemed to offer little advantage over shop distribution. Separate collars and cuffs were then distributed to laboratory personnel instead of Huck towels. Again, there seemed to be little advantage, particularly with regard to time. Finally, it was decided to make a list of objectives and try to devise a new procedure that would fulfill these conditions. These objectives were similar to those for the Dynamic Foam Test (15) and were: a) mechanization similar to present day washers; b) realistic soil; c) multiple washings; d) correlation with practical tests; e) complete application of soil in laboratory.

By using a Tergotometer for washing, padding on

a combination of airborne sebum type soil, washing for three soil-wash cycles and correlating the results with the towel tests, we hoped to fulfill the above listed objectives.

The literature reviewed gave no indication of the combination of airborne particulate combined with synthetic sebum having been used in any previous test procedure. One reason for this would be the fact that until air conditioning and electrostatic precipitators became commonplace, it was much easier to collect vacuum cleaner dirt or street dirt as a natural soil. However, the writers felt that this particulate was more representative of the soil embedded in collars and cuffs than most other natural particulate previously employed. The airborne soil used in this testing program was collected from the air conditioning units in three different locations. The soil was removed from the filters with a small vacuum cleaner and the entire contents of the "dust bag" were put into a large beaker partially filled with ethanol. The mass was alternately stirred and decanted until the supernatant liquid was clear. This removed all the oil and reduced the organic content. After drying on the steam bath, the contents were sieved through a 200 mesh screen to remove large particles. The particulate is then suspended in the emulsified sebum and this mixture is padded onto the cloth. Batch standardization is made by using a standard detergent.

Experimental

Apparatus. Tergotometer, laboratory wringer or padder (L&W Machine Works, Rock Hill, S. C.); print dryer (Gloss-O-Mat Beseler Co., East Orange, N. J.).

Reagents. Airborne soil obtained from air conditioners, air samplers, electrostatic precipitators, etc. This material is first washed free of oil with ethanol, dried on steam bath, then screened through a 200 mesh screen.

Synthetic Sebum.

Palmitic acid	— Fisher Tech A 224	10.0%
Stearic acid	— Fisher A-292 U.S.P.	5.0%
Coconut oil	— Armour Neo-fat 265	15.0%
Paraffin	— Fisher P-19 48C	10.0%
Spermaceti	— Fisher 0-475 U.S.P.	15.0%
Olive oil	— Fisher 0-111 U.S.P.	20.0%
Squalene	— Eastman 6966	5.0%
Cholesterol	— Fisher C-314	5.0%
Oleic acid	— Fisher A-215 U.S.P.	10.0%
Linoleic	— Fisher A-165	5.0%

Triethanolamine.

Procedure

Heat 50 g of the synthetic sebum until melted (not over 130F). Add 4 g oleic acid, 8 g of triethanolamine and 4 g of airborne soil. Thoroughly mix.

Add an amount of water equal to the volume already measured and stir. Then add 50 more ml of water and again restir. Homogenize this mixture twice with a hand homogenizer. Make up to 1000 ml with water at room temp and mix again. Pass 40—3 in × 6 in Indianhead swatches through the print dryer. Then soil these by immersing in a portion of the soiling medium and pass through the padder for 100% pickup.

Again pass through the print dryer (place between paper towels to avoid contaminating the apron).

Wash in sets of ten in the respective buckets of the

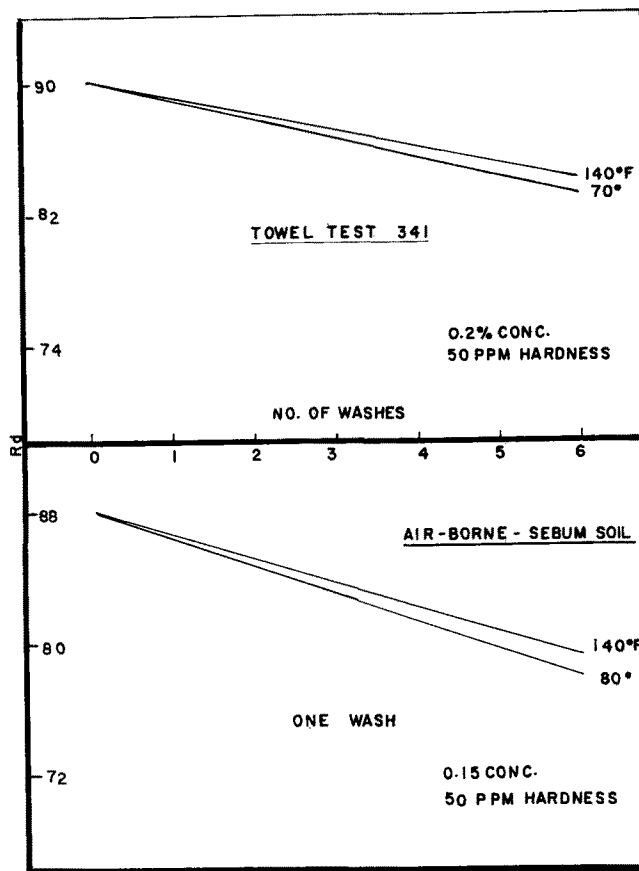


FIG. 4. Effect of temperature.

Tergotometer containing the experimental materials. Rinse-dry by passing twice through the print dryer. Repeat the soiling and washing procedure two more times.

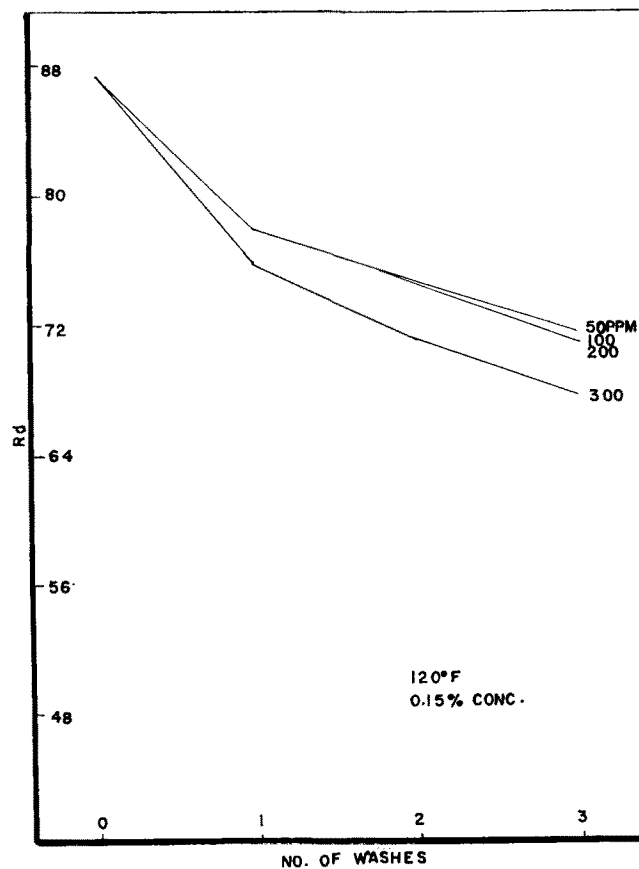


FIG. 5. Effect of water hardness.

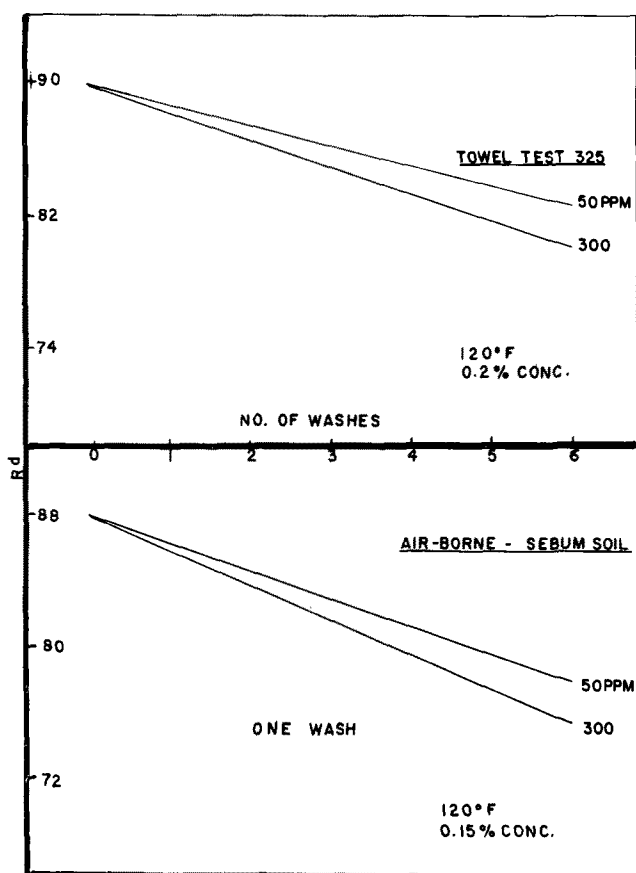


FIG. 6. Effect of hardness.

Measure the reflectance on a color difference meter. Calculate the mean and variance for each set of readings (12).

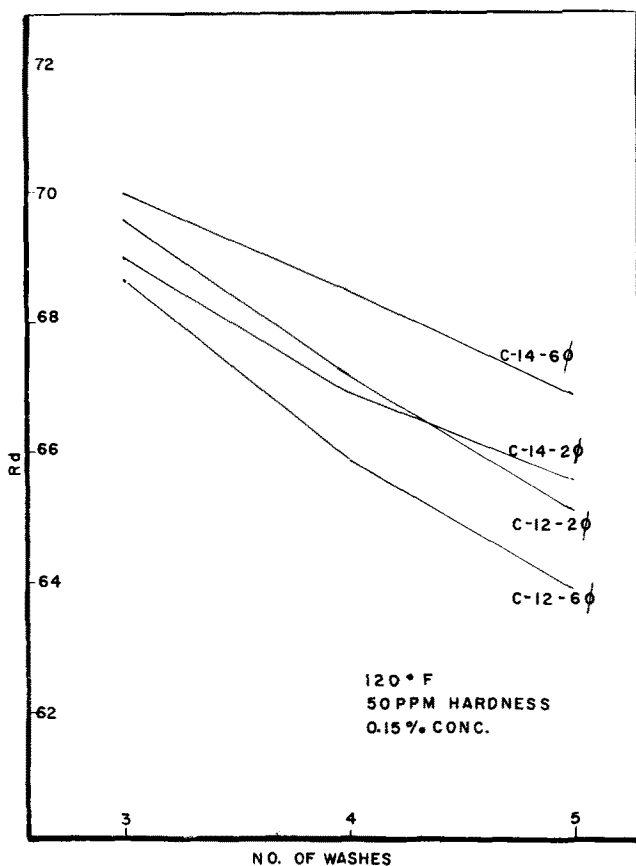


FIG. 7. Effect of phenyl position and chain length.

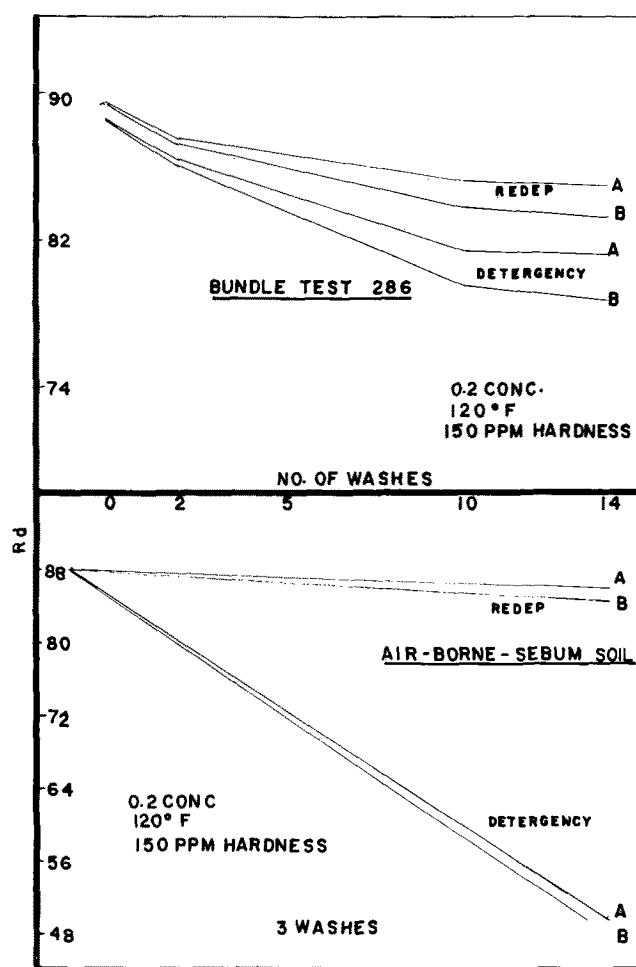


FIG. 8. Comparison of detergency and "redep."

Note: Control swatches may be included in each wash if it is desired to study redeposition and brightener effectiveness.

Results and Discussion

A typical high-foaming heavy-duty detergent was used to study the factors that have the greatest influence on detergency. These were detergent concentration, temperature, water hardness, phenyl position and chain length. The high foaming material contained 25% active ingredient of the alkylbenzene sulfonate type.

Figure 1 shows the effect of using the detergent at various concentrations in the wash solution. At the end of three washes, the results indicate that a 0.10% solution was a minimum effective level for detergency for this composition. This is equal to 0.025% active ingredient. Increasing the concentration failed to show much improvement. Figure 2 is a comparison of the test after one wash at 0.05% and 0.15% with a towel test at the same concentrations for six washes. The differences and final reflectance values indicate that one wash of the screening test approximates the results after six washes with the towel test.

Figure 3 depicts temperature effects in the range of 80°F to 140°F. There was approximately one reflectance unit difference for each 20°F increment of temperature after three washes. The data from this type of screening proved an advantage in modifying this standard type of heavy-duty product so that these temperature differences could be eliminated. Figure 4 is a comparison of one wash with the screening test and six washes with a similar type towel test. Again the differential and final reflectances are similar.

The effect of water hardness is more pronounced in the case of foam than detergent effects. Figure 5 shows a change from 50 ppm water hardness as CaCO_3 to 200 ppm produces a delta reflectance of approx 0.5 units after three soiling and washings. Progressing from 200 ppm to 300 ppm a delta Rd value of 4.5 units is indicated. Figure 6 again shows the same relationship existing to the towel test as previously shown.

The relationship of detergency to structure of straight chain alkyl benzene sulfonates is shown in Figure 7. These materials were formulated into a typical heavy-duty laundry composition at a 25% active ingredient level. It will be noted that both phenyl position and chain length are responsible for detergency effectiveness. These relationships are more fully discussed in a paper by Rubinfeld et al. (16).

Figure 8 was a comparison between a bundle test and the screening test with one half the amt of airborne soil and one half the water content. In other words 2 g of particulate were added to 500 ml of a 10% sebum emulsion. The Rd scale on the bottom chart is one half of the scale on the upper chart. In this comparison, both redeposition and detergency were measured in two products, A and B. Product A contained a different redeposition agent than product B. Both tests show approx the same reflectance difference between the two products for redeposition

and detergency. However, the screening test show the fabrics to have a reflectance in the upper forties after three washes, while in the bundle test, the clothes never go below 80% reflectance after 14 washes. Since the bundle test is composed chiefly of t-shirts, sheets, pillowcases, etc., one would expect the presence of very little particulate. A modification of this test will be presented at a later date, in which the particulate is omitted from the soiling mixture. This type of procedure more closely parallels so-called bundle testing.

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REFERENCES

1. Martin, A. R., and George P. Fulton, "Drycleaning," Textbook Publishers, Inc., New York, 1958, p. 49.
2. Diehl, F. L., and J. B. Crowe, *JAOCs* 31, 404 (1954).
3. Harris, J. C., "Detergency Evaluation and Testing," Interscience Publishers, New York, 1954.
4. New York Section AATCC, *Am. Dyestuff Repr.* 41, 322 (1952).
5. Washington Section AATCC, *Ibid.* 43, 751 (1954).
6. New York Section AATCC, *Ibid.* 44, 815 (1955).
7. Powe, W. C., and W. L. Marple, *JAOCs* 37, 136 (1950).
8. Davis, R. C., *Soap Chem. Spec.* 39, 47 (1963).
9. Walter, E., *Fette Seifen Anstrichmittel* 61, 188 (1959).
10. Oldenroth, O., *Ibid.* 61, 1142 (1959).
11. Lindner, K., *Ibid.* 65, 96 (1963).
12. Schwartz, A. M., and J. Berch, *Soap Chem. Spec.* 39, 78 (1963).
13. Michalik, W., and H. D. Cross, to be published.
14. Spangler, W. G., Colgate Research Report, unpublished, Oct., 1959.
15. Spangler, W. G., *JAOCs* 41, 300 (1964).
16. Rubinfeld, J. et al, Presented 1964 AOCs Meeting at New Orleans, April 19, 1964.

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Analyses of Fatty Acid Isomers in Two Commercially Hydrogenated Soybean Oils¹

E. P. JONES, C. R. SCHOLFIELD, V. L. DAVISON, and H. J. DUTTON
Northern Regional Research Laboratory,² Peoria, Illinois

Abstract

A conventional shortening and a hydrogenated winterized oil have been investigated to determine their composition of natural and isomeric fatty acids. Two solvent systems were applied in countercurrent distributions: the acetonitrile pentane-hexane system for separation of monoenoates from dienoates and the methanolic silver nitrate pentane-hexane system for separation of geometric isomers. While *cis* and *trans* monoenoates were well resolved, the separation of *cis,cis* from *cis,trans* dienoates was complicated by the presence of positional isomers. The fractions isolated were oxidatively cleaved, and the esters of the resultant acids were quantitatively analyzed by gas-liquid chromatography.

Although the amounts of saturated components of the two fat products were similar, the percentage of *trans* isomers of the shortening was more than twice that of the winterized oil. The amount of oleic acid (*cis*-9-octadecenoic) was 19.6% for the shortening and 25.4% for the winterized oil. The shortening contained 13.3% linoleic acid (*cis,cis*-9,12-octadecadienoic), whereas the winterized oil contained 30% linoleic acid.

Although our primary interest was in the estimation of *cis*-9-octadecenoic and *cis,cis*-9,12-octadecadienoic acids, the completeness of cleavage

data makes it possible to estimate all geometric and positional monoenoate and dienoate isomers in the two fat products.

Introduction

Hydrogenating fats produces many isomeric fatty acids because double bonds migrate and geometric isomers form. To increase our understanding of these complex changes, the composition of the unsaturated fats in two commercial products was studied and compared.

The complexity of the fatty acids formed on partial hydrogenation of methyl linolenate was described in previous studies (11,12,14) in which crystallization and countercurrent distribution (CCD) with acetonitrile and pentane-hexane and argentation CCD were used as fractionation tools. Kuemmel (8) in 1962 described the use of alumina chromatography of mercury adducts of fatty acid esters to perform quantitative separation of saturates, monoenoates, and polyenoates.

The use of silver nitrate for the separation of geometric isomers was initiated by Nichols (10) in 1952, but only recently has it been applied to mixtures of model compounds (4). An argentation CCD system has been described (13) and utilized to study partially hydrogenated methyl linolenate (12,14).

The effectiveness of this CCD system for the analysis of two commercially hydrogenated fat products is reported here. By applying various procedures to

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² A laboratory of the No. Utiliz. Res. and Dev. Div., ARS, USDA.