Detergency Measurement Using Artificially-Soiled Cloths[1]

F. L. DIEHL and J. B. CROWE, Procter and Gamble Company, Cincinnati, Ohio

ARTIFICIALLY-soiled cloths have found wide acceptance in the textile, laundry, and detergent industries in the evaluation of detergent products and methods. Manufacturer and operator alike faced with an optimum selection from a multitudinous array of soaps, synthetic detergents, detergency aids, and combinations thereof have resorted to the use of so-called "standard" soiled cloths in evaluation of detergency performance. Too often such cloths are "standard" only in name, in that they fail to meet one or more of the requirements usually expected of a soiled test fabric. These are:

1. The soiled cloths should rank detergent products in the same order as obtained in actual usage tests under practical conditions.
2. The soiled cloths should give reproducible results from batch to batch of cloth as well as within batches of cloth.
3. The soiled cloths should have sufficient sensitivity to distinguish known differences between detergents with a minimum expenditure of time and effort.

The first of these requirements, that of correlation with practical tests, is the most important of the three, since a wrong answer on soiled test cloths may result in serious economic losses. However the other requirements necessarily follow in order that the investigator will know when he has correlation with practical tests.

Few published papers on development of artificially-soiled cloths attempt correlation with practical tests. Exceptions are papers by Harris and Brown (4), Sanders and Lambert (6, 11), and Vaughn (14). Other investigators (5, 8, 15) have compared several types of soiled test fabrics in the evaluation of detergent systems or types of detergents. A number of the soiled cloths used are commercially-available and presumably were calibrated against practical tests on a given series of detergent products. The lack of agreement among test fabrics reported is an illustration of the limitations on their use; that is, successful correlation on a few detergent systems or types of detergents does not necessarily imply that application of the "standardized" soiled cloth to testing of other systems or types will continue to show correlation with practical tests.

The present paper serves to re-emphasize the lack of agreement between different types of artificially-soiled cotton test fabrics in evaluation of detergency performance of representative detergent products and the limitations on their use.

Experimental

Soiled Test Cloths. Four different types of artificially-soiled cloths were used. Three of these are commercially available; the fourth is from a private laboratory. Different batches of each test fabric were ordered at two-week intervals, such that two or three batches of each were available for test. The test swatches used were randomized within batches.

Wash Test Methods. The Launderometer (7) method used was essentially that described by Crowe (2) for cotton fabric, with certain exceptions:

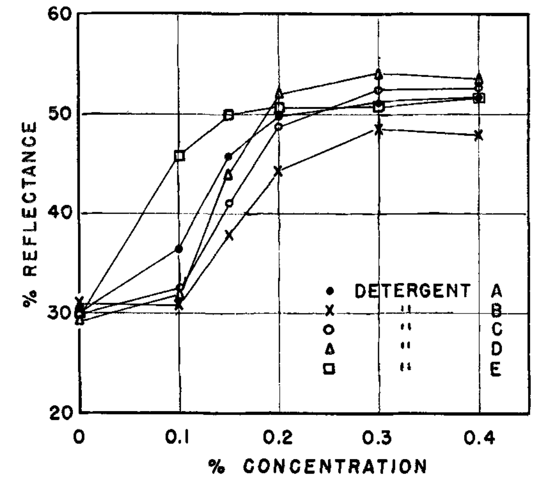

FIG. 1. Detergency as measured by fabric No. 1.

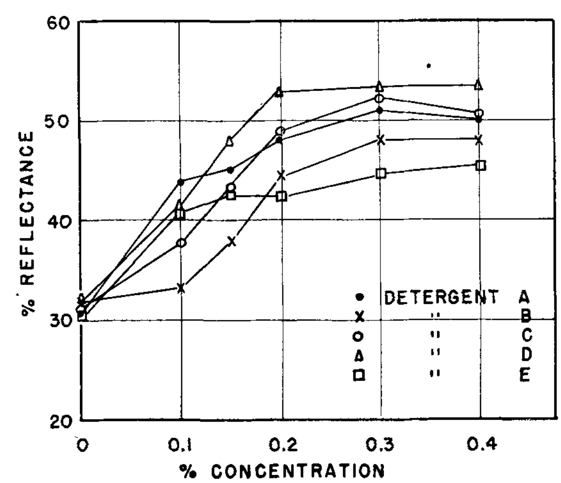

FIG. 2. Detergency as measured by fabric No. 2.

1. The water hardness was 7 gr./gal. (120 p.p.m.).
2. The temperature was 130°F. (54.5°C.).
3. Volume of test solution was 200 ml.
4. Duration of wash was 20 minutes.
5. Two 2½ in. x 2½ in. soiled swatches and two clean swatches of the same size were placed in each pint jar. The clean swatches were bleached white cotton print cloth, unsized, thread count 84 x 68, weight 3.0 oz./yd.

Detergents Used. The five detergents used are commercially available soaps and built synthetics. Among these are built and unbuilt soaps, built fatty alcohol sulfate, built alkyl aryl sulfonate, and built non-ionic.

Number of Tests. All four soiled test fabrics were evaluated by performance tests, on all detergent products at concentrations 0, 0.1, 0.15, 0.2, 0.3, and 0.4% on an "as-is" product basis. Duplicate tests were run at each concentration, with the exception of 0 and 0.4%.

In addition, two or three batches of each soiled cloth were evaluated in the same manner, with duplicate runs on at least one batch of each cloth.

Grading of Test Pieces. Reflectance measurements were made on the soiled test pieces and whiteness

[1] Presented at the 25th annual fall meeting, American Oil Chemists' Society, Chicago, Ill., October 8-10, 1951.

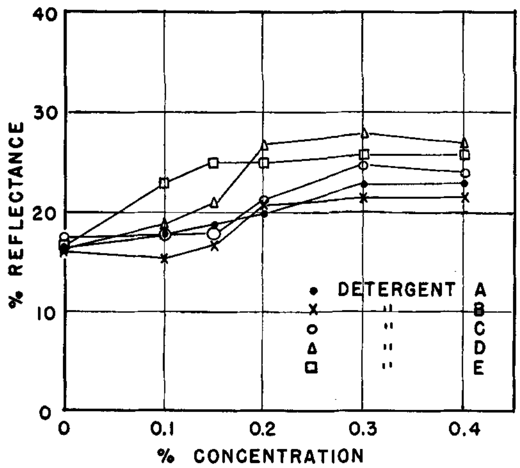

Fig. 3. Detergency as measured by fabric No. 3.

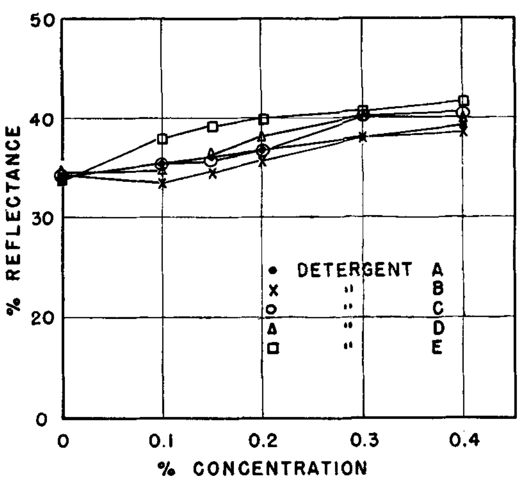

Fig. 4. Detergency as measured by fabric No. 4.

retention swatches after washing. The Photovolt Reflection Meter, Model 610 (10), was used for this purpose.

Comparative Ranking of Products as to Detergency

Results of wash tests on the four soiled fabrics are shown in Figures 1-4, respectively. Each point on the curves, with the exception of those at 0 and 0.4% concentration, is an average of the reflectance of 16 swatches. Each point at 0 and 0.4% concentration is an average reflectance of 8 swatches.

In general, it will be noted that all fabrics do not rank the detergents in the same order. The lack of agreement is best illustrated by selected pairs of detergents as in Figures 5 and 6.

In Figure 5, fabrics 1, 2, and 3 show an advantage for Detergent A compared to Detergent B whereas fabric 4 shows no difference. The situation is more serious where actual reversals of order are observed, as in Figure 6. Fabric 2 shows an advantage for Detergent A over Detergent E; fabric 1 shows substantially equal detergency whereas fabrics 3 and 4 show an advantage for Detergent E.

For purposes of simplicity, further discussion of Figures 1-4 will be confined to results at the 0.3% concentration since this point is approximately that at which maximum detergency occurs. At this concentration the comparative ranking of the various detergents may be summarized as in Table I.

TABLE I

Comparative Ranking of Five Detergent Products by Four Different Detergency Test Fabrics and Practical Tests as to Maximum Cleaning

Fabric No. 1		Fabric No. 2		Fabric No. 3		Fabric No. 4		Practical
Detergent	Reflectance	Detergent	Reflectance	Detergent	Reflectance	Detergent	Reflectance	
D	54.5	D	53.5	D	28.3	E	40.3	D
C	52.8	C	52.5	E	25.8	D	39.8	C
A	51.8	A	50.8	C	25.0	C	39.8	A
E	51.2	B	48.5	A	22.8	A	38.3	E
B	48.8	E	44.5	B	21.3	B	38.3	B
(Yardstick[a])	(2.4)		(2.5)		(1.1)		(.08)	

[a]An estimate of the reliability of the mean reflectance values given in Table I enables a judgment of the significance of the data. This is obtained by computation of standard error values for the means by statistical techniques described by Brownlee (1) and calculation of a "yardstick" applicable to the $k(k-1)/2$ contrasts, where k is the number of means to be compared. A conclusion as to the reality of a difference equal to the calculated yardstick will be in error only one time in 20 experiments. The yardstick is based on a method proposed by Tukey (13).

Note that detergents D, C, A, B are rated in that order by each of the four soiled fabrics. Detergent E is ranked successively fourth, fifth, second, and first by fabrics 1 to 4. Use of a bar in Table I to bracket several mean values indicates no experimental evidence of a significant difference within the group.

Correlation with Practical Tests

The comparative ranking of the detergent products by practical tests is also included in Table I. These ratings are based on wash tests on naturally-soiled clothes and practical laundry experience, both house-

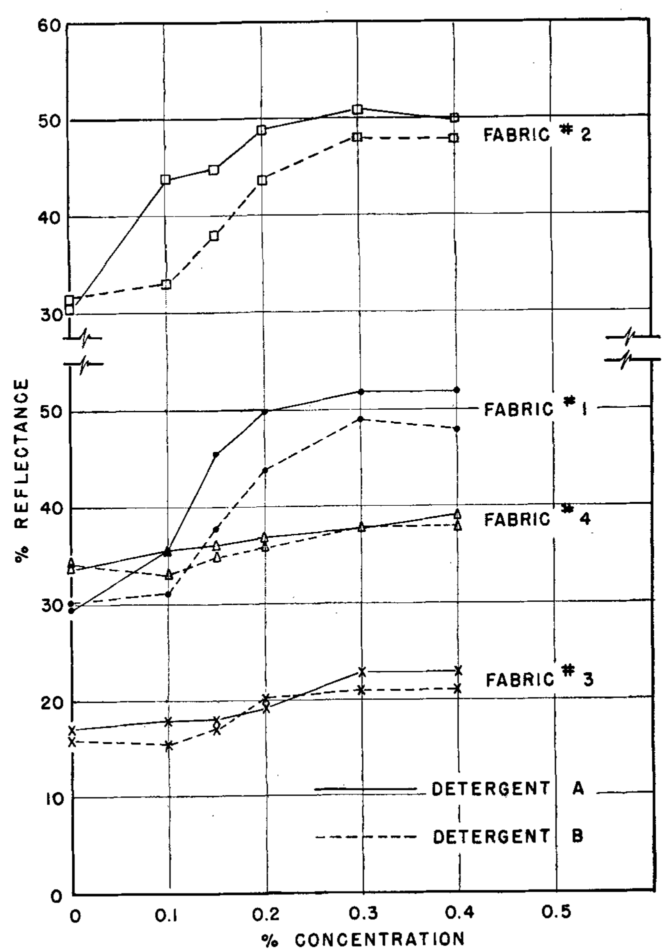

Fig. 5. Detergency comparison of detergents A and B on four test fabrics.

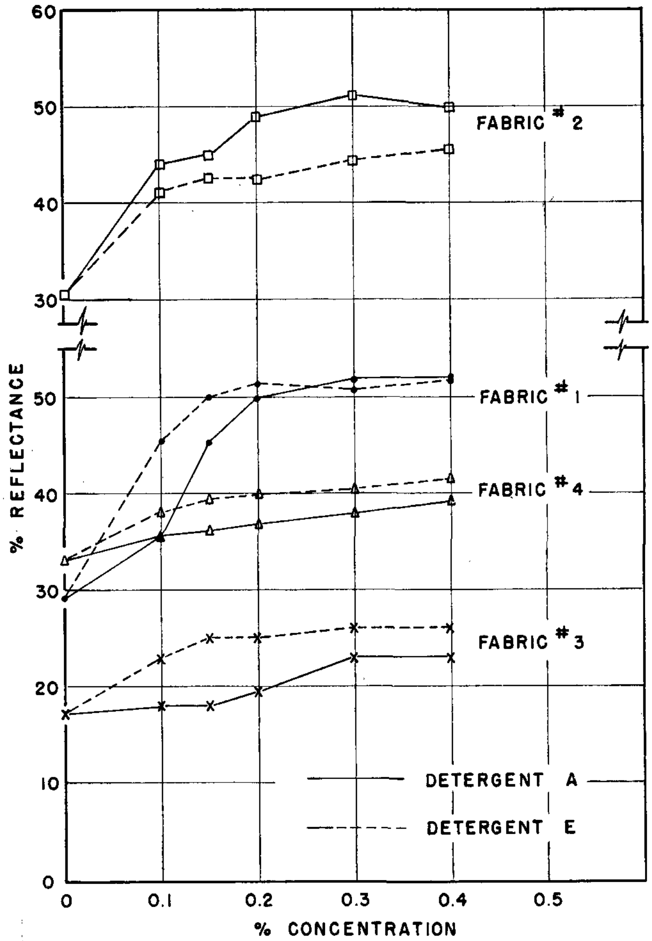

FIG. 6. Detergency comparison of detergents A and E on four test fabrics.

hold and commercial. The probable order of cleaning is D, C, A, E, B, with differences among C, A, and E probably not discernible except under favorable conditions.

Based on the above rating as the true one, the degree of correlation of the test fabrics with practical tests is that given in Table II.

Calculation of the correlation coefficient shows that only fabrics 1 and 3 give a significant correlation with practical tests as to ranking of the five detergent products. It should be emphasized however the correlation with practical tests is not implied for other than the specific group of detergents here employed. The better correlation with practical tests obtained on fabrics 1 and 3 will not necessarily apply to an expanded series of detergent products.

TABLE II

Rank Correlation of Detergency Test Fabrics with Practical Tests

Detergent	Practical tests	Fabric No. 1	Fabric No. 2	Fabric No. 3	Fabric No. 4
D	1	1	1	1	2.5
C	3	2	2	3	2.5
A	3	3	3	4	4.5
E	3	4	5	2	1
B	5	5	4	5	4.5
Correlation coefficient[a] with practical tests		0.90[b]	0.75	0.90[b]	0.55

[a] Spearman's rank correlation coefficient calculated as given in Snedecor (12).
[b] Significant at 0.05 probability level, *i.e.*, there is a probability of 1 in 20 that the correlation is zero, based on Olds (9).

Reproducibility

Reproducibility Within the Same Batch or Lot. Inspection of the standard error values given in Table III affords an estimate of the reproducibility of test results with the various soiled test fabrics within a given batch. The lower the standard error of the mean, the greater the precision of results based on a given test fabric. Thus precision obtained with the various test fabrics is in the order fabric 4, 3, 1, and 2 with 1 and 2 about equal in precision.

TABLE III

Statistical Values Applicable to Data from Wash Tests—for Means of Eight Jars (16 Swatches) as in Figures 1-6

	Standard error of mean	Confidence limits for means[a]
Fabric 1	.61	$\bar{X} \pm 1.2$
Fabric 2	.65	$\bar{X} \pm 1.3$
Fabric 3	.29	$\bar{X} \pm 0.6$
Fabric 4	.20	$\bar{X} \pm 0.4$

[a] The true value of the mean lies within the stated range subject to a risk of error of 1 in 20.

Reproducibility Among Batches. Wash test results on different batches of the same soiled fabric show that for each fabric, with the exception of fabric 2, the differences in cleaning levels among batches are no greater than the difference between duplicate runs on the same batch. With fabric 2 (Figure 7) however the first batch shows a considerably higher cleaning level than either the second or third batch.

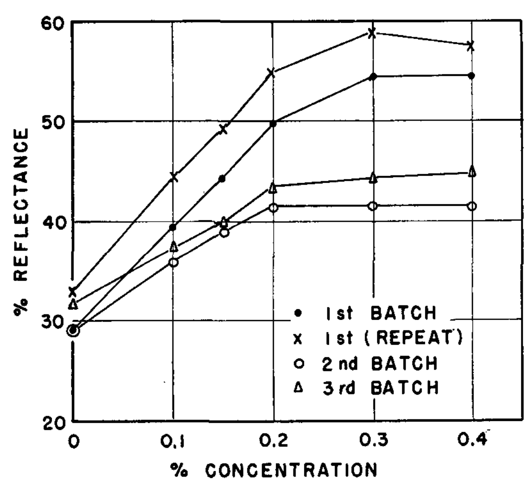

FIG. 7. Differences in detergency among batches of fabric No. 2.

Sensitivity

Equally as important as reproducibility in test results is the ability of the soiled test fabric to discriminate between products as to known differences in detergency. A test fabric may give very precise results, yet the very reason for the high precision may be insensitiveness to differences in cleaning. Very often an increase in sensitivity results in decreased precision such that a compromise between these two characteristics is necessary.

A choice can best be made by determining which soiled test fabric gives the greatest spread between given detergents in terms of the precision of test

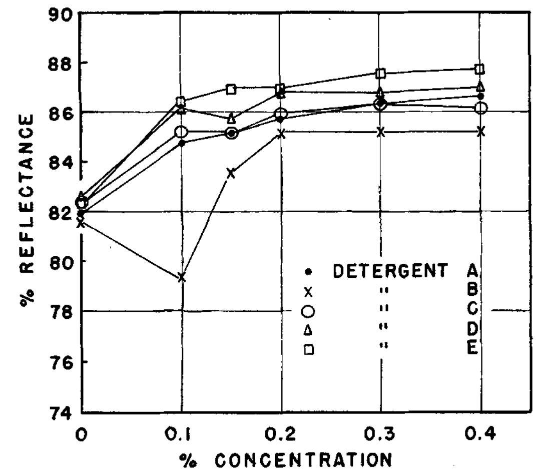

Fig. 8. Whiteness retention measured with fabric No. 1 as soil source.

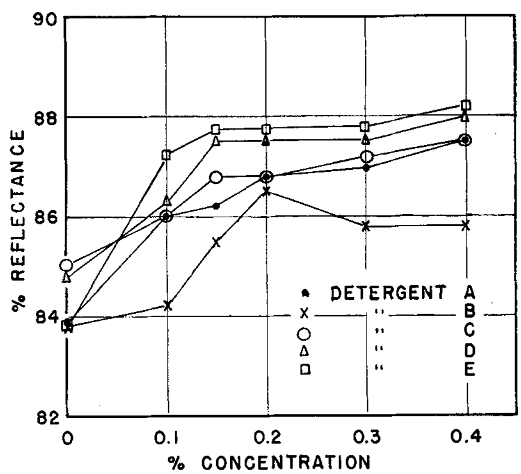

Fig. 9. Whiteness retention measured with fabric No. 2 as soil source.

results with the particular fabric. An alternative method of selection would be to determine the number of tests required to ensure detection of a difference between two specified detergents.

Both of these methods have been employed in Table IV in comparing the soiled fabrics. Detergents D and B were selected since the difference between them is the greatest in practical tests.

Fabric 3 represents the best compromise between precision and sensitivity inasmuch as the spread between detergents D and B is about 24 times the standard error of the mean. Furthermore only one launderometer run is required to detect a true difference of 7.0 reflectance units whereas three to four runs are required for the D-B difference with the other fabrics.

TABLE IV

Sensitivity of Soiled Test Fabrics with Respect to Detection of Differences Between Products

	(A) Observed spread Detergent D-Detergent B	(B) Standard errors	Method I (A)/(B)	Method II Number of launderometer runs[a] required to detect real difference of magnitude (A)
Fabric 1	5.7	.61	9.3	3
Fabric 2	5.0	.65	7.7	4
Fabric 3	7.0	.29	24.0	1
Fabric 4	1.5	.20	7.5	4

[a] Each run to consist of two jars, two swatches per jar. Prediction of number runs required based on Ferris, Grubbs, and Weaver (3).

Effect of Soiled Test Fabrics on Whiteness Retention Measurement

Results of whiteness retention tests with the various soiled test fabrics as load are shown in Figures 8-11. (Reflectance measurements have been made on originally-clean white swatches included in each jar. The source of redeposited soil is the soiled test swatches themselves.)

The most striking difference between the fabrics is the spread exhibited between detergent products with certain fabrics (fabric 3) while others give little or no spread, *e.g.*, fabric 4. For purposes of simplicity results are summarized in Table V for the 0.3% concentration only. (See footnote for Table I.)

There is some evidence of differences in ranking of detergent products as to whiteness retention with the various soiled test fabrics as load. However the differences between products are so small, except with fabric 3, that it is difficult to attach any significance

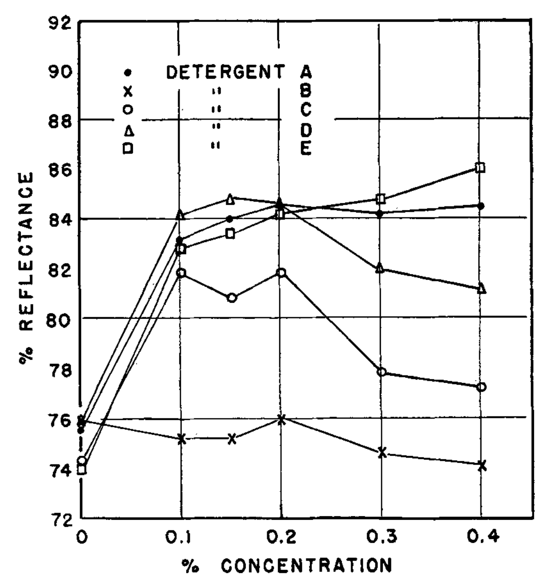

Fig. 10. Whiteness retention measured with fabric No. 3 as soil source.

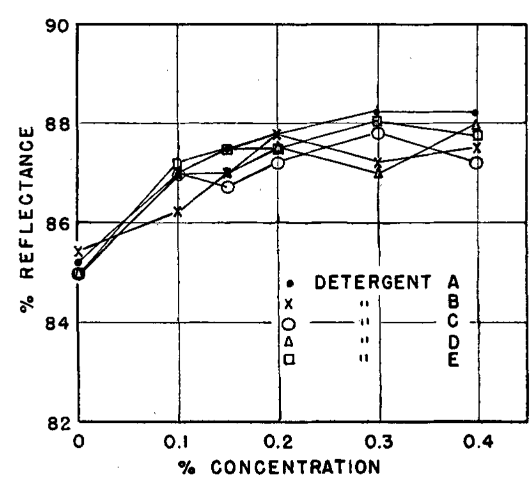

Fig. 11. Whiteness retention measured with fabric No. 4 as soil source.

to these ratings. As before, the use of a bar in Table V to bracket several mean values indicates no experimental evidence of a significant difference within the group. Statistical values for whiteness retention are given in Table VI.

TABLE V

Summary of Whiteness Retention Rankings with Four Detergency Test Fabrics as Soil Load

Fabric No. 1		Fabric No. 2		Fabric No. 3		Fabric No. 4	
Detergent	Reflectance	Detergent	Reflectance	Detergent	Reflectance	Detergent	Reflectance
E	87.5	E	87.8	E	84.8	A	88.2
D	86.8	D	87.5	A	84.2	E	88.0
C	86.5	C	87.2	D	82.0	C	87.8
A	86.5	A	87.0	C	77.8	B	87.2
B	85.3	B	85.8	B	74.5	D	87.0
(Yardstick)	(0.7)		(0.9)		(0.8)		(0.6)

TABLE VI

Precision of Whiteness Retention Data

	Standard error of mean	Confidence limits for means
Fabric 1	0.18	$\bar{X} \pm 0.4$
Fabric 2	0.24	$\bar{X} \pm 0.5$
Fabric 3	0.20	$\bar{X} \pm 0.4$
Fabric 4	0.16	$\bar{X} \pm 0.3$

Summary and Conclusions

Four types of artificially-soiled cloths are compared in their ability to evaluate cleaning of representative detergent products. Three of these cloths are commercially available while the fourth is from a private laboratory. These are compared in their ability to rate detergents in the same order as naturally-soiled clothes rate detergents. Sensitivity and reproducibility of the various soiled cloths in measurement of soil removal and whiteness retention are studied.

Results show that artificially-soiled cloths must be used advisedly. There is no substitute for actual performance tests of detergent products under practical conditions. At best, artificially-soiled cloths are useful for "screening" purposes where positive test results are confirmed by practical tests.

REFERENCES

1. Brownlee, K. A., "Industrial Experimentation," Chapters XI and XII, j, Brooklyn, New York, Chemical Publishing Company (1947).
2. Crowe, J. B., American Dyestuff Reporter, *32*, 237-241 (1943).
3. Ferris, C. D., Grubbs, F. E., and Weaver, C. L., Annals Math. Statistics, *17*, 178-197 (1946), Section 7, Power Function of the t-Test; $\alpha = 0.05$, $\beta = 0.05$.
4. Harris, J. C., and Brown, E. L., J. Am. Oil Chemists' Soc., *27*, 135-143 (1950).
5. Harris, J. C., and Brown, E. L., J. Am. Oil Chemists' Soc., *28*, 96-100 (1951).
6. Lambert, J. M., and Sanders, H. L., Ind. & Eng. Chem., *42*, 1388-1393 (1950).
7. Launderometer, Atlas Electric Devices Company, Chicago, Ill.
8. Merrill, R. C., and Getty, R., Ind. & Eng. Chem., *42*, 856-61 (1950).
9. Olds, E. G., Annals Math. Statistics, *20*, 1, 117 (1949); *9*, 2, 133 (1938).
10. Photovolt Reflection Meter, Model 610, Photovolt Corporation, New York, N. Y.
11. Sanders, H. L., and Lambert, J. M., J. Am. Oil Chemists' Soc., *27*, 153 (1950).
12. Snedecor, George W., "Statistical Methods," 4th Edition, p. 165, Iowa State College Press, Ames, Ia., 1946.
13. Tukey, John W., Method described by H. Scheffe, J. Am. Stat. Assn., *47*, 381-400 (1952).
14. Vaughn, T. H., *et al.*, Ind. & Eng. Chem., *41*, 112-119 (1949).
15. Woodhead, J. A., and Paichtel, H., "Some Inadequacies of the Soiled Cloth Detergency Test," Abstracts of Papers, XIIth International Congress of Pure and Applied Chemistry, New York, N. Y., Sept. 10 to 13, 1951, p. 146.

[Received December 29, 1952]

Fractionation of Castor Oil Methyl Esters by Liquid-Liquid Extraction

RALPH H. McCORMACK, University of Detroit, Detroit, Michigan, and
DON S. BOLLEY, Baker Castor Oil Company, Bayonne, New Jersey

METHYLATION of castor oil produces a mixture of methyl esters useful in reactions involving ricinoleic acid. The composition of castor oil, as given by Dean (5), ricinoleic 87.0%, oleic 7.0%, linoleic 3.0%, dihydroxystearic 0.5%, saturated 2.5%, and Bolley (2) shows the nature of this ester mixture. While the methyl esters, other than methyl ricinoleate, do not interfere particularly with the ricinoleic acid reactions, it is nevertheless desirable to remove them so as to have the purest possible starting material.

Since it is well known that compounds are most soluble in solvents which they resemble structurally, it is reasonable to suppose that the hydroxylated compounds, methyl ricinoleate and the methyl ester of dihydroxystearic acid, would be preferentially distributed in the alcohol phase in an alcohol-castor oil methyl ester-hydrocarbon system and that the non-hydroxylated compounds, methyl oleate, etc., would appear chiefly in the hydrocarbon phase.

Consideration of the possibility of separating castor oil methyl esters by liquid-liquid extraction is not entirely new. Cannon (4) discussed the separation of methyl ricinoleate and methyl 12-hydroxystearate in the hydrocarbon (pentane-hexane)-nitroparaffin (20% nitromethane-80% nitroethane) system. Methanol, of all of the alcohols, is the most like water and the least like a hydrocarbon. It is therefore the least soluble of the mono-hydroxy alcohols in hydrocarbons. The castor oil methyl esters are completely soluble in methanol and are produced in this solvent. Methyl alcohol is then preferred over other alcohols as one of the solvents in any liquid-liquid extraction system. There are a great many theoretical possibilities for a hydrocarbon solvent in such a system, but availability, ease of removal from castor oil methyl esters, and cost make pentane, hexane, and heptane the three practical solvents. Preliminary experiments showed that these three solvents were about equal in solubility in methanol and in selectivity for the non-hydroxylated methyl esters. Since this was the case, heptane was selected as the hydrocarbon solvent. It is being used for the extraction of castor oil from the press cake, and its use in fractionation would not involve handling a new solvent in the plant.

The first experimental work in this investigation was the determination of the solubility relations in the system methanol-castor oil methyl esters-heptane.