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Choice and Application of a Detergency Test Method[1]

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THE correct evaluation of detergent compositions in a variety of end uses is of vital and continuing interest to the detergent industry. A growing number of test procedures have been independently described in the literature (2, 3, 4), particularly during the past 10 years which have witnessed the greatest expansion of the synthetic detergent business. Some of these tests are relatively simple and closely parallel actual use conditions. Others are more complex, having diverged markedly from conditions simulating end application in the quest of more exact reproducibility. When properly interpreted however, the majority of these tests have proven to be capable of consistent results.

As a contribution to the information on detergency test methods herewith is presented a typical launderometer procedure which has been successfully applied over a number of years to the evaluation of detergents based on the Ultrawets, an homologous series of alkyl aryl sulfonates.

This test procedure was developed specifically for the evaluation of heavy duty detergents, that is detergents for heavily soiled white cotton goods. To be satisfactory it was considered essential that the test first, accurately evaluate the efficacy and utility of the products in the field of intended application; second, give consistent comparative detergency patterns with respect to a standard reference detergent; and last, be sufficiently simple in nature to permit rapid performance with a minimum of specialized equipment and skills.

To insure meeting the first and most important of these requirements, relative performance ratings on cotton were first established on an accepted proprietary detergent (a built fatty acid soap) and on a typical unbuilt alkyl aryl sulfonate (35% active, 65% sodium sulfate) known to be deficient in this application. This was accomplished by subjecting white cotton shirts and towels to repeated cycles of soiling, by normal wear and use in families including young children, and laundering in typical household equipment. Series of three, five, 10, and 20 cycles were employed to establish relative field performance ratings on different detergents. All field tests ratings were based on visual comparisons made significant by carrying the tests through a number of cycles sufficient to produce marked differences.

Working from these field ratings on products of different merit, a launderometer procedure was then sought which would show like differences in performance under test conditions approximating actual use conditions. Paralleling what was considered to be typical home laundry practice, use conditions of 100 p.p.m. hardness water, a temperature of 120°F., and a wash cycle time of 20 minutes were adopted.

The choice of test swatch size, 2″ x 4″, was based on the A.A.T.C.C. Method for Color-fastness to Domestic Washing of Cotton (6). The relatively small 2″ x 4″ swatch is sufficiently mobile in the Launderometer test jar to insure a uniform degree of mechanical flexing which is important to uniform detergency results. While the standard test swatch containing on the average 0.0215 g. (3.0 wt. %) of soil represents a light poundage load of soiled fabric on the volume of detergent solution used, this has proven to be a minor factor in test correlation with field performance. Then by experimentation a combination of test fabric and soil was found which was capable of giving the desired comparative detergent patterns which are plots of detergency versus detergent concentration. Using the above standardized conditions, experiments were run to find the combination of cloth plus soil composition which would give the results desired.

A white oxford cloth was adopted as the preferred fabric in this test because it seemed to give more uniform results, possibly because of the loose weave and the very light starch processing size which can be completely removed by simple means. Permanently sized cloth did not give the desired results with the varied soils tested.

The composition of, and detergency patterns obtained with a number of the different soils tested, are shown in Figure 1. The 1 AX soil was chosen for our test method since, with it, the satisfactory proprietary detergent gave a near white deterged swatch in a single wash cycle and yet left sufficient residual soil to permit the method to be used in evaluating improved or superior products; and, of most importance, the 1 AX soil gave clearly distinguishable differences in detergency patterns between the known satisfactory and unsatisfactory reference compositions. It is of interest to note in passing that

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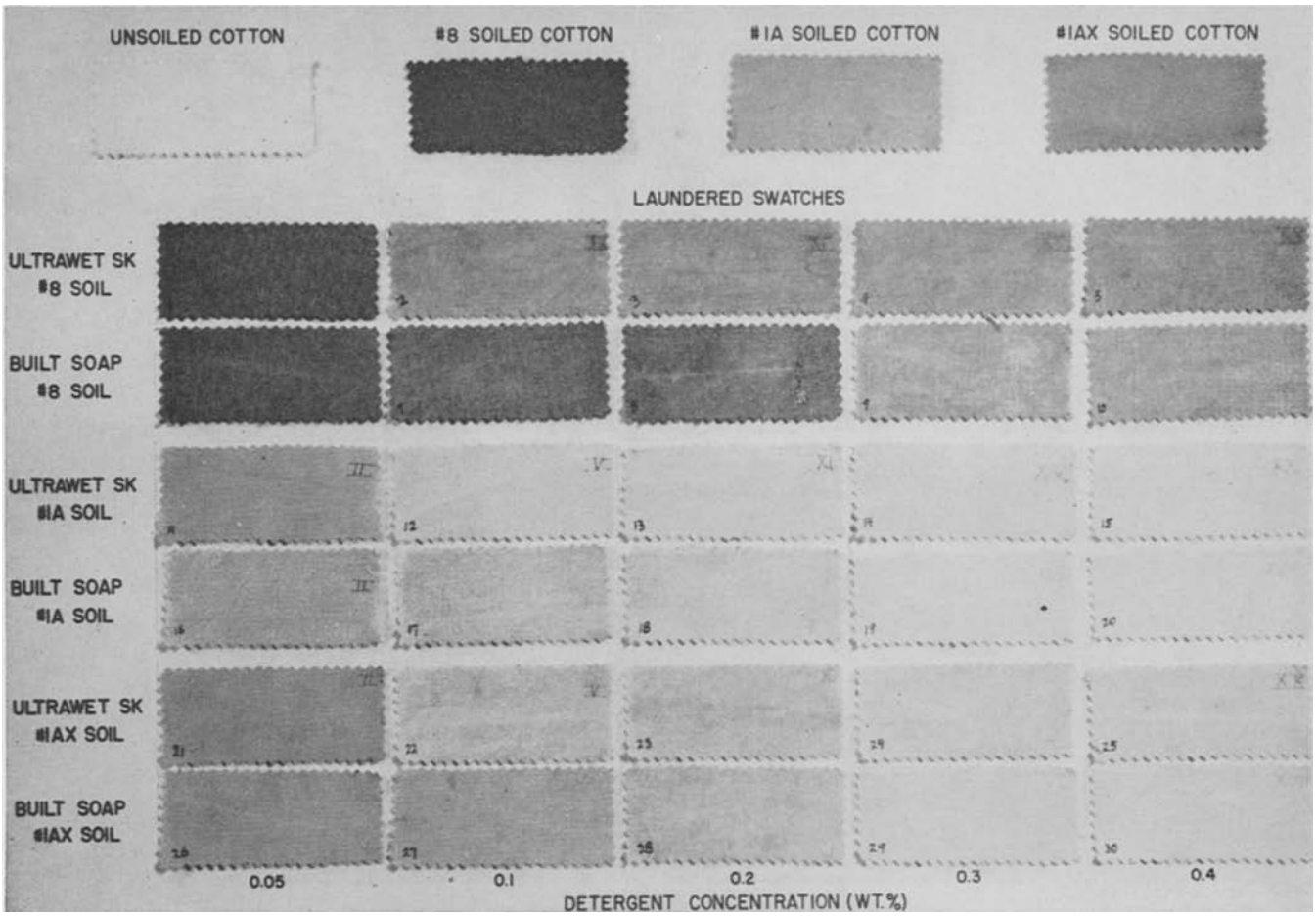

FIG. 2. Cotton detergency.

this same 1 AX soil was independently selected as the most suitable soil for detergency evaluation work on woolen fabrics.

The work on soil formulae led to these general observations, a number of which have been substantiated by other workers: (1)

a) Carbon black alone deterges from cotton very easily and is not therefore a satisfactory soil. Ease of detergency varies somewhat among different blacks and even among various brands of lampblack.

b) Either fatty or petroleum oil added to carbon black increases the difficulty of deterging the black from cotton.

c) Variation of the carbon black content of oil-black soil compositions changes the relative level of the detergency patterns.

d) Additions of materials such as proteins, urea, etc., merely complicate the soiling procedure.

e) Additions of dispersing or penetrating agents to typical soils usually result in heavily soiled swatches having a low key detergency pattern (dark laundered swatches).

f) Measurement of the light reflectance of lightly soiled swatches appears to be an accurate means for determining the whiteness of cotton as observed by the human eye.

g) Typical patterns are obtained when detergency is plotted against detergent concentration, and this relationship can be used to distinguish between various products which are relatively close in detergent ability. Usually the better products will exhibit higher detergency values at lower use concentrations.

These observations are portrayed in part in Figure 2. From this combination of data the test method described in the appendix was adopted.

In the development and application of this method all tests have been made on a comparative basis, obtaining results on at least one and usually two known reference detergents with each lot of soiled swatches. While the launderometer test exhibits its share of vagaries and inconsistencies of the type frequently lamented by people concerned with detergency testing, the occasional erratic results are usually accompanied by erroneous results on the reference detergents. About 85 to 90% of the detergency patterns obtained on a single reference sample over an 18- to 20-month period fell within the limits of variance indicated by the shaded zone in Figure 2A and were regarded as satisfactory reference patterns for comparative purposes. In the instances where detergency patterns have not been of typical shape or have fallen outside of the indicated zone, tests run on that lot of swatches have been repeated.

No advantage has been found in extending this test over a series of launderometer cycles on the same swatches in an effort to minimize the detergency variation from test to test. The detergency values at the different concentrations are capable of numerical reduction to performance numbers based on a reference detergent, but it is preferable to keep the actual detergency patterns before one for the evaluation picture. To facilitate comparison of results across a large number of samples run over a long period of time it has been demonstrated that the values in individual comparative patterns may

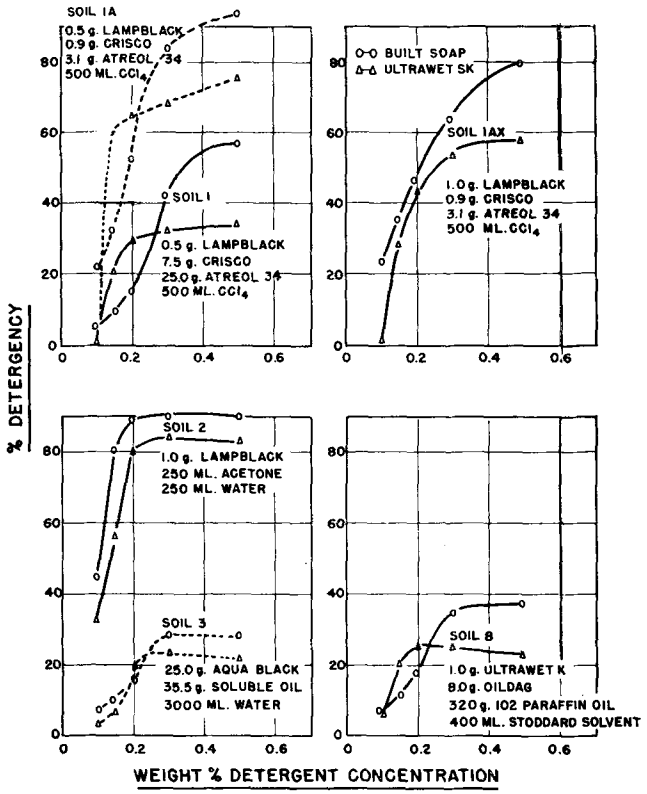

FIG. 1. Cotton detergency. Variant soils.

be adjusted in proportion to the adjustment necessary in values obtained on the reference product to correct it to the experimental mean value.

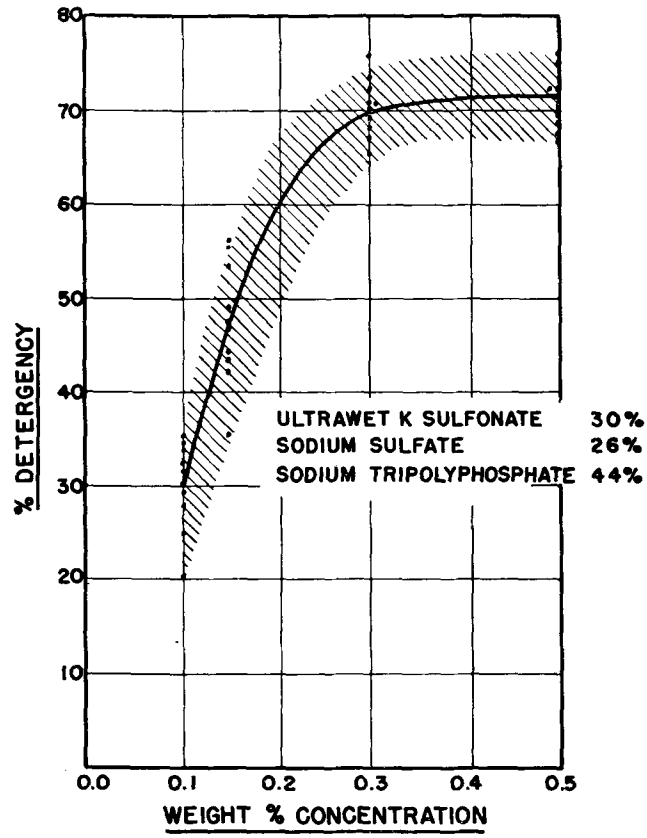

FIG. 2A. Degree of variance in cotton detergency patterns on a single reference detergent.

In the comparative detergency plots shown in this paper the relative pattern for a built fatty acid soap is shown in Figures 1 and 3. In these plots it can be seen that at a typical use concentration of 0.3%, a detergency rating of 70 is obtained. This same concentration of soap in practical tests in typical household washing machines satisfactorily washed white shirts and towels. Hence a detergency rating of 70 at any detergent concentration up to 0.3% was considered to be satisfactory for the job in question.

With these fundamentals in mind, development work on building the Ultrawets, typical alkyl aryl sulfonates, was initiated with the results illustrated in Figures 3 and 4. The detergency pattern plots in Figure 3 show that it was possible to build an alkyl aryl sulfonate to the point where it would perform satisfactorily in the launderometer test. It followed that if these materials behaved the same in practical tests as in the launderometer, a worthwhile laboratory procedure for evaluating the products in question would have been developed.

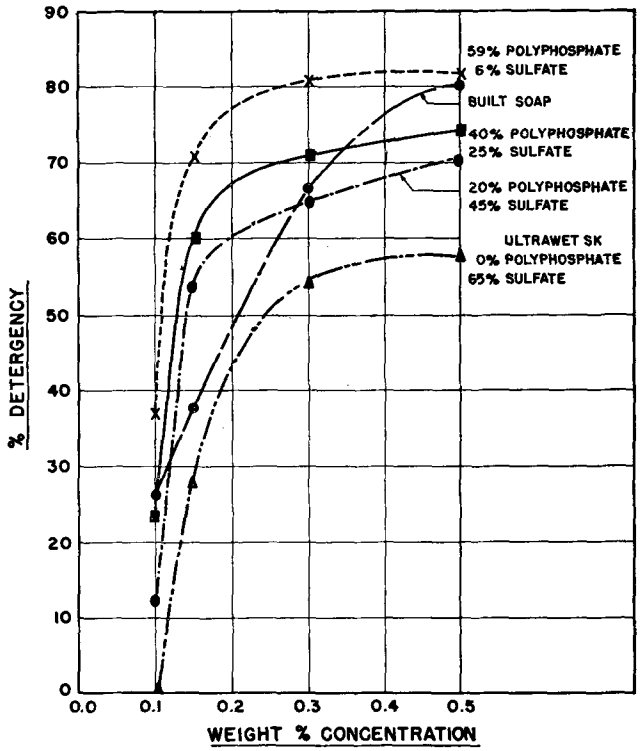

FIG. 3. Cotton detergency. Effect of substitution of sodium tripolyphosphate for sulfate in formula containing 35% active sulfonate—ultrawet K series.

In order to check this point household laundry field tests were again run on the original fatty acid soap, the unbuilt synthetic, and the built synthetic. The results closely paralleled those obtained in the launderometer, thus confirming the test method. A further check was made by running the built synthetic in a commercial laundry where satisfactory washing results were obtained on both light and heavily soiled cotton fabrics.

The relationship of household and commercial laundry temperatures as portrayed by this test are shown in Figure 4. The detergency patterns obtained upon building with different alkalies are compared at the

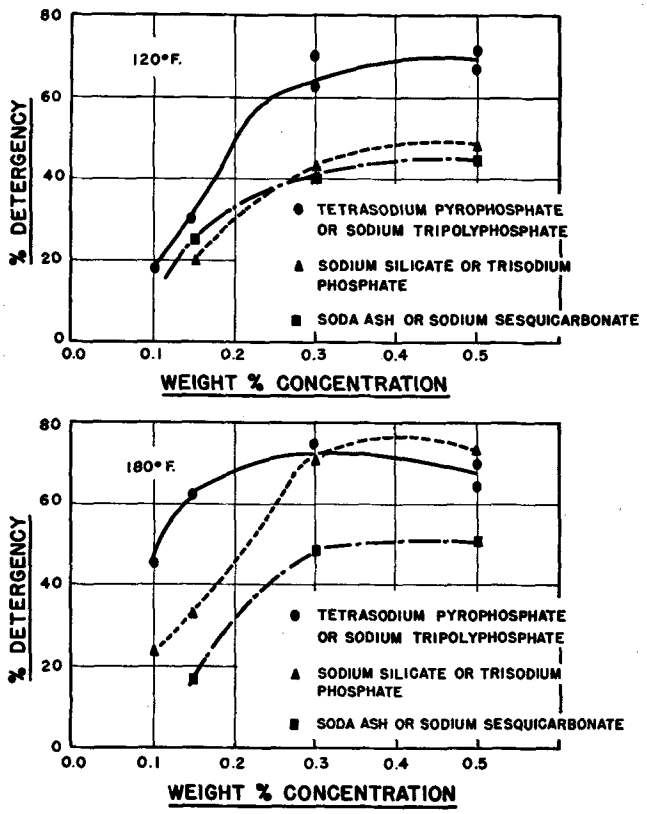

FIG. 4. Cotton detergency. Effect of temperature on alkali built ultrawet K series formulas—30 K sulfonate/26Na_2SO_4/44 alkali.

two different test temperatures, simulating household laundry work at 120° F. and commercial laundry work at 180°F.

In the course of the test development the measurement of soil redeposition was briefly studied by including the same clean white cotton test swatch in a series of successive launderometer cycles, using a freshly soiled swatch and fresh detergent solution as per the usual test method in each cycle. The soil redeposition on the white swatch is measured by noting its decrease in reflectance. The redeposition effects observed with a built fatty acid soap, an optimum alkali built Ultrawet detergent, an unsatisfactory formula for heavy duty work, and the latter two containing carboxymethyl cellulose are shown in Figure 5. These data indicated that in order to pick up differences of a minor degree multi-cycle testing had to be used. It also indicated that redeposition problems were minimized with a good detergent. These data were also borne out by practical washing tests.

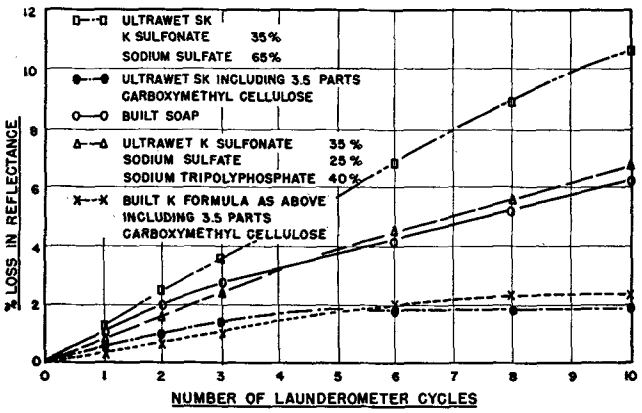

FIG. 5. Cotton detergency. Soil redeposition effects with variant heavy duty detergent formulae at 0.3 wt. % detergent concentration.

The described test method has also been used to evaluate the sudsing characteristics of a material along with its detergency. The suds volume measured in the launderometer test jar at the conclusion of the detergency cycle has been found to be representative of foaming characteristics observed in household laundering equipment. In Figure 6 the sudsing properties of two different polyphosphate built Ultrawets are illustrated along with their relative detergent properties. Their detergencies are essentially the same, but a significant difference in sudsing values is found between the two Ultrawets.

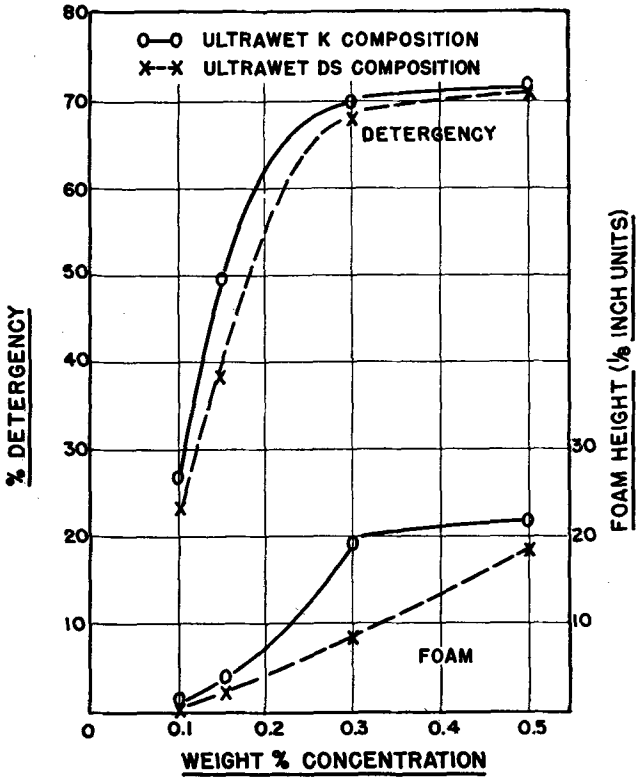

FIG. 6. Cotton detergency. Ultrawet DS and ultrawet K in sodium tripolyphosphate built formulae—30 sulfonate 26 Na_2SO_4 44 alkali.

The method described in this paper has been primarily applied to fatty acid soaps and mixtures of alkyl aryl sulfonates as represented by the Ultrawet series manufactured by The Atlantic Refining Company. It has also been applied to the evaluation of detergents resulting from research studies (5). While exhaustive data are not available on other types of detergents, numerous samples of proprietary compounds, many of unknown composition, have been rated both by the laboratory test described and by small scale practical home washing tests. Close correlation between the two evaluation methods has been found.

APPENDIX I

Cotton Detergency Test

White Oxford cloth[1] is desized and conditioned for use by:

a) Washing in a Bendix washer, using 0.1 wt. % Rhozyme DM No. 731[2] based on the weight of the fabric (about 5 lb.).

b) Repeating the wash, using 0.2 wt. % solution of Ultrawet K followed by a complete rinsing cycle.

c) Washing in 0.2 wt. % solution of a built fatty acid soap and thoroughly rinsing (until no suds remain in the water).

d) Cutting the cloth, while still damp, into four-inch (4") strips and ironing dry.

e) Drying strips in an oven for 2 hours at 150°F.

f) Storing in a dessicator until used.

The soiling is accomplished by dipping five successive times, without pause between dippings, in No. 1 AX soil prepared as follows:

Weigh—0.9 g. Crisco,
3.1 g. Atreol 34[3] and
1.0 g. Lampblack into sufficient carbon tetrachloride

from a 500-ml. portion to just dissolve the oil and fat. Pass this concentrated soil slurry through a small hand operated homogenizer to obtain good dispersion of the carbon black and then add the balance of the 500 ml. of carbon tetrachloride.

The soiled strips are immediately hung from one end to dry (do *not* put them through a wringer) at room temperature. When dry, the strips are cut into 2" x 4" swatches, and the soiled reflectance is read (once on each side) on the photometer.[4] The soiled swatches are now ready for testing and are to be used within 48 hours or discarded.

Detergents are usually tested at 0.1, 0.15, 0.3, and 0.5 wt. % concentration, using 100 cc. of test solution, one soiled swatch, and 10 three-eighth inch hard rubber balls in each pint test jar. Duplicate tests are normally run with occasional resort to quadruple testing. The jars are sealed, preheated, and transferred from the constant temperature preheat bath to the launderometer, which is run (at 40-42 r.p.m.) for 20 minutes at 120°F.

The jars are then removed from the launderometer, the height of foam above the detergent solution in each jar is noted (following one quick inversion of each jar), the swatches removed and thoroughly rinsed in 120°F. tap water, and then air dried. The reflectance of the air dried swatches is again measured and the detergency values calculated:

$$\text{Detergency} = \% \text{ reflectance regained} = 100 \times \frac{(\text{Reflectance, washed swatch} - \text{reflectance, soiled swatch})}{(\text{Reflectance, original swatch} - \text{reflectance, soiled swatch})}$$

[1] Manufactured by Everfast Mills Inc., Eddystone, Pa.
[2] An enzyme preparation used to hydrolyze starch and thus facilitate its solution. Manufactured by Rohm and Haas, 222 W. Washington Square, Philadelphia, Pa.
[3] Manufactured by The Atlantic Refining Company, Philadelphia, Pa.
[4] Manufactured by the Photovolt Corporation, 95 Madison avenue, New York 16, N. Y.

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Limitations of the Periodate Oxidation Method for the Determination of Monoglycerides in Fats and Oils

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THE periodic acid oxidation method for the determination of monoglycerides in fats and oils originally reported by Pohle, Mehlenbacher, and Cooke (1) and later modified by Handschumaker and Linteris (2) is apparently based upon the supposition that the periodic acid consumed in the method is attributable to monoglyceride only. Since it is possible, and very likely, however that small quantities of materials, other than monoglycerides, are present in oils that may react with periodic acid, calculated values for the monoglyceride content of naturally occurring fats and oils may be in error.

It is quite well known that other vicinal dihydroxy or ketohydroxy fatty acids or triglycerides thereof will react with periodic acid. These compounds may either exist naturally or may be formed during oxidation of unsaturated fatty acids. In the course of the present investigation the possibility of periodic acid reaction with such materials was considered. If a fat or oil which had a periodate value is saponified, the fatty acids isolated and washed thoroughly to remove the glycerol formed on hydrolysis, and the fatty acids treated with periodic acid by the accepted method, four possibilities may occur: a) The fatty acid fraction should have zero periodate value if all the periodate value is attributable to monoglyceride; b) the periodate value of the fatty acid fraction should be less than that of the unsaponified fat if only part of the periodate value is due to monoglyceride; c) if the periodate value of the fat is due to unsaponifiable material, then the periodate value of the fatty acid fraction should be the same as that for the fat; d) if there are substances present in the fat which contain vicinal or amino and hydroxy or ketohydroxy groups in which at least one of those groups is combined with some other material so as to prevent the periodic acid reaction, then on saponification those vicinal groups would be liberated and the periodate value of the fatty acid fraction should be greater than that of the original fat.

The purpose of the present investigation, in view of the above possibilities, was to assess the reliability of the periodic acid method as an indication of pres-

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