

Principles of Performance Testing of Laundry Detergents¹

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Introduction

THE use of laboratory performance tests for the evaluation of detergents for washing textiles has grown to a considerable magnitude in terms of effort expended and in technical and commercial importance. Several factors have contributed to this growth, one of which is the multiplicity of detergent materials which have become available in recent years. Since there is no single material of clear cut superiority which satisfies all requirements, even within a limited field such as that being discussed here, compounding is almost universally practiced either at the point of use, by intermediate agencies, or by the manufacturer of the basic materials. Important synergistic effects are known (3, 8), and systematic and precise evaluations are required in order that maximum advantage may be taken of this phenomenon. Most organic detergents do not consist of single molecular species; rather they consist of groups of related compounds, the performance characteristics of which may be affected by variations in raw materials or in the conditions of processing. These effects are not measurable with any degree of reliability by the usual chemical or physical determinations, and accordingly performance tests must be used for adequate production control. Further, it has been found that detergents within a given type or class may vary markedly in susceptibility to improvement with synergistic agents. In turn, different grades of synergistic agents may vary in their effect on a given detergent. Obviously for compounding such materials production control by means of performance tests is a prime requisite. Needless to say, performance tests are invaluable in guiding experimental syntheses of new detergents, where practically infinite variation in composition is possible.

Until recent years the use of laboratory performance tests for detergents was largely intra-organizational. Now because of interchange of materials and intermediates and because of the technical aspects of the sale of detergents, laboratory methods are frequently and importantly involved in inter-organizational negotiations. For such purposes the current status of industry-wide practice is quite unsatisfactory, not only because of lack of technical progress in the development and improvement of the testing methods but also because of lack of agreement as to their scope, objectives, and applicability to a given problem. Artificially soiled fabrics always have been and still are a subject of controversy. The validity of some types with respect to correlation with practice

has been seriously questioned. There is little agreement as to methods of carrying out the washing operation on the artificially soiled fabric or on methods of measurement of the results. There is no uniformity in the mode of expression of results and, perhaps the least excusable of all, no standard reference detergents have been established for industry-wide use.

In comparison with the progress which has been made in the development and standardization of performance tests in other fields, this presents a rather sorry picture. Extenuating circumstances are not lacking, considering the complexity of the effects which are involved and the lack of fundamental information on some of the most pertinent phenomena concerned. It is believed however that the general situation is worse than it needs to be. This paper is offered with the hope that it may be a small contribution to the resolution of some of the questions concerned. It is not a review of principles of detergency nor of published methods for its measurement. It is merely an exposition of the underlying philosophy of the methods currently in use in our laboratories and in some instances in the laboratories of other organizations. The details of our procedures have been published (8) without explanation of their development or a statement of reasons for choice of the conditions specified, and this paper is intended to supply some of the previously omitted background.

Scope

Like any laboratory performance test, detergency tests are used for screening, for guidance in laboratory development programs, and for control purposes. It is idle to criticize laboratory methods on the score that they are inconclusive, that the ultimate tests must be made in full scale equipment and under practical use conditions. For the purposes for which laboratory methods are properly used, full scale trials are usually cumbersome and prohibitively costly in time and materials. Laboratory performance tests are useful in increasing the probability of success in full scale trials and in minimizing the number of such trials which are necessary to yield optimum practical results. In performing these functions, such tests are useful only to the extent to which they fulfill the following requirements:

- a) The test should be reproducible either on an absolute or a relative basis.
- b) The test should yield an adequate spread of numerical results so as to cover the entire performance range, with sufficient precision to show the smallest differences which are significant in practice.

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- c) The test should be capable of correlation with practice in the specific field of use for which it is intended.

It is generally realized, and it has been frequently stated in the literature that cleaning operations are so diverse with respect to the nature of the surfaces to be cleaned, the nature of the soil to be removed, as well as other limitations and characteristics of the system in question, that any performance test for detergents can apply only within limited fields. The procedures under discussion here apply to detergents for use in the commercial laundering of cotton fabrics employing rotary wash cylinders. They have adequate range, precision, and sensitivity and have been correlated with practice over a period of several years in a highly satisfactory manner.

Simulation of Use Conditions

In performance testing it is generally considered desirable to simulate use conditions as closely as possible. Actually, close simulation is neither practicable nor necessary in this instance. Physical limitations of the laboratory scale of operation do not permit a close approach to the washing conditions which prevail in commercial laundering. Close correlation with field results has been achieved however with such attempted simulation being disregarded in favor of more important factors.

The mechanical action which is exerted on the detergent solution-soiled fabric system by commercial washing cylinders is not obtained when such cylinders are scaled down to sizes suitable for washing small artificially soiled swatches. In the former case the fabrics are partially lifted from the solution by the ribbed inner circumference of the cylinder and fall back into the solution with a rolling motion, thereby receiving scrubbing action from the cylinder wall and cleats, as well as between the fabric surfaces themselves, while detergent solution is forced through the fabrics. When scaled down to small diameters the scrubbing action is almost entirely lost. Further, the ratio of detergent solution to soiled fabric in commercial laundering is far lower than ratios which are convenient for laboratory purposes. A typical loading ratio in a commercial washwheel is of the order of 0.5 gallon per pound of fabrics. Attempting to reproduce this in the laboratory washing device such as the Launder-Ometer would result in almost complete lack of mechanical action, as well as require inordinately large amounts of artificially soiled test fabric. A typical Launder-Ometer loading ratio is two 2.5-in. x 3.5-in. swatches per 100 ml. of detergent solution, which is equivalent to approximately 6.3 gallons per pound of fabric. In the Launder-Ometer the nature of the mechanical action is quite different from that occurring in commercial wash cylinders, being exerted almost entirely by balls contained within jars (1).

The matter of detergent concentrations presents another difficulty insofar as simulation of practice is concerned. In commercial washwheels where low ratios of detergent solution to soiled fabrics are the rule, a considerable fraction of the detergent is consumed in dispersing the soil and by adsorption on the fabrics. Particularly in the case of soap, if large excesses over this amount are added, foaming becomes excessive and may actually prevent proper operation.

Thus in use the actual excess detergent concentration remains within rather narrow limits, which do not necessarily comprise the optimum range for comparison of detergents in the laboratory. Inasmuch as practical detergent solution-soiled fabric ratios cannot be conveniently duplicated in the laboratory, and more importantly, such small concentrations cannot be maintained at a constant level during testing due to variations in the consumption of various detergents, attempting to carry out laboratory tests at actual working concentrations would be needlessly restricting. Because of these considerations, in the development of the methods under discussion, primary emphasis has been placed on controlling the factors affecting the property to be measured rather than attempting to simulate field conditions. Since the Launder-Ometer provides a convenient means of carrying out a washing process under controlled conditions of temperature, time, and agitation, it is employed in both the soil removal and the whiteness retention tests.

Published criticism of the methods employing use of Launder-Ometer has not been lacking (2, 4). The shortcomings which have been pointed out however are concerned mainly with failure of different multi-component soils to yield concordant results in testing series of detergents and failure of some soils to correlate with practice. In the opinion of the authors, these findings are concerned to a greater degree with the soils and with the reflectance method for measurement of the results than with the Launder-Ometer itself. Our experience has not revealed any serious shortcoming of the Launder-Ometer as a laboratory instrument.

The chemical nature of soils encountered in actual laundering is complex and subject to wide variation. As a practical matter no close simulation can be accomplished and therefore, rather than use a multi-component soiling mixture as a gesture in this direction, we have sought to make the soil as simple as possible. Simplicity of soil is of considerable importance also from the point of view of lessening the amount of attention which must be given to the rigorous control of the characteristics of each component entering into the soiling mixture. Our goal has been to develop a standard soil rather than a typical soil. The soiling bath is intended merely to deposit carbon on the fabric and to do this in a controlled and reproducible manner.

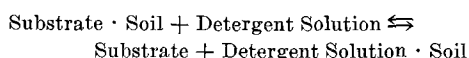
Recently, Utermohlen *et al.* (6) have published work which supports this view. They have shown that the removal of oily matter and pigments from cotton are separate phenomena and have pointed out the desirability of simplification of test methods in the direction which we have taken.

In actual washing operations the removal of the last traces of soil is more difficult than the removal of the bulk of the soil. In end use performance differences between detergents fall within this range in many cases. If it is attempted to design laboratory methods so that swatches washed with high performance detergents fall within this range of cleanliness, serious disadvantages result. For important reasons which will be set forth in detail in later parts of this paper, we have accordingly elected to ignore completely this phase of simulation of practice along with the others.

Separation of the Factors of Detergency

As has been stated in previous publications from this laboratory (8, 9), we consider it desirable to conduct separate determinations to measure the soil removal and whiteness retention properties of detergent systems. Such separation is of no great concern to the ultimate consumer of finished detergents, who can evaluate products by means of full scale washing trials and judge the results in terms of his own standards. The technical reason for failure, if it occurs, is usually of little concern to him. This is not true in the case of the manufacturer or in the case of the experimental investigator. It is highly advantageous in the case of experimental syntheses of detergents, the control of synthetic detergent production, or in the blending of materials to fulfill specific requirements, to be able to separate these effects. Some materials are effective in soil removal but ineffective in preventing redeposition, and with other materials the reverse is true. Accordingly, blending cannot be done intelligently by simple observation of gross effects. This is particularly true when synergism is involved in the system.

It has long been recognized that the detergency process comprises a reversible equilibrium of the following type:



The mechanism and factors affecting this process have been discussed in previous publications from this laboratory (9) and more recently by Schwartz and Perry (5). Removal of soil is represented by the forward reaction and redeposition by the reverse. The rates characteristic of the two opposing tendencies are dependent on numerous factors, some of which are interrelated. Among these factors, of course, is the composition of the detergent solution. In devising our tests, attempts have been made to hold all factors other than bath composition constant and to select conditions in each case which will tend to minimize the opposing tendency. In the simplest view the tests may be regarded as methods for study of sorption of carbon on cotton in aqueous systems. If this point of view is taken, the tests might be considered to be in a borderline position between performance tests and characterization tests, the results being distinguished from those of the usual characterization tests on detergents in that they are capable of correlation with actual washing performance.

Soil Removal Test

Since previous publication of our procedures (8) several improvements have been made. For this reason and for the sake of convenience in the discussion which follows, the current procedures are presented in detail.

Apparatus and Materials.

1. Indian Head muslin, bleached, unfinished. Count 58 x 47. Weight per sq. yd., 4.7 oz.
Manufactured by Nashua Manufacturing Company, 40 Worth street, New York 13, N. Y.
2. Shell Virgo Oil 38-P, Code 3263. (Soluble Oil).
Manufactured by Shell Oil Company, 154 Bagley street, Detroit 26, Mich.
3. Colloidal Black Dispersion No. 10, approx. 25% carbon.
Manufactured by Binney and Smith Company, 41 E. 42nd street, New York, N. Y.

[NOTE: Manufacture of this dispersion has been discontinued. To the present it has been used exclusively in this laboratory and because of stocks on hand will be used for some time in the future. Aqua Blak B (approx. 35% carbon), also a product of Binney and Smith is applicable although it may necessitate slight alteration in the soiling procedure in order to meet tenacity specifications.]

4. Tumbler, Huebsch, 36" diameter.
5. Washwheel—Monel, 24" x 34".
6. Raven 11 (Carbon black used in manufacture of Colloidal Black Dispersion No. 10).
Manufactured by Binney and Smith Company, 41 E. 42nd street, New York, N. Y.
7. Launder-Ometer Type 12QEF.
Manufactured by Atlas Electric Devices Company, 361 W. Superior street, Chicago, Ill.

[NOTE: The stainless steel balls and pint jars used in conjunction with this device may also be obtained from Atlas.]

8. Lumetron Colorimeter Model 402 E.
Manufactured by Photovolt Corporation, 95 Madison avenue, New York 16, N. Y.

Preparation of Standard Water Bound Carbon Soil Cloth. Bleached, unfinished Indian Head muslin is used without pre-treatment. Prior to soiling it is stored in the roll for at least 7 days under conditions of 65% relative humidity at 70°F. Thirty-five panels measuring 10.5 in. x 36 in., or equivalent total area, are cut from the roll of conditioned cloth. Two of the panels are weighed and identified with marking pins preparatory to the moisture determinations which will be described. Thirty-seven and three-tenths liters of softened water¹ having less than one grain as CaCO₃ per gallon is placed in the monel washwheel and 441.2 grams of Shell Virgo 38 P are added. The wheel is run for 5 min. in order to mix the ingredients, after which 306.3 grams of Colloidal Black Dispersion No. 10 are added and mixing is continued for another 5 minutes. During this operation the temperature is maintained at approximately 90°F. The cloth panels are added piece by piece to the soiling mixture, and the wheel is rotated at 42 r.p.m. for 30 minutes, stopping at 10-minute intervals to untangle the cloth. The speed of the wheel is then reduced to 15 r.p.m. and the carbon suspension is drained, with the wheel running, during a 30-minute period. The soiled panels are removed and passed one by one through a manually driven rubber roll wringer, the tension of which is adjusted so that the moisture retention is 120 ± 5% based on the weight of the dry fabric. The batch is then placed in the tumbler which is operated for 15 minutes at room temperature. One of the marked panels is removed and quickly weighed while continuing tumbling the remainder of the batch. Tumbling is continued until the moisture content is between 75% and 85% as determined on the second panel. The rate of decrease in moisture content is approximately 1% per minute. The total tumbling time is usually 20 to 25 minutes. The moisture test panels are returned to the tumbler immediately after weighing. When tumbling is completed, the panels are removed and allowed to dry by hanging edgewise at room conditions for 48 hours. On completion of drying, the cloth is cut into test swatches measuring 2.5 in. ± 1/32 in. by 3.5 in. ± 1/32 in., using a power-driven guillotine paper cutter. They are stored at 65% relative humidity and 70°F. prior to use.

On completion of each batch of soiled cloth it is necessary to determine its conformance with loading and tenacity specifications. This is done by means of the soil removal procedure, using two reference detergents. A standard sample of Kreelon 4D² is used at 2.5 grams per liter in distilled water and the test is conducted at 140°F. The carbon concentration in the wash liquor must be between 9.0 and 12.0 milligrams per liter. In a second test standard Kreelon 4D at 2.5 grams per liter together with standard Carbose² at 0.25 g. per liter is used. The ratio of carbon concentrations in the wash liquors between the

¹ Water prior to softening has the following composition (analysis furnished by Water Department, City of Wyandotte):

Total solids.....	140.4 ppm.
Calcium hardness as CaCO ₃	83.8 ppm.
Magnesium hardness as CaCO ₃	30.9 ppm.
Alkalinity as CaCO ₃	78.0 ppm.
Sodium and potassium as Na.....	5.6 ppm.
Silica.....	2.4 ppm.
Sulfate as SO ₄	20.6 ppm.
Chlorides as Cl.....	21.0 ppm.
pH.....	7.4 ppm.

² Manufactured by Wyandotte Chemicals Corporation, Wyandotte, Michigan.

first and second test must lie between the limits of 1.74 and 1.84. Any batches failing to conform to these specifications are discarded.

Procedure for Carbon Soil Removal Evaluation. The procedure is applicable to synthetic detergents or soaps, with or without builders and promoters. It is not recommended for testing soap systems in very hard water, where initial turbidities of solution may contribute a major portion of the total turbidity. The procedure consists of washing the test swatches in a Launder-Ometer and measuring the light transmittancy of the detergent solution by means of a photometer. A correction is made for the initial turbidity of the detergent solution. Results are expressed on a relative basis; standard reference detergents are measured concurrently. In these laboratories a selected and homogenized stock of Kreelon 4D (having an arbitrarily assigned value of 100) is ordinarily used as the reference detergent.

One liter of the detergent solution to be tested is prepared and 100 milliliters of this solution is transferred by means of a pipette to each of 10 one-pint Launder-Ometer jars. The jars are placed in a constant temperature bath and allowed to stand until thermal equilibrium is reached. Ordinarily a tolerance of $\pm 2^\circ\text{F}$. is allowed. Fifteen 18-8 stainless steel balls of $\frac{1}{4}$ " diameter are placed in each jar along with two swatches of standard soiled cloth in the case of nine of the jars. To the tenth jar two swatches of unsoiled, bleached, unfinished Indian Head muslin are added. The contents of this jar is used to determine the turbidity of the detergent solution. Immediately following the addition of the swatches, the jars are sealed and placed in the Launder-Ometer. The Launder-Ometer is operated for a 10-minute period at 42 ± 2 r.p.m. The jars are removed and again placed in the constant temperature bath. The contents of each of the nine jars containing soiled swatches is poured through a Buchner funnel without filter paper into a large beaker, which is also contained in the constant temperature bath. This removes the steel balls and soiled swatches. The composite suspension thus obtained is mixed thoroughly, and a specimen is placed in a 20-mm. photometer cell. (In order to minimize temperature effects the cell is kept in a beaker of distilled water in the constant temperature bath prior to use.) The cell is placed in the Lumetron colorimeter and the transmittancy determined in reference to distilled water contained in a similar cell. The multiplier filter which is supplied with this instrument is used if necessary in order to balance the instrument. It is left in place in balancing against distilled water. White light is used in these measurements. The light transmittancy of the solution from the jar containing the unsoiled swatches is measured similarly, and the transmittancy readings are converted to carbon concentrations by reference to a calibration curve or table. The calibration data is obtained by making measurements on a series of dilutions of a dispersion of 1 g. of carbon black (Raven 11) in one liter of distilled water containing 0.5 g. of Triton NE. The calibration should cover the range from 0 to 30 mg. of carbon per liter. It will be noted that the light transmittancy follows the Beer-Lambert law through part of this range, with deviation at higher concentrations due to light scattering. The net concentration of carbon in the detergent solution is calculated by deducting the carbon concentration equivalent to the turbidity of the detergent from that of the soiled suspension. This net carbon concentration is divided by a similar value obtained by use of the standard reference detergent determined concurrently on the same stock of standard soil. The carbon soil removal value is reported in terms of percentage of the reference material. (Note: If the detergent being tested contains soap, gelation may interfere with the light transmittancy measurements due to cooling during measuring. In this case the suspension and unsoiled solution are diluted with isopropanol to twice their initial volumes. A separate calibration curve prepared by the use of 50% isopropanol is used.)

Discussion. For several years in this laboratory soil removal tests were made according to a conventional method which has been used in many laboratories. The soil consisted of Norit C, lubricating oil, and hydrogenated cotton seed oil applied to the fabric from a medium of Stoddard solvent. After the washing process the light reflectance of the swatches was measured as well as the turbidity of the detergent solutions. Comparisons of detergents could be made by means of parallel measurements, using the same batch of soiled cloth. With different batches of soiled cloth,

discrepancies appeared which led us to investigate some of the variables involved in its preparation, including composition and concentration of the soiling bath, time of immersion, moisture content of the cloth, manner of carrying out the soiling operation, and aging of the soiled fabric. It was found that the moisture content of the cloth at the time of immersion had a pronounced effect on the tenacity of this type of soil. For example, soiled cloth prepared from cloth preconditioned at 20% relative humidity was considerably more tenacious and somewhat more uniform than when the cloth was preconditioned at 65% relative humidity, with other conditions constant. The use of completely dehydrated cloth seemed indicated, a fact which would involve some obvious difficulties. It was also found that the ratio of mineral oil and hydrogenated vegetable oil to carbon also affected the response to built soaps in comparison with soap alone. Inversion of results occurred if the ratios were varied over a considerable range. It was postulated that these factors were interrelated. The mechanism of the soiling process might be visualized as involving a phase boundary between the water immiscible solvent and a liquid film of water adsorbed on the fabric. This could constitute a barrier to the adsorption of oily material on the fabric, especially during the early stages of the soiling operation. Therefore variation in moisture content of the cloth might be expected to make for erratic behavior by affecting the bonding of the pigment to the fabric.

Studies of the effect of soiling time indicated that tenacity increased with soiling time beyond the period when the cloth was increasing its total load, suggesting that as equilibrium is approached, finer particles of carbon were displacing coarser ones from the cloth. Norit C was therefore considered to have too broad a range of particle sizes from the standpoint of soiling as well as regularity of optical response in measuring soil removal.

Although the degree of initial soiling could be readily controlled by selection of soiling bath concentration and soiling time, choice of conditions presented some uncertainties. A water wash back was used to remove superficial soil and to bring reflectance values within a suitable range for measurement. It was found to be rather difficult to reproduce the soil load remaining after the water wash back, and in the event of distinct differences at this stage inconsistent results were sometimes obtained in the comparison of detergents. This was particularly true if final reflectances approached the initial reflectances of the unsoiled cloth, in which case it became apparent that redeposition effects were contributing significantly to the gross effect, thus reducing the specific nature of the test.

In general, the precision left a great deal to be desired, particularly in the case of the reflectance method where small differences in instrumental readings were involved in single wash tests. The turbidity method yielded more concordant results, with better spread of values.

The reflectance method is subject to some inherent weaknesses. The precise relationship between soil content and reflectivity is still a subject of some uncertainty although it has been fairly well established over a limited portion of the working scale for some soils (7, 9). Utermohlen has reported a logarithmic relation in the case of an iron oxide soil. The Ku-

belka-Munk equation is used by some workers. Perhaps the most serious objection to the use of the reflectance method is the disproportion between quantities of carbon which are redeposited and their effect on reflectance, which may arise from the physical state of the redeposited soil and its distribution over the most accessible and therefore most visible portions of the fabric. When testing detergents having good soil removal and poor whiteness retention properties with lightly soiled cloth, we have experienced decreases in reflectance values while actually removing soil as evidenced by the accumulation of carbon in the wash liquor. At best, reflectance measurements are based on a secondary effect rather than a direct measurement of the desired quantity, presuming of course that the objective of the test is to determine the actual quantity of soil removed.

These considerations, in the judgment of the authors, pointed to the adoption of an essentially single component soil to be applied from aqueous medium and to the use of the turbidity method in measurement of results. These steps were taken in 1943, and since that time the procedures here reported have been under development and in use in our laboratories. It is recognized of course that other workers have advanced the type of procedure which we abandoned to a better degree of reliability than existed then, while our efforts have been devoted to working out procedures embodying the departures mentioned. In some recent instances close agreement has been experienced in cooperative testing, the other laboratory using the reflectance method, with refined technique.

A number of advantages accrue from the use of an aqueous soiling medium. It probably represents a closer approach to natural soiling conditions than the use of organic solvents although that is not considered to be an important factor. Certainly it is secondary to the considerations of reproducibility and appropriate tenacity and range of response to detergents known to have varying degrees of effectiveness.

The effect of moisture content of the cloth on the soiling process is drastically reduced but not entirely eliminated. A minor effect of tenacity remains, and for this reason the cloth is preconditioned at 65% relative humidity at 70°F. in our current procedure. Completely dehydrated cloth is not necessary or desirable as the possibility of disproportionation of soiling ingredients, that is pigment, fats, and oils, is completely eliminated by the simple soil system used.

A very important benefit of the use of water applied soil coupled with turbidity measurements is the freedom of choice of soiling levels which is permitted. In the reflectance method one is restricted by very small changes in reflectivity with relatively

large changes in soil content at high loadings, which amounts to poor sensitivity. The situation is reversed at the other end of the scale. This is illustrated by Figure 1, taken from work previously published by

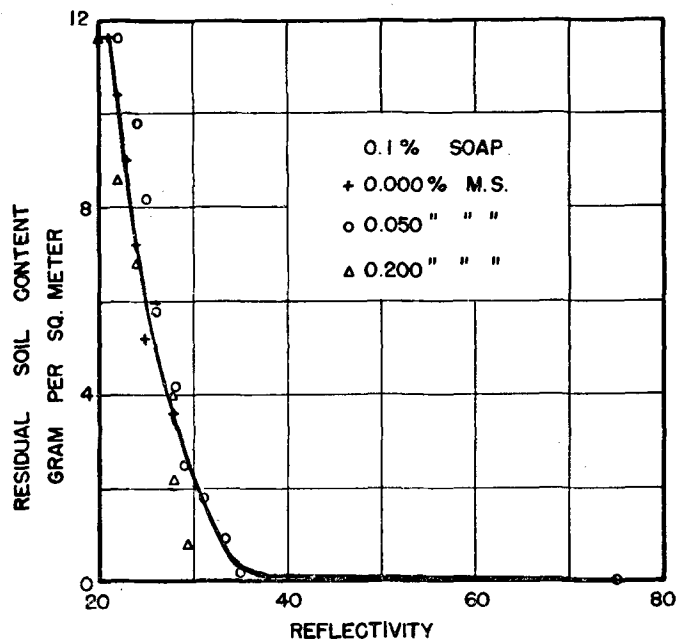


Fig. 2. Relation between soil content and light reflectance of artificially soiled cloth, as determined by multiple wash tests using soap and modified soda.

this laboratory (9). The same conclusion can be drawn from the work of Utermohlen (7). Freedom from these restrictions permits the use of rather heavily loaded fabrics, which is a distinct advantage in minimizing redeposition. The rate of deposition is a function of the soil concentration in the solution and on the fabric. For a given concentration in solution it is naturally at a maximum for perfectly clean cloth.

The characteristics of soiled cloth prepared according to the procedure given above are shown in Table I. In these multiple wash tests the detergent solutions were replaced after each 10-minute washing period. The degree of loading and general tenacity characteristics can be judged from the reflectance values which are quite low and do not change materially in a single 10-minute washing period. They cover but little of the useful working scale of the reflectometer through the series of washes.

On the other hand, the transmittancy of the detergent solutions encompasses the entire working range of the Lumetron colorimeter. This provides sensitiv-

TABLE I
Effect of Multiple Washing of Water Bound Carbon Soiled Cloth
Detergent concentration, 2.5 g. per liter distilled water. Temperature, 140°F.

Washing time, min.	Distilled water			Kreelon 4D			L-1386*		
	Reflectance, % of MgO	Transmittancy, % of distilled water	Carbon concentration, mg. per liter	Reflectance, % of MgO	Transmittancy, % of distilled water	Carbon concentration, mg. per liter	Reflectance, % of MgO	Transmittancy, % of distilled water	Carbon concentration, mg. per liter
0.....	11.7	11.2	11.2
5.....	15.8	45.8	5.3	24.8	9.7	13.1	14.3
10.....	17.2	32.5	7.8	12.5	18.2	11.8	14.6	32.0(M)†	21.3
20.....	18.3	23.4	10.1	13.1	13.5	14.1	15.7	17.0(M)	25.9
30.....	19.4	19.5	11.5	13.2	12.0	15.0	16.0	12.5(M)	28.1
40.....	19.9	15.0	12.5	13.9	10.5	15.8	17.4	9.9(M)	29.8

*A laboratory reference detergent containing Kreelon 4D, Carbose, and modified soda.

†(M) indicates readings taken without multiplier filter in Lumetron Colorimeter.

ity and precision well in excess of that inherent in the other steps of the procedure and obviates the necessity for any elaborate statistical approach to this phase of the test. The solutions from the nine jars involved in the single test are easily and reliably averaged by merely mixing the solutions prior to the transmittancy measurements.

The transmittancy measurements are reproducible within 0.3% of the transmittancy of distilled water, corresponding to a range of uncertainty of 0.045 mg. of carbon per liter. The precision of this measurement alone, for the average amounts of carbon removed in single wash tests, is in the order of one part in 400.

Excluding errors involved in handling swatches, Hunter reflectometer readings are reproducible to 0.1% on the magnesium oxide scale. Therefore to reach purely instrumental precision of 1 part in 400, it would be necessary to wash the swatches through a reflectance change of 40% of magnesium oxide. Also it would be necessary to measure the reflectance of each side of 18 swatches to equal the precision of the turbidity method.

By proper choice of cell thickness in the light transmittancy measurements, one is free to select any degree of loading of the cloth which is desired. As previously stated, we have chosen to use rather heavily loaded cloth in order to minimize redeposition. An additional advantage in providing a rather large reservoir of carbon lies in the fact that during the washing procedure in the Launder-Ometer there is little change in the soiled fabric with respect to tenacity and total removable soil.

The data from Table I are shown graphically in Figure 2, in which the cumulative amounts of carbon

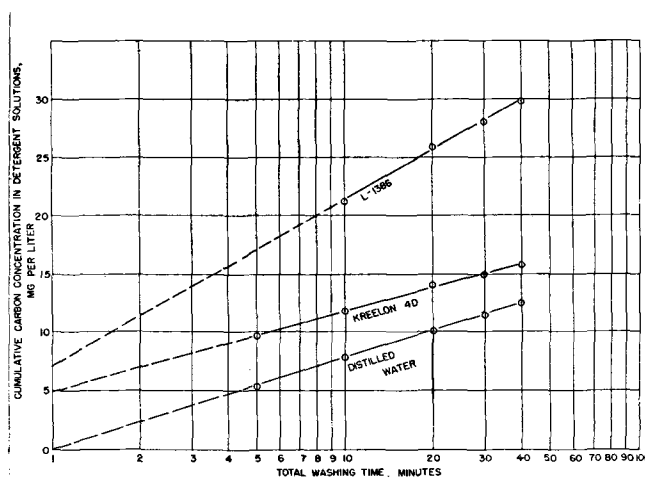


FIG. 2. Effect of multiple washing of water bound carbon soiled cloth. Detergent concentration, 2.5 g. per liter in distilled water. Temperature, 140°F.

removed are plotted against the logarithms of the time intervals. The ordinate is intersected at the 1-minute period in which case no datum points were obtained because of manipulative uncertainties. The regularity of response is clearly evident, and it is apparent that multiple wash tests are unnecessary with this technique. The differences between the detergents are amply shown by a single 10-minute wash period. It is evident that these differences are in the nature of rate or intensity of soil removing action and

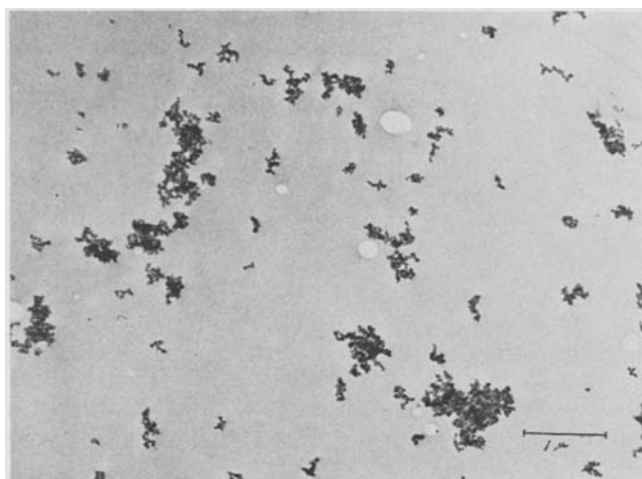


FIG. 3. Electron photomicrograph of Raven 11 (dry carbon black).

that prolonging the test would only serve to broaden the differences.

For the sake of rigor, it might be argued that the soiled cloth should be subjected to a water wash back prior to use in order to remove any superficial carbon along with any soluble oil and dispersing agent picked up from the soiling bath. Although this can be done, we have not found it to be necessary for ordinary purposes. The quantities of soluble oil and dispersing agent present in the cloth are such that their concentration in the detergent solution being tested is less than 0.20 g. per liter. Their effect on the light transmittancy is small, and it is cancelled out when the results are expressed in terms of the reference detergent. The effect of the carbon which is removed by water alone is significant, however its removal would only serve to change the slope of the curves without altering their relative positions. Except when working at extremely low concentrations, where the traces of dispersing agent might interfere, we have no evidence to indicate that the extra labor of making a water wash back is warranted.

It is believed that an important factor contributing to the behavior of the soiled cloth is the fine particle size and the range of particle size distribution of the carbon which is used. Figures 3, 4, and 5 are electron micrographs of Raven 11, the dry carbon, Aqua Blak B, and Dispersion Number 10. In the dispersed forms

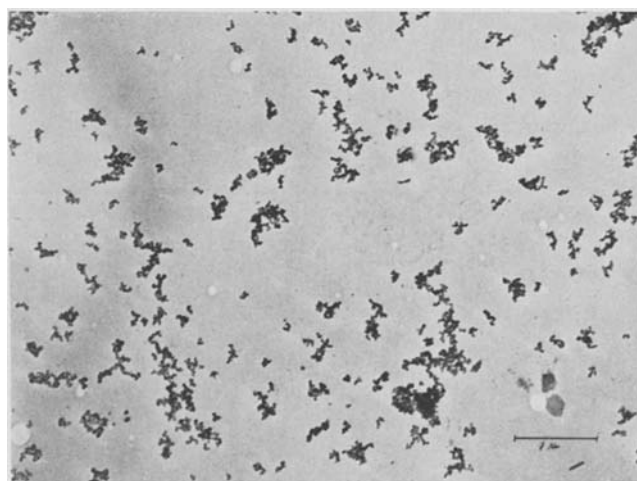


FIG. 4. Electron photomicrograph of Aqua Blak B.

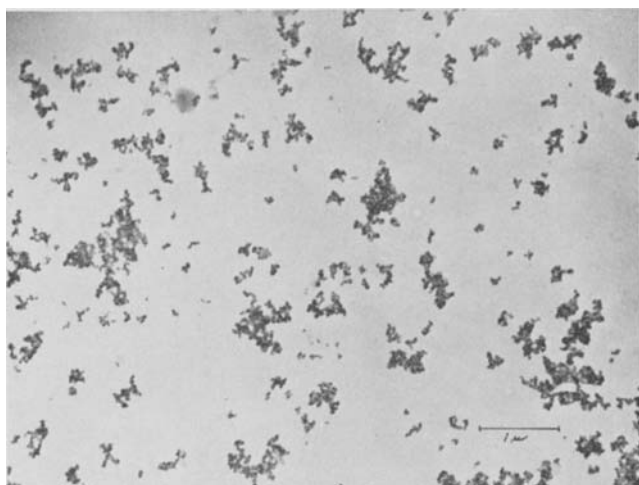


FIG. 5. Electron photomicrograph of Colloidal Black Dispersion No. 10.

there is no appreciable agglomeration in comparison with the dry form. The particle size range is from 0.02 to 0.08 microns.

The extent to which redeposition has been excluded from the soil removal test has been estimated by means of experiments designed to reveal the maximum possible redeposition effect. Soiled swatches were washed according to the regular procedure and the carbon concentrations of the resulting suspensions measured. The suspensions were returned to the Launder-Ometer jars and two clean white swatches added to each jar. After running in the Launder-Ometer for another 10 minutes, the carbon concentration was again measured. The results are shown in Table II. It is seen that the redeposition effect is

TABLE II
Maximum Possible Redeposition During Soil Removal Test
Detergent concentration, 2.5 g. per liter in
distilled water. Temperature, 140°F.

Soiled cloth	Detergent	Carbon concentration after washing soiled swatches, mg. per liter	Carbon concentration after washing white swatches, mg. per liter	Difference, mg. per liter	Percentage of total effect
346	L-1386	21.1	20.9	0.2	0.95
352	L-1386	17.3	17.1	0.2	1.16
348	Kreelon 4D	10.9	9.5	1.4	12.8
346	Kreelon 4D	11.7	10.3	1.4	12.0
352	Kreelon 4D	8.3	7.1	1.2	14.4

greater in the case of Kreelon 4D than in the case of the compounded detergent (because of the presence of Carbose in the latter) which is in accordance with expectations that interference would increase with decrease in whiteness retention properties. Since the opportunity for redeposition in the tests shown in Table II is greatly exaggerated by the use of white swatches rather than the heavily loaded cloth which is actually present during the soil removal test, it is reasonable to assume that redeposition does not occur to any significant extent in this test.

The ability of a detergent system to remove fats or oils from fabric is not measured by this test. It is our belief that where information on this property is required, it is best determined separately, excluding pigments, in which case the results are readily measured by means of solvent extraction procedures.

Whiteness Retention Test

Apparatus and Materials.

1. Hunter Multipurpose Reflectometer.
Manufactured by Henry A. Gardner Laboratory inc., Apparatus Division, 4723 Elm street, Bethesda, Md.
2. Gyrosolver.
Manufactured by Fisher Scientific Company, Pittsburgh, Pa.
3. Prosperity Pony Press, Model 219-PO.
Manufactured by Prosperity Company inc., Syracuse, N. Y.
4. Other materials and apparatus as listed under soil removal test.

Procedure. Bleached, unfinished Indian Head muslin is cut into swatches measuring $2.5 \pm \frac{1}{32}$ " by $3.5 \pm \frac{1}{32}$ ". The light reflectance of each side of each swatch is measured by means of a Hunter Multipurpose Reflectometer, using a standard white backing having a reflectance value of 68.8% of magnesium oxide behind the cloth. The green filter supplied with the instrument is used. The reflectance of the front and back of each piece is averaged, and the swatches are classified in a multi-compartment box marked off in 0.1% units. The swatches for any single test are drawn from one compartment. A standard soil suspension is prepared by diluting 28.55 grams of Aqua Blak B to 1 liter with distilled water. A weighed quantity of the detergent to be tested is placed in a 1-liter volumetric flask and dissolved in 200 or 300 ml. of distilled water. The soil suspension is shaken vigorously, and 50 ml. are transferred to the flask containing the detergent solution by means of a pipette, after which the mixture is diluted to one liter. One hundred-ml. portions of the suspension are transferred to each of 5 Launder-Ometer jars, 15 stainless steel balls are added, and the jars are placed in the constant temperature bath and heated to the test temperature. The jars are placed in the Launder-Ometer and rotated for 5 min. at 42 ± 2 r.p.m. The Launder-Ometer is stopped, and, without removing the jars from the machine, the lids are opened and two pieces of cloth added to the contents of each jar. Immediately prior to their addition the swatches are soaked for one minute in distilled water. The covers are replaced on the jars and the Launder-Ometer rotated for 30 minutes. The jars are removed from the Launder-Ometer and the swatches transferred immediately to one of the flasks of the automatic rinsing device. This device consists of a gyratory shaker holding four 1-liter Erlenmeyer flasks, each of which is equipped with outlets to the drain and inlet connections to receive water from individual 3-liter distilled water reservoirs. Three liters of distilled water is passed continuously through the flask containing the 10 swatches while shaking, the operation being completed in 5 minutes. The swatches are removed and placed flat on clean paper towels and allowed to drain, then are pressed until dry on a Prosperity press at 328° to 338° F. The reflectance of each side of the 10 pieces of cloth is measured and the whiteness retention value for the detergent under test calculated. This value is equal to the ratio of the average reflectance after washing to the original reflectance, multiplied by 100. Finally the results are expressed in terms of percentage of whiteness retention relative to a standard reference detergent determined concurrently.

Discussion. In principle the whiteness retention test is less involved than the soil removal test. The soil concentration in the detergent solution is relatively high, approximately 0.50 g. of carbon per liter. This provides a large reservoir of soil, thereby minimizing any change in rate in deposition during the course of the test which might originate from this source. Since there is very little change in the carbon concentration during the test, it is not feasible to determine the quantity deposited on the cloth by photometry of the dispersions, and therefore the results are determined and expressed in terms of reflectance. The carbon concentration and the duration of washing are such that the reflectance values lie between 20% and 80% reflectivity on the magnesium oxide scale, in the case of poor and good detergents with respect to the whiteness retention property. The conditions are intended to favor deposition with the exclusion of soil removal, based on consideration of the equilibrium concerned. The soil content of the solu-

tion is high and nearly constant through the test, and the system reaches equilibrium, within experimental error, during the 30-minute washing period.

The rinsing procedure is intended to standardize this operation in the interest of precision. The steam press is used in preparing the swatches for final reflectance measurements in order to avoid the effects which any sliding or rubbing on the surface might have on the observed reflectance.

We believe this procedure to be superior in principle to tests in which white swatches are included with soiled swatches in a detergent solution, in which case the soil content of the solution rises continuously during the test period and is dependent on the soil removal property of the detergent being tested.

Precision

The precision of the test methods described is not considered adequate for expression of the results in absolute terms. Therefore control determinations are carried out regularly, and all results are expressed relative to a standard reference detergent. This compensates for differences in lots of standard soil test fabrics as well as other sources of systematic error.

The precision of the soil removal test is shown in

TABLE III
Precision of the Carbon Soil Removal Test
Detergent concentration, 2.5 g. per liter in distilled water. Temperature, 140°F.

Sample	No. of operators	Sample population	Arithmetical mean, percentage of Std. Kreelon 4D	Mean deviation, per cent
Experimental Non-ionic detergent	1	8	212	±2.9
Kreelon 4D (Laboratory A)	6	29	99.5	±3.5
Kreelon 4D	1	22	105	±2.1
Blended detergent No. 1 (Laboratory A)	3	19	143	±4.0
Blended detergent No. 1 (Laboratory B)	1	22	150	±1.6
Blended detergent No. 2 (Laboratory A)	3	19	182	±6.7
Blended detergent No. 2 (Laboratory B)	1	20	183	±2.7
Average.....				±3.4%

Table III. These data which were collected over a period of several months were determined by 7 operators, on 7 batches of soil and in 3 Launder-Ometers. The determinations were made on a routine basis in two separate laboratories which are under separate supervision, one being a control laboratory and the other a research laboratory. With the exception of the experimental non-ionic detergent, the samples were carefully homogenized materials which were specially prepared for the purpose of obtaining statistical data. The average mean deviation over a wide range of levels is ± 3.4%. Satisfactory agreement may be obtained between laboratories, the largest difference between the arithmetical means reported by the two laboratories on the same material being 5.5%.

It may be noted that the degree of precision obtained by a single operator is slightly better than that obtained among a group of operators.

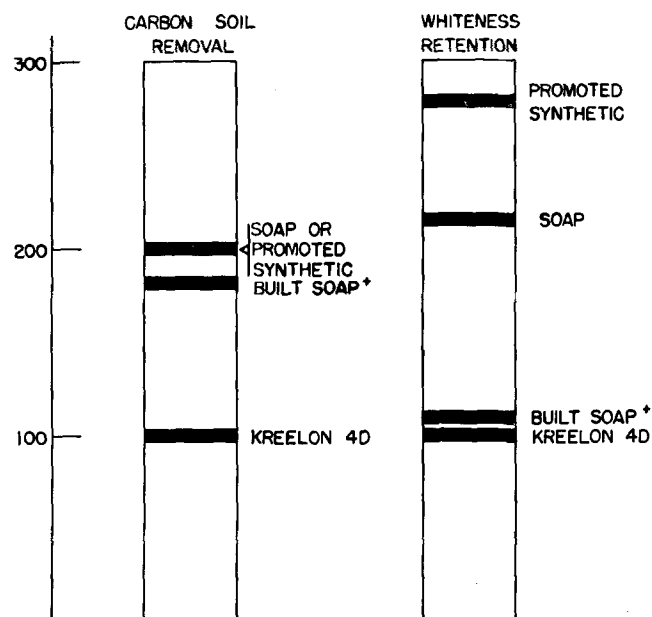
The precision of the whiteness retention tests is shown in Table IV. The average mean deviation is ± 5.1%.

TABLE IV
Precision of the Whiteness Retention Test
Detergent concentration, 2.5 g. per liter in distilled water. Temperature, 140°F.

Sample	No. of operators	Sample population	Arithmetical mean	Per cent mean deviation
Blended Detergent No. 1	2	11	342	±4.8
Blended Detergent No. 2	2	19	212	±5.3
Average.....				±5.1%

Interpretation of Values

The results of the soil removal and whiteness retention tests should be interpreted with full realization of the nature of the tests, that is, that they are essentially comparisons of the rates of soil removal and redeposition between detergents. Satisfactory levels in both respects does not constitute final proof that the detergent will perform satisfactorily in the field. They are however reliable indications that the detergent will be satisfactory with respect to these two properties and that the probability of overall successful performance is extremely high. Results may be used very effectively in predicting field performance if they are used in comparison with values for materials for which clear cut field performance patterns have been established. This is illustrated in Figure 6 which shows typical ranges of values for



† 2 PARTS SOAP, 1 PART SODA ASH

FIG. 6. Performance levels of detergents. Measurements made in distilled water at 140°F., at total concentrations of 2.5 g. per liter.

high titer tallow soap, built soap, and a synthetic detergent composition containing sodium carboxymethyl cellulose. The whiteness retention properties of built soaps are critically dependent on the composition of the builder and the ratio of builder to soap used. By assuming average values for built soap as a criterion of acceptable performance, acceptance levels are readily apparent. It follows of course that comparisons

made at single arbitrarily chosen concentrations and temperatures are not adequate for complete evaluation of a given detergent, and such investigation in the laboratory can be of great value in pointing the way to obtaining optimum results in actual use.

In our experience, for successful use in commercial laundries, a detergent must have soil removal and whiteness retention properties of the order of magnitude of built soap as first requirements. We have also found that the higher the values, the more satisfactory the product is likely to be in actual service.

In correlating laboratory tests with practice the practical aspects of laundering have not been neglected. Because of commercial relationships with thousands of laundries and because of the use of the test methods for production control of synthetic detergents, sodium carboxymethyl cellulose, laundry builders, and completely formulated built and promoted synthetic laundry detergents, as well as for experimental purposes, a considerable fund of correlated information has been collected. In many cases actual laundry performance has been determined by the use of test bundles carried through 20 or more washes in accordance with the generally accepted practices in the trade, in addition to direct observation. Within the limits of their applicability the laboratory tests have not once failed, in the past several years, accurately to reflect field performance.

The tests do not measure the tolerance of the detergent solution to soil loading especially for oil or greasy matter. This must be determined by other tests or by actual field trials.

Summary

Laboratory performance tests for laundry detergents can fill important needs in laboratory development programs and in control testing, in which cases full scale practical testing is inapplicable. It has been found to be unnecessary and undesirable to attempt close simulation of practice conditions. In order to be most useful to the experimental investigator or the manufacturer of detergents the soil removal and whiteness retention properties should be measured by separate tests.

A soil removal test has been devised in which the soil, which consists essentially of carbon black, is applied to the test fabric from aqueous medium. Soil-

ing from aqueous medium has advantages with respect to reproducibility in tenacity and in variation and susceptibility to removal by detergents having different degrees of effectiveness. The quantity of soil removed is measured directly by means of light transmission measurements on the soiled detergent solution. This eliminates uncertainties and limitations inherent in the reflectance method and permits the use of high soil loads in the test cloth, which minimizes redeposition effects. Multiple wash tests are not required.

The whiteness retention property is determined by agitating unsoiled swatches in the detergent solution containing carbon black dispersion and measuring the reflectance change of the swatches.

The results of both tests are expressed in relative terms, reference detergents being used as controls.

The precision of the soil removal tests is approximately $\pm 3.4\%$ in terms of mean deviation and that of the whiteness retention test approximately $\pm 5.1\%$. Both tests have been used over a period of several years for research and control purposes and have been successfully correlated with actual results in commercial laundries.

Acknowledgment

A large number of individuals in our laundry research organization have made substantial contributions to the development of the test procedures described in this paper and to the accumulation of the large mass of laboratory and field data which has made practical correlation possible. We are particularly indebted to Clifton E. Smith and Maurice G. Kramer for their contributions. The electron photomicrographs are the work of L. E. Kuentzel of our physics laboratories.

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Report of the Smalley Foundation Committee, 1949-50

FOLLOWING the custom initiated a year ago, the reports of the five subcommittees of the Smalley Foundation Committee are combined into one report. In doing this it appears desirable to discuss the activities of the various subcommittees individually and briefly. In most cases individual detailed reports covering grades, methods of grading, etc., have been mailed to the individual collaborators by the subcommittee chairmen. About 3,200 samples were distributed by this committee.

R. T. DOUGHTIE JR.	S. W. GLOYER
W. C. AULT	R. W. BATES, <i>chairman</i>
A. S. RICHARDSON	

REPORT OF THE SUBCOMMITTEE ON OIL SEED MEAL

This year 15 samples were distributed instead of 30. It was believed that this number of samples distributed over the same period would be more desirable than 30 samples. At the end of the period we submitted a questionnaire to the collaborators asking their comment on the number of samples preferred. The results are listed:

Per cent returning the questionnaire.....	89
Per cent preferring 15 samples.....	91
Per cent preferring 30 samples.....	7