Report of the Detergents Committee to the American Oil Chemists' Society

By J. G. Vail, Chairman

The Detergents Committee, as at present organized, inherited from its predecessor, a body of experience and information which was largely negative but none the less valuable on that account. It has been found that it was necessary to soil cloth in some uniform manner before it was possible to devise a standard method of cleansing. No soiling method could hope to duplicate all of the endless varieties of dirt which are met with in practice. In choosing a definite method of soiling, certain pigments, cloth, oily materials, vehicles and procedures had been selected and tried. The results obtained by various operators were not sufficiently uniform to be satisfactory.

With such a basis, it was to be expected that the results of washing should also be more or less lacking in agreement.

Judging the washed specimens was also a source of uncertainty. Even supposing that people's perceptions of color were the same, no method of judging by direct inspection could give a good basis for numerical averages.

With this history as a background, the present committee approached its task with a sense of the complicated character of the problem and the need of simplifying methods wherever possible. On the other hand, the simple tests which have been employed for determining individual characteristics, such as emulsifying power, effect on surface tension, etc., seemed inadequate. The reason for this view is that actual detergent efficiency manifestly depends on the interplay of some or all of these features, and not on any one alone. Any attempt to evaluate detergents must, therefore, include some element of compromise.

The earlier washing tests had shown that the oily materials were removed with comparative ease, but that the last portions of certain pigments were held by the cloth with great tenacity. It was therefore concluded that if thoroughly clean fabric was desired, the capacity of a detergent to remove pigment only, was a most important feature. The influence of oily materials, especially during the early stages of the washing process, was clearly recognized. The use of such materials in a standard method of soiling, however, seemed sure to introduce complications if not actual uncertainties. It was therefore concluded to try the simplest possible soil, applied in the simplest effective manner, giving a product containing nothing but cloth and pigment.

Extracted carbon black was selected as a pigment which was not too easily removed, and was as nearly inert to chemical influences as any intensely colored substance that could be secured.

It was found that a suitable grade of carbon black could be suspended in water without the help of any deflocculating agent, and that unsized sheeting would take up a certain amount of the pigment when properly treated, but no more. (This was judged by depth of color and not by chemical analysis.)

This made it possible for widely separated operators to obtain closely similar specimens for their washing tests, if they had the same cloth and pigment, and opened the way for a trial of washing procedure.

Temperature and the mechanical treatment of a fabric undergoing a cleansing process were recognized as features of such importance that close control of them was essential. The use of the Launderometer (already described to the A. O. C. S.—See Oil & Fat Industries, Nov. 1931, page 414) helped greatly toward this end. With certain changes, aimed at securing constant speed of rotation, this machine should prove satisfactory.

To attain greater accuracy in judging the color of specimens, either before or after washing, and to make possible the securing of averages, various optical devices have been available.

With the foregoing considerations in mind, the committee has conducted two trials in which a number of people in various parts of the country cooperated. Cloth and pigment have been supplied from a central source, but each operator has performed his own soiling and washing processes. In the first trial there seemed to be some misapprehension in regard to certain parts of the method, and much irregularity due to various speeds of rotation in washing. At first sight, the results appeared to have little, if any, meaning. On more careful analysis, however, it developed that the four detergent solutions had been placed in a certain order of efficiency.

In the second trial, the method was modified slightly, and the same solutions used. Some operators who had secured the right order of efficiencies (as the matter was interpreted) in the first trial, declined to repeat their test. This is to be regretted since some of them are those who have had most experience with the method. The results of the second trial confirmed those of the first in every respect. Two of the solutions are so nearly alike in efficiency at the temperature selected that they may be considered identical. In such a case it is to be expected that the findings as to their relative efficiencies should vary from one operator to another.

Although the procedure employed by the committee has not given uniform results in different laboratories, it is felt that real progress has been made and that a method of studying detergency has been developed which should prove a valuable research tool when used with discretion. It is of course realized that no single test can be applied to a detergent that will fully determine its value as a cleansing agent. A true picture can be obtained only when a number of tests are made under a wide variety of conditions of temperature, concentration, hardness of water, type of soil, etc., such as are met with in practice. Consideration must be given also to the action of the detergent upon the fabric as well as upon the soil. It is urged that in applying the processes which have been worked out by the committee, the limited applicability of the results to any other set of conditions should be borne in mind. If this is fully realized, it is believed that the method of washing herein described will be of definite aid in classifying detergents. It may be added that this has proved to be true in more than one instance of commercial practice.

The committee does not presume to think that the last word has been said in regard to the method. Some may feel that the elimination of oily materials from the soiling mixture was a mistake. Others may prefer a pigment, such as umber, which may be removed more easily than carbon black. Alternative procedures have been suggested by members of the committee, and others, which have not been fully tried out. Improvements no doubt will be found.

The chairman wishes to express his appreciation of the cooperation extended by other members of the committee, and by a number of laboratories who have given

valuable help in making trials of the methods proposed.

The chairman feels that the detailed results of the two trials referred to above should be made available to any who may be interested. These results are therefore appended, with the method as applied by the committee, and the unproved suggestions which have been offered.

Procedure for Evaluation of Detergents.—This test depends upon the soiling of cloth with a water suspension of carbon black to the point of saturation, under given conditions, removal of part of the pigment, and comparison of the test pieces on the basis of color.

Cloth.—The cloth used is bleached cotton sheeting weighing about 1.5 grams per square decimeter, and having about 27 threads per centimeter in the warp and 25 threads per centimeter in the filling ("Utica" brand sheeting from the Utica Steam and Mohawk Valley Cotton Mills, Utica, N. Y., was used in the work of the committee.) The sheeting should be substantially free from size before soiling.

Soiling Material.—The soiling material is an extracted carbon black. (Grade "J," supplied by L. Martin Company of Philadelphia, has been found satisfactory.) It is essential that the pigment shall disperse readily in water, without the addition of a deflocculating agent.

Washing Apparatus.—The washing machine used by the committee consists of a horizontal shaft that can be rotated at a speed of 40 r.p.m., arranged to hold one pint jars placed radially about the shaft, with the base of the jars two inches from the center of the shaft. Provision is made for maintaining the temperature of the wash solution in the jars to within plus or minus 2° F., of that specified for a given test. One pint, glass-topped jars about 6 inches in height and about 3½ inches in diameter are used. (The Launderometer manufactured by the Atlas Electrical Devices Co., Chicago, Ill., and Atlas E-Z Seal jars, were used in this work.) In order to secure a definite and constant speed of rotation, a chain, or other equally effective device, should connect the speed-reducing mechanism with the main shaft. It is believed that this is necessary if concordant results are to be obtained by different operators.

Method of Soiling.—The cloth is cut into strips, about 3½ inches wide and 13 inches long. Not less than 10 nor more than 12 grams of carbon black are suspended in 500 ml. of distilled water in any suitable vessel. Each strip of cloth is thoroughly wet in distilled water, then stirred for a few moments in the suspension of pigment, and passed between the closely-set rolls of a clothes wringer or similar device. The treatment with pigment and the rolling are repeated until the color of the cloth ceases to become deeper. Five passes have usually been found sufficient. If more than 5 or 6 pieces are to be soiled, the suspension of pigment should be renewed. Without drying, each piece is shaken in a jar or wide-mouthed bottle with successive portions of distilled water, until only very small amounts of pigment appear in the rinsing. The strips are then dried on a smooth surface at room temperature. This method should give soiled specimens of a nearly uniform gray color, showing from 20 to 25 per cent whiteness, as compared to magnesium carbonate, in the Hess-Ives Tint-Photometer. The pieces needed in a comparative test should be so assembled that each group will have the same average reading.

Preparing the Specimen.—The soiled cloth is cut into pieces of 3 inch by 6 inch size, folded crosswise and sewed along three sides to form a bag, 3 inch by 3 inch in dimension. Enclosed in each bag are 50 balls of Monel metal of ¼ inch diameter, weighing about 60 grams. (Atlas Ball Co. of Glenwood Ave. and Fourth St., Philadelphia, Pa., are suppliers.)

Preparing the Detergent Solution.—The work on this method has been done with soap solutions made by dissolving 2 grams of the detergent in 100 ml. of boiling-hot distilled water, and diluting to 1,000 or 2,000 ml. The washing has been done at 60° C. (140° F.). Other detergents, temperatures, or concentrations may be employed, as desired.

The Washing Test.—(In this test it is intended that a washing machine of the type described above, shall be used. There is some evidence to show that satisfactory results may be obtained with other forms of mechanical washers.) Heat the water in the Launderometer to 140° F. (60° C.). In each jar place two of the cloth bags and 100 ml. of the detergent solution. Close the jars and make them fast in the machine, loading the shaft so as to secure approximate balance. (Tendency of the jars to leak may be checked by forcing down the wing-nuts.) Allow a few minutes for the temperatures within the jars to become equalized. Rotate by means of motor for 20 minutes at 40 r.p.m. Remove the jars, pour out the liquids, squeeze the bags by hand, recharge with detergent solution and repeat the process until 6 washes have been given. The bags should not be allowed to dry between treatments. After the sixth wash, each pair of bags is rinsed by placing for a few minutes in 3 successive 100 ml. portions of distilled water at 140° F. The bags are then cut open and spread on a flat surface of glass or enamel to dry. Not less than 10 bags should be used with each detergent solution.

Judging the Results.—When dry, the specimens may be compared by any method which is available to the operator. When this is done directly by the eye, care must be taken that the pieces receive exactly the same illumination. Mechanical or optical devices are very helpful, especially in giving numerical values and thus making it possible to obtain averages. The Hess-Ives Tint-Photometer has been found satisfactory (Palo-Myers, Inc., of 81 Reade St., New York City, are suppliers of this instrument). Plotting of results in terms of percentage of white, has been found useful.

Suggested Alternative Procedures.—The cooperators did not all obtain the same depth of color in their soiled cloths. Incomplete rinsing is at least a partial explanation. One or more laboratories have found that cloth will take up and hold more carbon black under some conditions than it will under others.

In view of these circumstances it has been suggested that the conditions of soiling should be more definitely fixed, especially in regard to the pH of the distilled water used, the temperature of the soiling suspension, and the number of pieces of cloth which may be treated simultaneously or consecutively with one portion of carbon black.

As previously indicated, it has been the belief of the committee, that a given cloth will take up a certain amount of pigment under conditions which it is not necessary to fix with very great rigidity. In order to place this phase of the matter beyond doubt, more tests should be made.

Until the precise effect of each variable can be determined, it may be desirable to define narrowly a soiling procedure which can be tentatively employed as the nearest possible approach to uniform practice. Should it be found that some precautions are unnecessary, the rigidity of the method may be relaxed.

In line with this thought, it is suggested that the suspension of the carbon black should be made up with 11 gm. of pigment, 500 ml. of distilled water, at 20° C. (68° F.), that pieces of cloth should be treated one at a time, and that not more than 6 pieces should be treated in a given suspension. Other operations and details would

remain the same as those given above under "Procedure for Evaluation of Detergents."

An alternative method of soiling, suggested on the basis of the experience of one laboratory, is as follows:

Bags are made before the cloth is soiled rather than after. In each jar are placed 100 balls, a weighed amount of carbon black, 100 ml. of distilled water and two of the bags, each containing 50 balls. The jars are then rotated in the machine at 60° C. for one hour. Three 15 minute rinses with water are given. The bags are then ready for use without drying. Several of the bags may be dried, if measurement of their color is desired. It may be found possible to reduce the duration of the treatments.

O. M. Morgan, in the Canadian Journal of Research, 6, 292-305, 1932, advocates a soil containing oily materials, the use of a machine for soiling which employs a long strip of cloth, and a miniature wash-wheel for the washing process.

It has been suggested that the results of judging the specimens should be expressed as the efficiency E of a detergent under specified conditions of use, by the following equation:

$$E = \frac{B_s - B_w}{B_s - B_0} \times 100$$

In which B_s, B_w and B_0 are respectively the negative logarithms of the ratios of the brightness of the soiled, the washed, and the original unsoiled cloth to that of a white standard.

In view of the wide differences in the results secured by the various cooperators, it might, at first sight, seem that the figures are quite without meaning. Further study, however, reveals some significant features. If the figures on specimens from all the cooperators, as found in the Philadelphia Quartz Co. laboratory, are averaged, the results are:

	Per Cent
.1% cocoanut	38.8
.2% cocoanut	36.8
.1% tallow	40.5
.2% tallow	39.7

From this it appears that the four solutions, placed in order of their efficiency are .1 per cent tallow, best, .2 per cent tallow next, .1 per cent cocoanut next, and .2 per cent cocoanut, poorest.

For reasons which are given more fully below, it seems certain that very low figures, say below 30, cannot be right. Omitting the figures from cooperators 1, 2, 7 and 13, the averages become:

	Per Cent
.1% cocoanut	43.9
.2% cocoanut	41.0
.1% tallow	46.1
.2% tallow	44.3

The order of efficiency is found to be the same as before.

Taking the figures from the 6 cooperators who obtained the most complete washing (No. 3, 4, 10, 11, 14 and 15) the averages are:

	Per Cent
.1% cocoanut	48.3
.2% cocoanut	46.9
.1% tallow	53.6
.2% tallow	50.2

Again the order of efficiency is the same as before.

From the foregoing it seems reasonable to conclude that this order of efficiency represents an actual fact.

Figures from cooperators Nos. 10, 11 and 15 agree with this order. Figures from Nos. 6, 8 and 14 almost do so. Eight cooperators found .2 per cent cocoanut to be least efficient and 7 found .1 per cent tallow to be the best.

When attempt is made to explain the widely dissimilar results obtained by the several cooperators, the element of conjecture enters. In the course of other work 960 pieces of cloth have been soiled in the laboratory of the P. Q. Co. by the method supposedly used in the A. O. C. S. test. After soiling, rinsing and drying, as prescribed, the average of the 960 pieces was 25.1 per cent, as read in the Hess-Ives Tint-Photometer. These were used, day by day, in groups of six. The highest average for any such group was 27.6 per cent, and the lowest 23.6 per cent. This may be taken as showing the degrees of consistency of the soiling method, when applied over several months. It also indicates that something must be wrong when figures on washed specimens are below or near 25 per cent. A series of soiled, rinsed and unwashed specimens, sent in by one of the cooperators, averaged 25.4 per cent.

There are no available figures showing what the result would be if the loosely attached carbon black were not rinsed away before washing began. The influence of differences in color of well-rinsed specimens, has, however, been observed to some extent. In the course of work not connected with the A. O. C. S. test, there were many cases in which a lighter and a darker piece were washed together in the same jar. In 27 such cases the results were:

Average before washing 27.9. Average after washing 61.8.

Average before washing 22.0. Average after washing 59.3.

A difference of 6 per cent at the start may thus produce one of 2.5 per cent in the washed pieces.

Another source of discrepancy in the specimens from different cooperators, seems to have been in the speed of the Launderometers. In the writer's experience there is often more or less slippage of the round belts of these machines as originally designed. Most of the cooperators did not state the exact r.p.m. which they used. One (No. 2) used 16 and another (No. 11) ran at 45 r.p.m. The former secured the lowest figures (averaging 16.7 per cent) and the latter the highest (averaging 54.4 per cent), of the entire 15 series. On the other hand, one cooperator, using a chain drive and 65 r.p.m. obtained intermediate results (35.0 per cent average). It would therefore appear that there is an optimum speed. If low speeds are used, longer times are necessary to get the same amount of washing. If higher speeds are used, a point is finally reached at which the centrifugal force is great enough to prevent the bag from traveling the full length of the jar on each revolution. In any case, it seems clear that the speed of the machine should be constant to obtain comparable results.

Result of Second Cooperative Trial of the Method.— In this test, reports and specimens were received from 5 cooperators; another made the test, but unfortunately the specimens were apparently lost in transit. One of the 5 just mentioned did not take part in the first trial. The figures obtained by one of the cooperators were low (averaging 29 per cent). For reasons given under the "First trial," it seems that these may properly be omitted from the averages. These figures were:

.1 per cent cocoanut 31.9 per cent, .2 per cent cocoanut 27.4 per cent, .1 per cent tallow 28.4 per cent, .2 per cent tallow 28.3 per cent.

Readings on specimens in Hess-Ive Tint-Photometer in laboratory of Phila. Quartz Co.:

Cooperator	.1% Cocoanut	.2% Cocoanut	.1% Tallow	.2% Tallow
No. 1	42.2	34.9	43.2	41.0
No. 2	39.4	36.5	42.0	40.2
No. 3	41.0	40.6	44.8	43.0
No. 4	32.9	31.5	33.9	32.3
No. 5 Average	38.8	35.8	40.9	39.1

RESULTS OF FIRST COOPERATIVE TRIAL OF THE METHOD

The readings on washed specimens, as obtained by the co-operators and in the laboratory of the Philadelphia Quartz Company, are as follows:

	.1% Cocoanut Soap		.2% Cocoanut Soap		.1% Tallow Soap		.2% Tallow Soap	
No. of Co-operator	Cooperator's Reading	P. Q. Co. Reading	Cooperator's Reading	P. Q. Co. Reading	Cooperator's Reading	P. Q. Co. Reading	Cooperator's Reading	P. Q. Co. Reading
1	....	25.8	....	29.7	....	28.3	....	33.0
2	....	20.2	....	19.4	....	16.2	....	21.0
Note 4								
3	45.8	45.8	50.2	50.25	52.8	52.8	54.6	54.6
4	....	49.0	....	42.8	....	56.9	....	47.8
5	....	41.4	....	35.1	....	40.1	....	38.7
6	....	38.9	....	35.0	....	39.0	....	39.2
Note 1								
7	....	29.7	....	27.7	....	31.6	....	27.6
Note 1								
8	35.9	36.4	34.4	35.2	36.3	36.2	35.8	36.2
9	44.6	41.4	36.70	31.2	41.0	36.8	40.9	35.1
Note 2								
10	50.9	50.5	49.2	48.7	52.7	52.9	50.5	50 6
11	....	52.0	....	51.2	....	58.8	....	55.7
Note 5								
12	37.5	35.5	34.5	34.0	33.5	*25.5	37.5	37.0
Note 6								
13	18.98	22.9	21.75	24.7	21.54	24.8	23.37	26.6
Note 7								
14	50.35	50.4	52.35	49.2	52.35	53.4	52.50	48.5
15	39.2	42.4	36.1	39.2	42.9	46.7	42.1	44.2

1. Extracted with diastase. 2. Extracted with water. 4. 16 r.p.m. 5. 45 r.p.m. 6. Very few specimens sent in. 7. Used 60 gm. glass beads instead of Monel metal balls.

*This figure is probably affected by some mistake. In computing averages, the cooperator's figure (33.5) is used.

The cooperator whose specimens were lost, reported that non-instrumental comparison of them showed the following order: .1 per cent tallow best, .2 per cent tallow next, .1 per cent cocoanut next, and .2 per cent cocoanut poorest.

By comparison with the results of the first trial it will be seen that the same order of efficiency was found in both tests, when averages are considered.

In the second trial, all four cooperators gave first place to .1 per cent tallow, all agreed in finding .1 per cent tallow better than .2 per cent tallow, .1 per cent cocoanut better than .2 per cent cocoanut, and .2 per cent cocoanut the poorest of the four. The only disagreement in rating was in comparing .2 per cent tallow with .1 per cent cocoanut. These two solutions were apparently so nearly alike (.3 per cent in the averages) that entire agreement in regard to them was hardly to be expected.

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By R. B. Birch, Jr.

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