three methods gave the correct values. These fats have widely divergent physical characteristics, and one is an animal fat and two are vegetable fats. It is therefore not unlikely that the method can be successfully applied to all natural fats such as these, in which C_{16}–C_{18} acyl groups are in great excess. Whether it can be applied to others of greater or lesser chain length remains to be seen.

There is presently no way of testing the accuracy of the values for the isomeric forms. It is worthy of note however that the values for the glyceride types are the values, or the sums of values, derived by calculations based on the structures of the molecules. Thus the proportions of GS_2U are the sum of the proportions of SUS and SSU, the isomeric forms. If the value for GS_2U is correct, it is likely that the values for SUS and SSU from which it is derived are also correct.

Because no saturated acyl groups are present in the 2-positions in Hypothetical Fat No. 2, there can be no GS_3 in it. This fat therefore represents the extreme in "restriction" of GS_3. The values for the glyceride types calculated by the method of Kartha (3) for a fat in "restricted random" distribution with respect to the S and U are approximately, but not exactly, the same as those calculated by the present method. The values for the isomeric forms are grossly different; those calculated by the present method are obviously correct if it be assumed that those for the glyceride types are correct.

When a method of calculation gives correct results, the assumptions upon which it is based are presumably also correct. Therefore, in those fats to which the present method can be successfully applied, the saturated and unsaturated acyl groups in each of the three positions, no matter what their proportions, may very well be distributed therein at random. It is also quite possible that the proportions of S and U in the 1- and 3-positions are identical. If these characteristics were to prove common to natural fats generally, regardless of their origin, it would indicate a common synthetic pathway to the triglycerides. The present results suggest a mode of triglyceride synthesis common to both the animal and vegetable C_{16}–C_{18} fats.

The fat from the rat fed a fat-free diet is probably endogenous. The distribution of the saturated and unsaturated acyl groups therein is the most nearly random of all the fats investigated. Deviations from random distribution are largest in the proportions of the isomers, and the differences in these values are very small. It is of interest to note that the proportion of S in the 2-monoglycerides is slightly greater than that in the whole fat, which makes it resemble, in this respect, the distinctive pig fats more closely than the vegetable and other animal fats.

The calculated and observed values for the triglyceride types in kokum butter agree very well with those calculated for restricted random distribution. The calculated values for the isomeric forms are however greatly different. A similar relationship in cacao butter was pointed out recently by Vander Wal (7).

Summary

Evidence has been presented that the proportions of the glyceride types and isomeric forms in some fats in which C_{16}–C_{18} chains are greatly in excess can be determined by calculations based on a) the percentage of saturated acyl groups in the whole fat, b) the percentage of saturated groups in the 2-monoglycerides which can be derived from the fats by hydrolysis, c) the assumption that all the saturated and unsaturated acyl groups (S and U) present in each of the three positions in the molecules are dispersed therein at random, and d) the assumption that the proportions of S and U in the 1-positions are identical with those in the 3-positions. The method may apply to all predominantly C_{16}–C_{18} fats and to other fats as well.

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Some Factors in the Measurement of the Suspending Power of Aqueous Detergent/Fabric Systems

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THE LABORATORY-SCALE measurement of detergency for the purpose of assessing the efficiency of detergent products or processes, used in aqueous systems for removing soil from textile fibers, has long remained an incompletely solved problem, and in spite of the large amount of work that has been devoted to the problem, no completely satisfactory test method has yet been evolved. Not only do variations in test conditions or types of soil give variations in data that may lead to entirely contradictory results, but even when the same test is carried out by different laboratories under supposedly identical conditions, surprisingly variable results have been obtained.

It is generally recognized that the "suspending power," *i.e.*, the ability of a solution of detergent to prevent the redeposition of suspended soil onto a washed fabric, is a major factor contributing to the over-all efficiency of a detergent. Laboratory measurements of suspending power have been of two general types: a) a piece of white fabric is washed along with soiled fabric in a solution of the detergent under test, or b) a piece of white fabric is

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[1] Deceased.

washed with a measured quantity of soil dispersed in the detergent solution. In both of these methods the extent of deposition of soil, hence the suspending power of the solution, is measured by the decrease in reflectance of the white piece. The former method has been used extensively (1, 2, 3, 4) but is subject to at least one objection. The amount of soil available for assessing the suspending power of the detergent depends on the ability of the same detergent to remove soil. This latter property depends not only on the detergent itself but also on the soil and fabric used in the preparation of the soiled swatches. A low degree of deposition therefore does not necessarily represent good suspending-power; it may represent poor soil-removing power.

The other method, b) above, also has been used extensively (5, 6, 7) and is the method used in work previously reported from these laboratories (8, 9, 10). This method has provided in the past, and is still providing, much useful information. However its precision or reproducibility is such that only gross effects can be characterized with certainty. For detecting small differences between detergents, the method, at least as it has been applied in these laboratories, is not considered completely suitable.

The distinction between precision and accuracy in a test method has been stressed by Lambert and Sanders (11). Precision may be regarded as the extent of agreement between replicate determinations and is indicated by the standard deviation of the mean. Accuracy, on the other hand, indicates the extent to which the test results approach the "true value" of the property being measured.

Many examples of the low order of precision generally obtained by method b) might be quoted; the results of a cooperative testing program (15) carried out recently in Canada by six independent laboratories and given in Table I are typical.

It will be seen that the five laboratories that used the Launder-Ometer rated the three detergents in the same order of merit, *i.e.*, A<C<B, but the range of values assigned to any one detergent by the various laboratories was, in many cases, greater than the differences found between the three detergents. The range of values obtained, in any one laboratory, in the 16 replicate readings on a given detergent varied from 2.4 to 11.0 units with the average about 6.5 units. While this indicates an undesirable variability in the individual data obtained, some compensation can be provided by carrying out a larger-than-usual number of determinations. Thus, with 16 replicate determinations, the largest probable error of the mean recorded was only ± 2.0 units.

The variation in mean value for any one detergent obtained by different laboratories was considerably larger, amounting in one case to 18.7 units. It is true that different types of reflectometers were used by some of the laboratories, but, judging from the readings obtained on the unsoiled swatches, this source of variation could account for not more than three or four units.

TABLE I
Results of Cooperative Trials (15)

Laboratory	1	2	3	4	5	6
Detergent A						
Ro[a]	87.9	84.4	85.5	84	88.2	86.4
R[b]	39.6	36.1	44.3	45	41.0	59.4
Detergent B						
Ro	87.7	84.4	85.9	85	88.3	87.3
R	47.5	39.6	58.3	54	45.1	60.9
Detergent C						
Ro	87.7	84.4	85.7	85	88.3	87.1
R	46.8	39.5	54.0	52	41.6	61.3

[a] Ro = initial reflectance of white cotton. [b] R = final reflectance of soiled cotton. Launder-Ometer used except Laboratory 6 (Determeter). Temperature 60°C. Solution 0.2% by weight of detergent in distilled water. Test solution contained 0.02% graphite derived from Aquadag. Values shown are the mean of 16 readings.

This seems to indicate that in addition to an appreciable random variation that is inherent in the method, there is also a further source of variation that is characteristic of each laboratory. Since the compositions of the materials supplied are believed to have been reasonably uniform throughout, it is believed that the above-mentioned variations are related to an incomplete specification of the essential details of the method to be followed.

The above case thus illustrates the need for a more complete understanding of the factors affecting the precision of the suspending power test, and this was the purpose of the work reported in this paper. It is believed that the information obtained may be useful in the selection of testing conditions for specific purposes, also in interpreting the data obtained in such tests. In addition, some observations of more academic interest have been made, and it is felt that these should be reported. This work has been carried out over a considerable period of time, with the results of one trial suggesting further trials. Consequently a certain lack of organization of the work has been unavoidable.

Experimental

Materials and Methods. The majority of the measurements were carried out in a Launder-Ometer, using either one-pint glass jars or stainless steel cylinders (12). Some work was done by using vacuum bottles and a mechanical shaking machine (9), but this technique was rejected because the soiling appeared to be less uniform than that obtained with the Launder-Ometer and the temperature was more difficult to control.

Fabric. The fabric used, except where otherwise noted, was Town and Country cloth, a bleached unfinished cotton, having 54 × 46 threads per inch, weight 4.8 oz./sq. yd., supplied by Montreal Cottons Ltd., Montreal, Quebec. This cloth is normally given a resin finish to impart crease-resistance, but this was omitted in the cloth used in this work. It is very similar to the Indian Head muslin that has been used in many of the published methods. The cloth was extracted for 18–24 hrs. in a Soxhlet apparatus with 1:1 (by volume) methanol-benzene, dried, boiled for ½ hr. in 1% acetic acid, rinsed 3 times, boiled for ½ hr. in water, and finally rinsed 4 times in cold water. Distilled water was used throughout. The fabric was dried but not ironed and was then cut into 3 × 4-in. swatches with the 4-in. dimension in the warp direction. Two of these swatches were agitated in 100 ml. of detergent-soil mixture in a Launder-Ometer jar for 30 min., followed by a 5-min. rinse in water.

Soils. The behavior of a number of types of soil has already been studied in relation to the suspending power of pure soaps (9). Of these, Standard Micronex carbon black, uncompressed, was selected as the most suitable for use in suspending-power tests. This material is a channel black, having a mean particle diameter of 28 mμ and is manufactured by the Columbian Carbon Company. Aquadag, a colloidal graphite in the form of an aqueous paste, supplied by the Acheson Colloids Corporation, has also been used extensively. Both of these soils have been used in the present work.

Ilmenite, a ferro-titanium pigment, has also been used as a soil (13). In comparison with either Aquadag or Micronex the degree of soiling obtained is light even when used in relatively high concentration. Hence there is a tendency for the readings obtained with it to be crowded into the upper portion of the reflectance scale, thus decreasing the possibility of differentiating between different detergents. In some cases the data obtained with ilmenite do not agree even qualitatively with those obtained with carbonaceous soils. For example, sodium oleate is a somewhat better suspending-agent than sodium stearate when tested against Micronex, but the reverse is true when they are tested against ilmenite (9). Likewise a number of nonionic detergents are excellent suspending-agents for Micronex but are only mediocre for ilmenite (14). It is difficult to say which of these results are the more "accurate," in the sense previously defined, but the need for careful selection of soils and careful interpretation of data is obvious.

Preliminary Trials. In some of the earlier work carried out at these laboratories, using Micronex soil at 0.1% concentration, it was observed that the soil was not deposited uniformly over the surface of the cotton. In an attempt to improve this a number of minor modifications of the basic procedure were investigated. These included investigation of: a) type of fabric (fine sheeting, heavy drill, flannelette, Indian Head muslin with and without permanent finish, and Town and Country cloth); b) size of swatch; c) wetting out of swatch in boiling water prior to addition to detergent-soil mixture; d) elimination of possible oily contaminants on fabric arising from excessive handling; and e) hemming or coating the edges of the swatches with collodion to prevent ravelling and tangling. None of these modifications led to any appreciable improvement in the uniformity of soiling.

The Indian Head muslin with permanent finish was of some interest in that the degree of soiling obtained was very intense. Reflectances in the order of 11–12% were obtained as compared with 55–60% for similar fabric without the permanent finish. This difference is presumably the result of modification of the surface properties of the cotton and serves to emphasize the need for careful selection of fabrics used in soil deposition work.

Effect of Soil Concentration and of Number of Washes. Previous work on suspending power had employed relatively high concentrations of carbon, for the most part in the range of 0.02–0.1%. These higher concentrations, when used with a poor, or even a fair, suspending-agent, lead to a heavy deposition of soil on the cotton. From one point of view this is acceptable since the wider portion of the reflectance scale put into use should lead to a greater differentiation between detergents. However these heavy loadings not only fail to simulate practical laundering conditions but may be responsible, in large part, for the poor reproducibility of the data since the irregular deposition of soil mentioned previously appears to be accentuated by heavy loading.

Accordingly trials were carried out in which the carbon concentration was reduced to the extent that a barely perceptible darkening of the cotton swatch was obtained in one wash. Then, to increase the degree of soiling, multiple washes were carried out. In this way it was hoped to combine the uniform deposition characteristics of very light redeposition soiling with the differentiation potentiality of a reasonably wide reflectance range.

The soil concentration used was either 0.0005 or 0.001% (5 or 10 p.p.m., respectively) carbon derived from Aquadag. Aquadag, as supplied, contains approximately 22% solids. A 1% dispersion was prepared by dilution of this material with distilled water. The concentration was checked by evaporating 25-ml. aliquots to dryness at 105°C. and weighing the residue. The stock dispersion was then further diluted as required for use. Two detergent formulations were compared: Formulation A contained 0.2% Nacconol NR[2] in distilled water, and Formulation B contained 0.2% Nacconol NR plus 0.002% sodium carboxymethyl cellulose,[3] also in distilled water. The detergent-soil mixtures were prepared at least 18 hrs. before use and were agitated for 30 min. in the Launder-Ometer before adding the cotton swatches. This was done to insure that the carbon particles would be thoroughly dispersed. It has been shown (16) that the particle-size distribution of suspended carbon changes with the changing concentration of the detergent used to suspend the particles. In the present case it was expected that this would involve deflocculation of carbon since the soil mixture is made up initially as an aqueous dispersion, and this is then added to the detergent solution. However subsequent work on the dispersion of carbon would suggest that these steps were unnecessary. (See later section). The swatches were rinsed by immersion for a few seconds in a beaker of distilled water at 60°C. and were then spread first on paper towels and then on wire screens to dry. They were not ironed. This method of rinsing was adopted rather than the longer process of rinsing in the Launder-Ometer because it was found that, except for a small amount of loosely held soil, very little soil was removed in the rinsing operation. Three consecutive washes were given; the swatches were dried, and their reflectances were read after each wash. The whole procedure was repeated twice more, over a period of about 12 days, using freshly prepared and aged soil-detergent mixtures.

The data are given in Table II, in which each value is the mean of eight reflectance readings. The highest standard deviation obtained was 1.03 while the average for the whole series was 0.49. These values indicate a considerable improvement in uniformity of soiling, and this was confirmed by visual examination of the soiled swatches. The reproducibility is indicated by the agreement between the replicate determinations a, b, and c (Table II), which were carried out at different times and with different lots of solutions and is considerably better than has been obtained previously.

The data of Table II also show that differentiation

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[2] National Aniline Division, Allied Chemical and Dye Corporation.
[3] Carboxel D-435, Chemical Developments of Canada Ltd.

TABLE II

Soiling of Cotton by Dilute Aquadag Suspensions

Detergent formulation Soil concentration p.p.m.	A 5			B 5			A 10			B 10		
No. of washes	1	2	3	1	2	3	1	2	3	1	2	3
Reflectance %												
a	65.6	57.7	52.2	81.9	80.9	80.1	58.3	49.6	45.0	79.9	78.7	76.8
b	65.6	58.0	52.0	81.4	80.7	80.2	58.5	48.9	44.3	79.5	77.7	76.3
c	65.4	56.9	51.9	81.8	80.4	80.4	58.2	49.2	44.6	78.7	77.5	76.4

Temperature 60°C. One hundred ml. of detergent-soil mixture used. Two 3 × 4-in. cotton swatches. Fifteen steel balls. Stainless Launder-Ometer tubes. Time of agitation with detergent-soil mixture 30 min.

between Formulations A and B may be increased by increasing the soil concentration or by increasing the number of washes. Thus in selecting test conditions, from the point of view of precision and of time required to carry out tests, it is desirable to use the highest soil concentration compatible with a uniform deposition of soil and to give only as many consecutive washes as may be necessary to obtain a satisfactory depth of soiling. However from the standpoint of simulating the soil concentrations normally encountered under practical conditions and thereby possibly improving the accuracy of the test, it is better to employ low soil-concentrations with a number of multiple washes.

Effect of Type of Carbon. In order to study the effect of varying the soil concentration for both types of soil, suspending-power tests were carried out, as outlined above, on Detergent Formulations A and B and also with distilled water alone using, respectively, Aquadag and Micronex soils at concentrations varying from 5 to 80 p.p.m. Reflectance values were measured after two consecutive washes. The amount of soil deposited on the cotton was calculated in relative weight units by means of the Kubelka-Munk equation. (See later section on calculation of data.) The results are given in Figures 1 and 2.

The data for Micronex (Figure 1) are generally in accord with the anticipated behavior of the materials used, *i.e.*, it would be expected that carbon would be deposited most readily from a suspension in water only, less readily from the Nacconol solution, and least readily from the solution of Nacconol plus carboxymethylcellulose.

The results for Aquadag (Figure 2) are not as readily explained. It is apparent that Aquadag forms a remarkably stable suspension in distilled water as indicated by its low deposition on cotton in comparison to that of Micronex. The graphite particles in Aquadag are suspended with the aid of ammonia and dextrinous materials (17), and this probably accounts for, or at least contributes to, the low degree of deposition from water. However it does not explain the high degree of deposition from the Nacconol NR solution at low soil-concentrations (Figure 2). It would therefore seem that some component of the Nacconol NR causes deposition of the soil to such an extent that this tendency cannot be overcome by the surface-active properties of the alkylaryl sulfonate active ingredient of the Nacconol NR but can be overcome by the combination of alkylaryl sulfonate and carboxymethyl cellulose. The component most likely to cause this excessive deposition is sodium sulphate (7), which is present to the extent of about 60% in Nacconol NR. The effect on the deposition of soil of sodium sulphate and of a salt-free surfactant is shown in Table III. The concentrations of Na_2SO_4 and of Nacconol NRSF (which is similar to Nacconol NR except that it is free of inorganic salt) were chosen to approximate the concentrations of these materials present in a 0.2% solution of Nacconol NR.

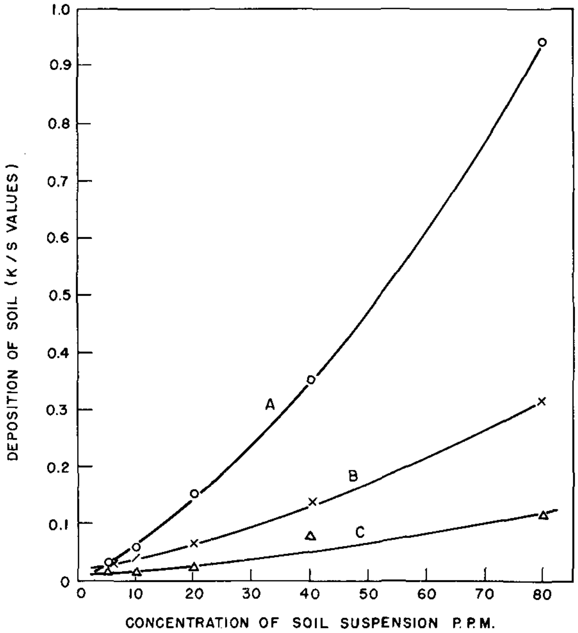

Fig. 1. Deposition of Micronex soil. A, distilled water; B, 0.2% Nacconol NR; C, 0.2% Nacconol NR plus 0.002% carboxymethyl cellulose.

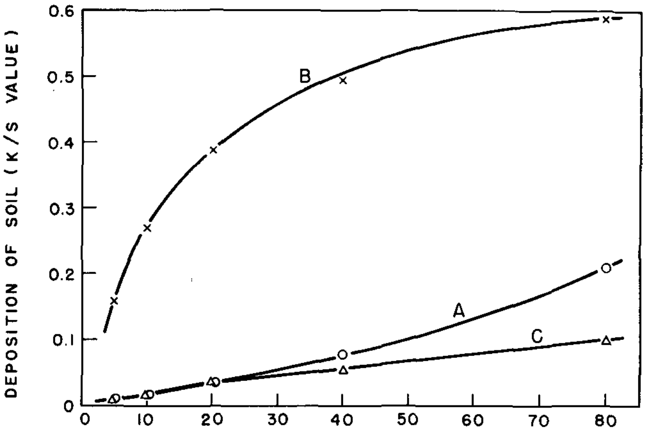

Fig. 2. Deposition of Aquadag soil. A, distilled water; B, 0.2% Nacconol NR; C, 0.2% Nacconol NR plus 0.002% carboxymethyl cellulose.

TABLE III

Deposition of Soil During Two Consecutive Washes[a]
Relative Weight Units (K/S values)

Type of soil	Aquadag		Micronex	
Soil conc'n, p.p.m.	10	80	10	80
Nacconol NR, 0.2%	0.2533	0.6240	0.0343	0.3371
Nacconol NRSF, 0.087%	0.0657	0.2166	0.0337	0.2153
Na_2SO_4, 0.12%	0.5028	3.8054	0.4571	3.4723

[a] Experimental conditions as shown in Table II.

Considering first the Aquadag suspensions, it is obvious that the presence of Na_2SO_4 causes a heavy deposition of soil on the cotton even from suspensions containing initially only 10 p.p.m. of graphite. Similarly heavy depositions have also been obtained in the presence of NaCl and of calcium and magnesium salts used to simulate hard water. This effect would thus appear to be analogous to the well-known effect of electrolytes in deflocculating colloidal suspensions. The deposition from the suspension containing the salt-free Nacconol NRSF is considerably lower than that from the suspension containing Nacconol NR. Hence, in the case of Aquadag suspensions, it may be concluded that the suspension in distilled water is quite stable, that it is very sensitive to precipitation by electrolytes, and that the presence of an alkylaryl sulfonate only partially overcomes this tendency to precipitate.

TABLE IV

Effect of Hard Water on the Deposition of Soil[a]

	Reflectance after 2 consecutive washes			
Soil	Aquadag		Micronex	
Water	Distilled	Hard	Distilled	Hard
Water only	79.6	41.4	69.6	39.0
Nacconol NR, 0.2%	49.3	45.4	70.1	69.7
Nacconol + CMC, 0.002%	78.2	70.8	80.2	75.5
Nacconol NRSF, 0.087%	68.5	48.5	74.8	49.8
Nacconol + CMC, 0.002%	80.5	72.0	77.8	69.4
Na_2SO_4, 0.12%	37.8	35.1	39.4	37.0
Na_2SO_4, 0.12% + CMC, 0.002%	56.0	......	52.2	......

[a] Experimental conditions as shown in Table II.

The data for Micronex (Figure 1 and Table III) suggest that this carbon shows considerably more tendency to deposition from distilled water than does Aquadag, particularly at higher soil concentrations, that it is equally sensitive to precipitation by electrolytes, and that this precipitation is inhibited by the presence of an alkylaryl sulfonate to a much greater extent than is the case with Aquadag suspensions.

This last effect is possibly related to the extent of adsorption of the surfactant by the two types of soil. The graphite particles in Aquadag have a mean diameter of 1 μ or slightly less (17) while Micronex particles have a mean diameter of 28 mμ (9). Micronex particles in aqueous solutions are undoubtedly agglomerated into particles of much larger size, but the surface area available for adsorption appears to be determined by the size of the ultimate particles (18, 19). Hence it would be expected that a surfactant would be adsorbed to a greater extent on Micronex than on Aquadag particles.

From the standpoint of selecting suitable testing conditions it may be concluded that with low soil-concentrations and multiple washes the use of Micronex leads to results that are, in some respect at least, more nearly in agreement with practical experience. However, for certain specific tests, *e.g.*, for showing the effect of additions of CMC to a detergent, the use of Aquadag may be preferable since certain effects tend to be magnified by this soil.

It should also be noted that the data obtained with Micronex appeared to be somewhat more variable than that obtained with Aquadag.

The Influence of Hard Water on Soil Deposition. The suspending powers in distilled and in hard water were compared for the various formulations listed in Table IV. The hard water contained $CaCl_2$ and $MgSO_4$ in sufficient quantity to give a total hardness of 300 p.p.m. as $CaCO_3$ with a Ca:Mg ratio of 60:40. Both Aquadag and Micronex soils at a concentration of 10 p.p.m. were used. It may be seen that the effect of the hard water on the deposition of these soils is approximately the same as that of 0.12% Na_2SO_4 in distilled water. In molar units these concentrations correspond to 9.1 millimoles/liter of Na_2SO_4 and 3.0 millimoles/liter of combined Ca and Mg salts. With respect to the electrical charge 1 mole of Na_2SO_4 is equivalent to 1 mole of $CaCl_2$ or $MgSO_4$, but divalent ions are more effective than monovalent ions as precipitating agents for carbon suspensions because they are more strongly adsorbed.

With regard to testing methods a choice is usually made between distilled or hard water. Occasionally both are used, but this is usually limited to specific cases where the resistance of a detergent to hard water is being studied. From the data given in Table IV it would appear that, in general, suspending power is lower in hard water than in distilled water. However tests have been carried out with a built domestic detergent in which no significant difference between hard and soft water could be detected, and this, together with other data obtained in the course of the work, suggests that the effect of hard water varies from negligible to appreciable, depending on the particular detergent compound or formulation.

In addition to the possible ionic effects referred to above, the use of hard water may accentuate the effect of other components of the detergent formulation. For example, the presence of carboxymethyl cellulose leads to improved suspending power in all cases where hard water is used. With Nacconol NRSF and Aquadag soil this improvement is twice as great (in terms of reflectance units) in hard water as it is in distilled water. On the other hand, with Nacconol NR, the improvement is slightly greater in distilled water than in hard water.

Likewise if the difference between Nacconol NR and Nacconol NRSF is attributed to the effect of Na_2SO_4, this effect is large in distilled water and small in hard water. Similar effects are also obtained with Micronex soil.

Dispersion of Particles in Soil Suspensions. Use of Waring Blendor. It has been pointed out already that the ultimate particles in Micronex are very small but that in aqueous suspensions they coalesce into much larger aggregates. This was demonstrated by agitating a dilute suspension of Micronex (10 p.p.m.) in distilled water in a Waring Blendor at 15,000 r.p.m. for 1–2 min. The suspension, which was initially almost water-clear, became quite perceptibly darker. Apparently the carbon aggregates are partially dispersed by the action of the Blendor with a resultant increase in light absorption.

In order to study further the effect of aggregate size a series of 0.02% aqueous suspensions of Micronex were made up and agitated in the Waring Blendor for times varying from 30 sec. to 4 min. These suspensions were then used to carry out suspending-power tests at 20 p.p.m. soil concentration in distilled water and in 0.2% Nacconol NR solution. Although the data showed more than the usual variation, this appeared to be purely random, and there did not appear to be any correlation with the time of agitation in the Blendor. Since it was obvious from the slower rate of settling of the carbon particles that the average aggregate size had been decreased by the Waring Blendor treatment, it was concluded, in agreement with Vold and Phansalkar (19), that the aggregate size has little effect on the extent of deposition on cotton.

Effect of Presence of Fabric in Increasing Dispersion of Soil. In measurements of suspending power of soil-water systems in which no detergent was present it was observed that the Micronex suspension became noticeably darker after agitation in the Launder-Ometer with the cotton swatches. This was also found to occur with suspensions containing 0.2% Nacconol NR, but here the effect was obscured by the presence of foam.

To study this effect further, suspensions were made containing 10, 20, and 30 p.p.m. Micronex in distilled water alone. After thorough mixing on a mechanical shaker the optical density of each suspension was read on a Fisher Electrophotometer, using a green (525 mμ) filter. A portion of each suspension was then agitated in the Waring Blendor for 2 min. at 15,000 r.p.m., and the optical density was again read. The usual suspending-power tests were then carried out in the Launder-Ometer, using both the original and the Blendor-"dispersed" suspensions. The optical density of the residual suspension was read, and the reflectance of the soiled swatches was determined. The results are given in Table V.

TABLE V
Effect of Launder-Ometer Treatment in Presence of Fabric on Dispersion of Soil

Soil concentration p.p.m.	Original suspension (Mechanical shaker)			Dispersed suspension (Waring Blendor)		
	Optical density		Reflectance of cloth[a]	Optical density		Reflectance of cloth[a]
	Initial	Residual[a]		Initial	Residual[a]	
10	3.3	50.0	69.7	33.5	62.0	71.2
20	7.8	102.8	59.5	61.2	119.6	62.2
30	11.5	166.0	51.1	94.0	198.0	54.9

[a] After shaking in Launder-Ometer in presence of fabric.

It is obvious that, while agitation in the Waring Blendor produces an appreciable darkening of the Micronex suspension, agitation in the Launder-Ometer with steel balls and cotton swatches is much more effective in this respect. This interesting effect apparently can be attributed to the presence of the fabric, or to the combination of fabric and steel balls, although in the absence of fabric only a very slight darkening of the suspension was obtained.

It should be noted that, although the Waring Blendor-processed suspensions were initially considerably darker than the corresponding suspensions before being put through the Blendor, these differences tended to be very much smaller after agitation with fabric in the Launder-Ometer. Furthermore the cotton swatches that were agitated in the darker suspension (Waring Blendor) came out slightly lighter than those agitated in the suspension which had not been put through the Blendor although this difference may not be significant. If it is true, as these results seem to indicate, that carbon aggregates are dispersed much more completely by agitation with the fabric in the Launder-Ometer than by other seemingly more vigorous means, then the reason for the lack of correlation between aggregate size and depth of soiling becomes apparent since agitation with the fabric would seem to bring all of the aggregates to nearly the same particle size regardless of their initial condition.

In a further series of experiments a variety of fabrics were solvent-extracted, thoroughly rinsed in water, dried, and cut into 3 × 4-in. swatches. In addition, one swatch of Town and Country cloth was ravelled into individual yarns and another was reduced to individual fibers by chopping the yarns into lengths of about 1 mm. These were run in the Launder-Ometer in the usual way except that only one fabric swatch (or equivalent weight of yarn or fiber) was used in each container, with 100 ml. of 20 p.p.m. Micronex suspension. The optical densities of the residual suspensions are given in Table VI.

TABLE VI
Optical Density of Micronex Suspension after Agitation with Various Textile Materials

Material	Optical density
Initial suspension before agitation in Launder-Ometer	7.7
Initial suspension after agitation without fabric in Launder-Ometer	10.0
Cotton, plain weave (Town and Country), fabric	89.0
Cotton, plain weave (Town and Country), yarn	150.0
Cotton, plain weave (Town and Country), fiber	130.0
Cotton, plain weave, light (nainsook)	64.0
Cotton, duck, 10 oz.	46.4
Cotton, flannelette	114.0
Glass fabric, coarse[a]	154.0
Glass fabric, fine[b]	57.0
Wool flannel	30.3
Nylon taffeta	31.2

[a] 18.9 oz./sq. yd.; 46 × 35 threads/inch.
[b] 2.1 oz./sq. yd.; 79 × 73 threads/inch.

All the fabrics were lightly-to-moderately soiled except the wool and nylon, which were very heavily soiled. The low optical density of the residual suspensions from these two fibers is apparently the result of depletion of carbon from the suspension by deposition rather than lack of dispersion of carbon aggregates. It is obvious that the ability to increase the dispersion of carbon aggregates is not unique for cotton, also that the physical condition of the textile material has a pronounced effect.

Similar tests, using cotton fabric (Town and Country), were also carried out with 20-p.p.m. suspensions of various carbon blacks, also with Ilmenite and Aquadag. Owing to the extremely high optical density reading of the initial Aquadag suspension, this material was used at a concentration of 1 p.p.m. instead of the usual 20 p.p.m. Some carbons that would not wet out in water were dispersed in a 0.01% solution of Nacconol NR. The results are shown in Table VII.

TABLE VII
Optical Density of Various Suspensions

Soil	Original	Agitated in Launder-Ometer		Agitated 1 min. in Waring Blendor
		Without cotton	With cotton	
A-20 p.p.m. suspensions in distilled water				
Royal spectra	5.6	9.7	38.0	34.3
Micronex	7.7	10.0	89.0	42.9
Neo spectra	2.5	7.8	45.7	48.4
Superba	4.0	12.3	83.0	48.1
Excelsior	5.8	10.2	73.0	45.8
Ilmenite	2.5	3.1	17.2	5.7
Aquadag	140.0	......	......	......
Aquadag (1 p.p.m.)	6.7	7.5	11.3	8.0
B-20 p.p.m. suspensions in 0.01% Nacconol NR solution				
Statex B	2.8	7.1	32.6	35.7
Acetylene black	3.9	22.3	44.2	55.4
P-33	1.8	8.1	26.5	35.5
Lampblack	6.5	19.7	32.5	32.2

The original suspensions were made by adding a weighed quantity of dry carbon to water or Nacconol solution and stirring or shaking gently by hand. With the exception of the Aquadag all the other suspensions gave initial optical density readings within the range 1.8–7.7. While the optical densities of all the suspensions were increased by agitation in the Launder-Ometer, the extent of this increase varied widely with the various carbons.

Aquadag appears to be unique among the soiling materials studied. The extremely high optical density of the initial suspension, together with the almost negligible increase on agitation in either the Launder-Ometer or Waring Blendor, suggests that the graphite particles in Aquadag do not form aggregates but have been almost completely dispersed in the material as received. This may account for the observation, previously made, that fabrics are soiled somewhat more uniformly from Aquadag than from Micronex suspensions.

The surprising efficiency of textile materials in various forms in producing deflocculation of most carbons is of considerable interest in view of the numerous detergent processes involving the agitation of textiles with aqueous detergent solutions. Of these, the one involving conditions most similar to those of the experiments described above is laundering, and it would be of interest to explore the bearing of this deflocculatory phenomenon on the laundering and cleaning industry.

Calculation of Data. In the calculation, from reflectance data, of suspending power (S.P.), redeposition factor, or whiteness retention as it is variously described, two formulas are commonly used, *viz.*: a) S.P. (etc.) = 100(R–Rw)/(Ro–Rw) and b) S.P. = 100R/Ro, where Ro is the reflectance of the original white fabric and R and Rw are the reflectances of the fabric after washing in a suspension of soil particles in the test solution and in water, respectively. With regard to the first formula 100% represents no deposition of soil, 0% represents the suspending power of water. In many cases this formula gives comparative data that have some physical significance. However, as is evident from the data for Aquadag (Table IV), there are cases where the assigning of zero suspending power to water leads to negative values for compounds that do, in fact, have appreciable suspending powers. The second formula is preferable for use with Aquadag since the "water value" does not enter into the calculation. Both formulas include Ro and therefore presumably take into account variations in the initial reflectance of the white fabric. However standard deviations calculated for a large number of determinations, using both "R" and "100R/Ro" values, indicate that no improvement in variability was obtained by use of the latter formula. Consequently it is concluded that the reflectance "R" is just as satisfactory a measure of suspending power as are the values calculated by the above formulas.

A third method of calculation that has received some attention in recent years involves application of the Kubelka-Munk equation (20), $K/S = (1-R)^2/2R$ to the reflectance data. In this equation K is the coefficient of absorption of light, S is the scattering coefficient, and R is the reflectance. It has been shown (21) that

$$K/S - K^1/S = XG/S$$

where K/S and K^1/S refer to the soiled and clean fabrics, respectively, G is the weight of soil retained by a given weight of fabric and X is the specific absorbance of the soil. As long as a single type of fabric is used for all tests, the value of S remains essentially constant and relative values of GX can be calculated from reflectance data. These values have been used as an index of the weight of soil deposited on the fabric, but it is obvious that this is only valid if the specific absorbance of the soil remains constant. In general, the latter is not constant but varies with the concentration of the detergent used to suspend the soil (16). The term GX should be regarded as representing the "soiling capacity" of the deposited soil or the "effective soil content" of the fabric rather than the weight of soil. For many purposes this is a more useful and informative value than the reflectance or suspending-power index derived from reflectance data. Examples of its use are shown in Figures 1 and 2 and in the following calculation. It was stated above that the variability of the suspending-power index (100R/Ro) was not improved by taking into account the initial reflectance of the individual swatches. The reason for this becomes apparent when the pertinent K/S values are considered. Suppose that the initial reflectance is 87 ± 2% and that the fabric is soiled to an average reflectance of 50%. It is desired to calculate the variation in the final reflectance which results from ±2% variation in the initial reflectance.

The initial reflectance of 87 ± 2% corresponds to a K/S value of 0.0097 with a range of 0.0133 to 0.0068. A final reflectance of 50% corresponds to a K/S value of 0.2500. Hence to reduce the mean reflectance to 50% requires the addition of an amount of soil equivalent to a K/S value of 0.2500 − 0.0097 = 0.2403. Adding this amount to each of the above K/S values and converting back to reflectance units, the final reflectance is found to be 50 ± 0.2%. Since the variation in the initial reflectance is usually less than 4 units, its effect on the final reflectance is negligible.

Conclusions

In view of the complexity of the detergent process and of the many factors that influence its operation, it seems unlikely that a single universal test for suspending power can be specified that will be applicable under all conditions and for all detergent materials. It is suggested instead that the one basic procedure should be modified to suit particular needs by varying the type and concentration of soil used and the number of consecutive washes given. For example, the data given in Table II show that a soil concentration of 5 p.p.m. Aquadag with three consecutive washes is a suitable choice for demonstrating the effect of carboxymethyl cellulose on the suspending power of an alkylaryl sulphonate detergent. However, if two highly efficient suspending agents were being compared, use of the above conditions would probably result in a very small degree of soiling, hence in very little differentiation between the two detergents. It would be necessary to go to higher soil concentrations, to a greater number of multiple washes, or perhaps to a different type of soil. In general, the soil concentration should be low enough to give a uniform deposition on the fabric, and the number of consecutive washes should be great enough to bring out any differences between the materials being compared. A thorough familiarity with the behavior of the soiling material under varying conditions of testing is thus essential, not only for the selection of the optimum testing conditions but also for intelligent interpretation of the results obtained.

Summary

The variability associated with the usual methods for measuring the suspending power of aqueous detergent solutions used to remove soil from textile fibers is pointed out, and a modified method, using multiple washes with very low concentrations of soil, is proposed. Two commonly used artificial soils are compared. Micronex, a typical fine particle carbon black, appears to give data in reasonable accord with practical experience while Aquadag, a suspension of graphite particles, tends to magnify some effects and therefore is more useful for specific tests. Aquadag is found to be highly dispersed in dilute aqueous

suspension while Micronex (as well as other carbon blacks) forms relatively large aggregates in water. These aggregates are partially dispersed by vigorous agitation in a Waring Blendor but are more completely dispersed by rotation in the Launder-Ometer in the presence of fabric, yarn, or fiber of cotton or other textile material. The influence of hard water and of other inorganic salts on suspending power data is discussed. The need for careful selection of type of soil and fabric and for careful interpretation of data is stressed.

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Preparation of Pure Fatty Acid Methyl Esters by Countercurrent Distribution[1]

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COUNTERCURRENT DISTRIBUTION constitutes a useful physical tool for the isolation and preparation of pure fatty acids and methyl esters because of its inherently mild fractionating-conditions, high resolving power, and comparatively large sample-capacity. Like chromatographic methods and fractional solvent crystallization, it separates unchanged the naturally occurring isomers of unsaturated acids. In contrast, chemical methods involving the polybromides give products containing some unnatural isomers, and urea fractionation usually gives products containing at least small amounts of other fatty acids.

Various solvent combinations have been used for the separation of fatty acids and of methyl esters. Ahrens and Craig (1) studied systems formed by mixing heptane with acetic acid, methanol, and either formamide or acetonitrile for the countercurrent distribution of the higher fatty acids. Cannon, Zilch, and Dutton (3) reported the use of a nitromethane, nitroethane, pentane-hexane system for the separation of methyl esters.

This communication describes the use of acetonitrile and pentane-hexane for the analytical countercurrent distribution of methyl ester mixtures as well as the preparative separation of methyl esters of pure fatty acids. Acetonitrile is selective for esters of different degrees of unsaturation. It has a low boiling-point and forms azeotropes with the hydrocarbon solvents so that it is easily removed by evaporation. It is stable under the conditions used, and when the fractions are removed in portions of upper pentane-hexane layer by the single withdrawal procedure (4), the lower layer may be re-used. Thus operations are considerably simplified, and it is not necessary to empty the apparatus and refill with fresh solvent for each successive batch.

Experimental

Methyl Linolenate. Since preparations of this ester have frequently been required in this laboratory, experience with this ester and the acetonitrile-pentane-hexane system is most complete. Because the weight of esters that can be fractionated per batch is limited by the size of the tubes of the countercurrent distribution apparatus, it is advantageous to start with esters having as high a concentration of methyl linolenate as possible. For this reason a methyl linolenate concentrate, prepared by the urea-complex procedure that was devised by Parker and Swern (10), was used as the starting material. This concentrate contained 84.7% methyl linolenate, 15.4% methyl linoleate, and 0.2% methyl oleate as measured by gas chromatography.

Countercurrent distribution was carried out in a 200-tube apparatus which contains 40 ml. of lower layer in each tube. To study separation under optimal conditions, only 10.0 g. of methyl linolenate concentrate were used. The concentrate was dissolved in 200 ml. of lower phase and 50 ml. of upper phase of the solvent system and was placed in the first five tubes of the instrument. Seven hundred transfers were applied, using 10-ml. portions of upper phase for each transfer. After the first 200 transfers the upper layers were withdrawn from the apparatus according to the single withdrawal procedure. These fractions were caught, one in each tube of the collector, and were evaporated in tared flasks. Because nothing was found in fractions corresponding to transfer 200 through 300, these fractions are not

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