Studies in the Comparison of Detergents

Degree of Cleanliness Obtained Throughout Washing Process of Same Order as That After Maximum Number of Washes

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THE problem of determining the detergent properties of a soap or washing material is of great interest to soap manufacturers and users. For several years a committee of the American Oil Chemists' Society has been considering the solution of this problem. Numerous methods have been tried out in the past and gradually a method has been evolved step by step.

A little over a year ago a method of making wash tests was worked out by the committee which seemed to be a great step ahead in the solution of the problem. A reproducible method of soiling specimens was worked out by Mr. Carter and with equipment and washing procedure which had been pretty well standardized previously it was possible to make comparisons of detergents which were reproducible and apparently of considerable accuracy. The results obtained with this test were expressed as the number of washes required to wash the soiled specimens to the same color as unsoiled specimens which were carried through the test (complete cleanliness). It was found however that the method required such a long time to wash the specimens that it was valueless from a practical standpoint. It was also found that the amount of soil removed per wash, as the specimens approached complete cleanliness, was so little that the endpoint could not be determined within a range which would not comprise the endpoints of most of the common detergents.

The results during the early washes however seemed quite consistent and the differential between different detergents was quite marked. It was felt therefore that the detergent properties of different detergents could be compared satisfactorily if it could be shown that the degrees of cleanliness obtained at any fixed number of washes were in the same order as the number of washes required to obtain complete cleanliness. In order to demonstrate this, several series of washing tests were made and the color of the specimens determined after each wash. The results were expressed graphically in a coordinate system with the number of washes and percent white as coordinates. For comparison a C.P. anhydrous sodium-tallow soap and a C.P. anhydrous sodium-coconut oil soap were chosen.

Since difference in washing action is more pronounced with a pigment that is difficult to remove, carbon was decided on, the cloth (Utica sheeting) being soiled to saturation in accordance with the method worked out and demonstrated by Carter. The Launderometer was used and the washing performed according to specifications with the exceptions that all washes lasted twenty minutes and that the specimens were dried between washes. For reading the color the Hess-Ives Photometer was used, 100 percent white being indicated by a block of Magnesium Carbonate. Distilled water was used throughout the experiments, and the strength of soap solution was 2 g. in 1000 cc.

IN ORDER to determine color readings it was of course necessary to dry the specimens. To ascertain whether there was any difference when the specimens were washed in successive washes when they were dried between the washes a preliminary test was made with the coconut oil soap. Forty specimens were given eight twenty minute washes in succession and forty specimens were given the same number of washes but rinsed and dried after each wash. When the color was read it appeared that the average color of the specimens washed in successive washes was lighter (43.26% white) than the average color of the rinsed and dried specimens (40.76% white). Realizing that incomplete rinsing, leaving soap to dry on the specimens, would complicate the process, a second test was made. In the first test the rinsing water had room temperature, in the second test it had a temperature of 150° F.

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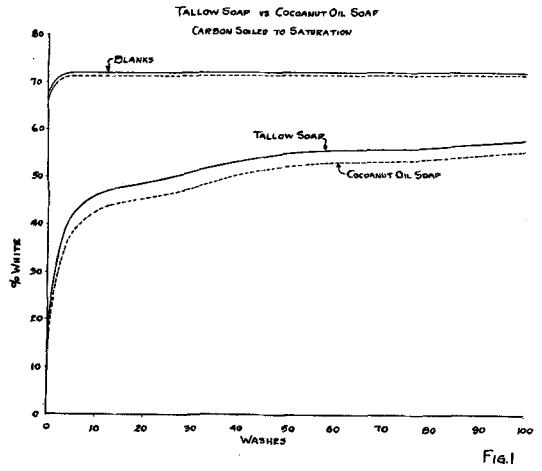

FIG. 1

When rinsing, mechanical action of course was avoided as much as possible so as not to remove part of the pigment. Therefore the specimens were soaked in the water for fifteen minutes and then squeezed lightly. The result of the second test was 43.87% white for the successive washes and 42.54% white for the intermittent ones. These results were considered close enough to justify the assumption that there is no appreciable difference in washing action whether the specimens be dried after each wash or not.

In the main test sixteen soiled and four unsoiled specimens were used for each soap. The results shown are averages of sixteen individual readings of the soiled specimens and of four individual readings of the blanks. Up to and including the twelfth wash colors were read after every wash but from the twelfth up to the one hundredth the washes were made in blocks of three, four or five with no rinsing and drying after the individual washes. If during the washing test a jar broke or started to leak the specimens were immediately discarded, this of course to eliminate disturbing factors as much as possible.

Figures 1 and 2 show the results obtained in graphical and numerical form. It will be noted that the results as shown (*Figure* 2) are not absolutely consistent. Interfering factors are many, such as mechanical action, inconsistencies in color readings etc., but the curves plotted (*Figure* 1) seem to show very definite characteristics. It should be remembered that

COMPARISON OF RESULTS. TALLOW SOAP VS. COCONUT OIL SOAP
SPECIMENS SOILED TO SATURATION WITH CARBON

Wash No.	Blank—Color % White		Soiled Cloth—Color % White		
	Tallow Soap	C.N.O. Soap	Tallow Soap	C.N.O. Soap	Difference
0	66.0	66.0	7.8	7.8	0 0
1	69.6	68.2	25.7	24.5	1.2
2	67.5	67.6	32.3	30.2	2.1
3	70.0	67.7	35.4	33.7	1.7
4	67.5	69.2	38.6	36.5	2.1
5	70 5	70.8	41.5	39.0	2.5
6	75.7	73.4	42.3	39.3	3.0
7	74.2	73.2	44.0	42.4	1.6
8	76.2	73.7	45.5	41.2	4 3
9	72.9	71.9	46.0	42.7	3.3
10	73.9	73.9	45.8	43.8	2.0
11	74.7	73.9	47.7	43.2	4.5
12	73.9	71.2	45.7	42.7	3.0
14	73.4	70.7	46.9	43 3	3.6
17	73.4	71.7	48.4	45.3	3.1
20	71.4	72.9	48.5	45.6	2.9
23	71.2	69.4	49.6	46.1	3.5
26	68.7	70.4	50.3	47.4	2.9
29	69.7	69.9	50.9	47.8	3.1
32	70.2	70.2	51.8	48.7	3.1
35	72 2	73.7	53.1	50.7	2.4
39	68.4	66.4	52.1	50.7	1.4
43	67.9	67.9	52.7	52.7	0.0
46	72.2	72.2	54.4	52 4	2.0
49	70.4	73.2	55.9	53.8	2.1
53	68.9	70.7	55.3	52.9	2.4
58	69.4	72.4	58.8	54.3	4.5
61	72.9	—	57.4	—	—
65	69.4	70 7	53.9	52.2	1.7
72	65.9	69.2	55.9	51.9	4.0
75	68.9	68.2	55.6	53.0	2.6
80	70.2	69.7	56.2	52.8	3.4
85	71.5	69.4	55.9	54.0	1.9
90	71.9	73.7	56.3	54.5	1.8
94	70.4	69.7	57.6	54.9	2 7
100	70.7	71.4	57.7	55.7	2.0

FIGURE 2

the color readings are averages. There is a distinct difference between the results with the different soaps after the first wash. This difference seems to reach a maximum between the eighth and fourteenth washes. From this point on the curves remain practically parallel, possibly converging slightly.

A second series of tests was run using a soap this time consisting of 50% C.P. anhydrous sodium tallow soap and 50% C.P. anhydrous sodium coconut oil soap. In one case this soap was mixed 75% soap and 25% sodium carbonate solids and in the other case 75% soap and 25% "N" brand sodium silicate solids. The strength of the solutions was again 2 grams in 1000 cc. The procedure was repeated exactly as in the first series of experiments except that the test was carried to only twenty washes. *Figures* 3 and 4 show the results obtained in graphical and numerical form. The results follow very closely in every respect with those obtained in the first series.

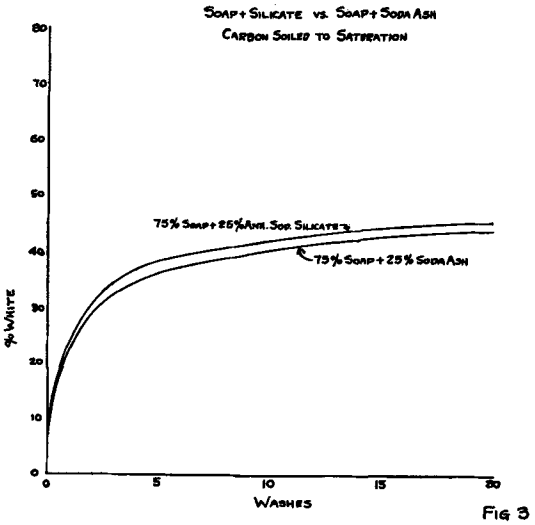

FIG 3

COMPARISON SOAP AND SILICATE VS. SOAP AND SODA ASH
SPECIMENS SOILED TO SATURATION WITH CARBON

Wash No.	Soap and Silicate Color % White	Soap and Soda Ash Color % White	Difference
0	7.48	7.48	0.00
1	24.29	22.09	2.20
2	31.76	29.52	2.24
3	34.52	32.56	1.96
4	36.58	34.85	1.73
5	38.69	36.02	2.67
6	38.02	37.19	0.83
7	38.97	37.47	1.50
8	39.80	39.07	0.73
9	39.97	39.19	0.78
10	41.41	40.36	1.05
12	42.40	42.02	0.38
14	43.52	43.08	0.44
16	44.25	43.41	0.84
20	45.30	44.19	1.11

FIGURE 4

IT WILL be noted that in none of the tests, even those run to 100 washes, did the color come up to complete cleanliness (the color of the blank). It had been expected when the tests were started that the point of complete cleanliness would be reached. It is apparent that the color of the washed specimens is not going to reach the color of the blanks within any reasonable number of washes. In fact it seems doubtful if this point can ever be reached when the specimens are soiled to saturation with carbon. It is desirable though to try to obtain some definite demonstration that the degrees of cleanliness obtained with different detergents at any fixed number of washes are in the same order as the number of washes required to obtain complete cleanliness.

Two additional sets of tests were then run using specimens less heavily soiled so that they could be washed more rapidly. The specimens for one set were soiled to saturation with umber and for the other set were lightly soiled with carbon. Two series of washes were run on each set, one series with C.P. anhydrous coconut oil soap and the other with C.P. anhydrous tallow soap. The washes were continued to as near complete cleanliness, that is, the color of the blanks, in each series as possible. The results of each series are expressed graphically and numerically in *Figures* 5, 6, 7, and 8. It will be noted that the umber soiled specimens show numerous discrepancies during the early washes. This is to be expected since the soil is so easily removed. But that the curves are in the proper order during the latter washes and that the curve representing washes with tallow soap meets its blank after about seventeen washes whereas twenty-eight washes are required for the curve representing coconut oil soap to meet its blank.

The series lightly soiled with carbon show reasonably consistent results throughout but time was not available to carry the results quite to the point of complete cleanliness although

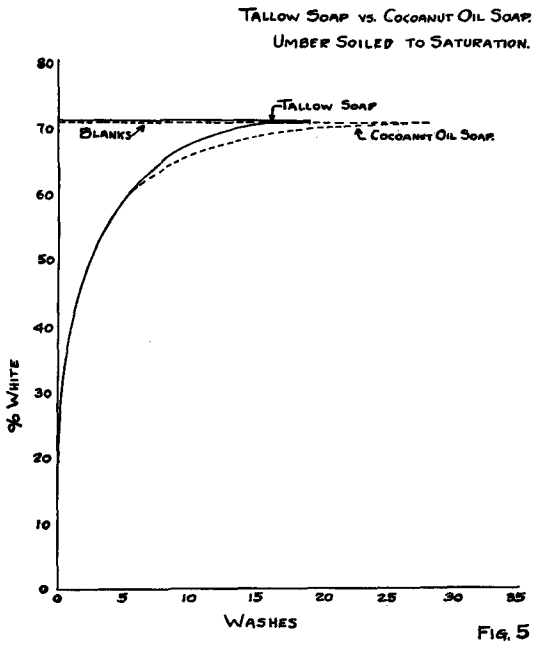

FIG. 5

they have approached very closely and the results remain in the proper order. In fact it looks doubtful again whether the color of the washed specimens even lightly soiled with carbon will ever reach the color of the blanks. Apparently the last traces of carbon soil are too difficult to remove and even if sufficient washes could be made to accomplish this the results as the color of the specimens approaches the color of the blanks would not be sufficiently accurate to be reliable.

In conclusion therefore it seems that the majority of the data supports the original hypothesis that the degrees of cleanliness obtained with different detergents remains in the same order throughout the washing process so that detergents may be correctly compared after a limited number of washes. It will be noted that the results are most consistent in the majority of the tests during the early washes due to the fact that the most soil is being removed per wash during this time.

IT SEEMS logical therefore to recommend the following procedure as a standard test for comparing detergents.

1. Use standard method as detailed in 1930 except all washes twenty minutes. No unsoiled blanks required.
2. Soil specimens to saturation with carbon black as worked out by Carter. Do not use less than ten specimens.
3. Make six twenty minutes washes in succession.
4. Compare average color of washed bags after drying either by color readings or by eye and rate detergents accordingly.

If standard equipment, standard methods, standard sheeting and standard carbon black are used the results may be expressed numerically since no trouble has been experienced in checking results if an average of a number of washes is used. It has been found that the test may be carried out in different washing equipment using different sheeting and different soil with equally satisfactory results relatively, although of course the results will not check numerically with results run by the standard method. It has been suggested that an index wash be run in each series either with C.P. sodium stearate or plain water which

COMPARISON OF RESULTS. TALLOW SOAP VS. COCONUT OIL SOAP
SPECIMENS SOILED TO SATURATION WITH UMBER

	Blank—Color % White		Soiled Cloth—Color % White	
Wash	Tallow Soap	C. N. O. Soap	Tallow Soap	C. N. O. Soap
0	70.99	70.99	19.54	19.44
1	71.19	71.19	41.69	43.33
2	73.44	70.44	50.83	49.08
3	71.44	71.19	58.65	56.86
4	70.94	70.69	57.70	58.65
5	71.19	71.44	60.85	60.15
6	70.69	70.94	62.86	63.23
7	71.19	71.19	64 54	64.84
8	71.19	71.19	65.12	63.38
9	71.19	70.94	66.56	65.86
10	70.94	71.19	68.04	67.20
11	71.19	71.19	67.82	67.39
12	70.19	70.69	66.75	65.90
13	69.34	69.19	65.81	67.66
14	70.19	70.19	67.40	69.12
17	71.19	70.19	70.82	69.46
20	71 00	70.19	70.07	68.07
23	71.00	70.19	70.20	68.80
28	—	70.19	—	70.70

FIGURE 6

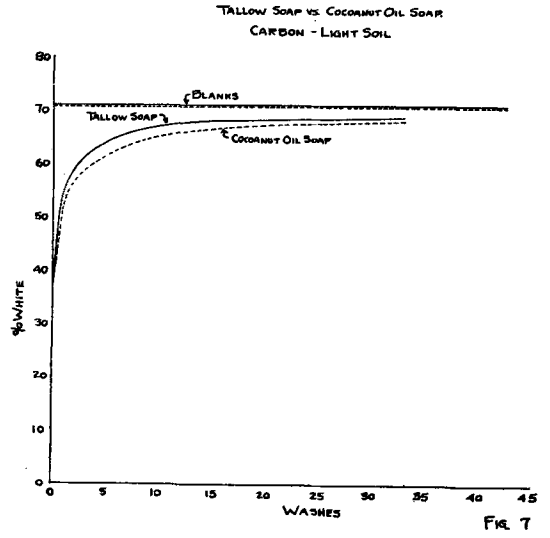

FIG. 7

can be used as an index from which all results can be expressed. In this case numerical results can be obtained under any conditions. Some work done along these lines shows considerable promise. It may be interesting to note that while color readings are desirable they are not necessary since a large number of tests have indicated that the eye can distinguish a difference of 1 percent whiteness easily.

It should be borne in mind that there are certain limitations to the above method namely:

1. That only one general type of soil has been tried i.e., inorganic materials, umber and carbon black and on only one type of fabric. Whether the same results would be obtained with soils containing greasy material is questionable. It has been suggested that in view of the difficulty of removing carbon black all other soils, except possibly stains, would come out long before the carbon in which case the results with carbon would be a true index of detergency regardless of the type of soil.

2. An average of a number of not less than ten specimens must be taken to correct inconsistencies in individual washes.

3. The procedure and results obtained are known to hold only with the common types of washing materials usually dealt with and may not be satisfactory for detergents of special types such as those containing solvents, bleaching materials, etc.

It is felt that the test as outlined above supplies a tool which is practical and which if used with discretion by an intelligent operator who understands its limitations will give comparisons of detergents which are dependable.

COMPARISON OF RESULTS. TALLOW SOAP VS. COCONUT OIL SOAP
SPECIMENS SOILED LIGHTLY WITH CARBON

	Blank—Color % White		Soiled Cloth—Color % White	
Wash	Tallow Soap	C. N. O. Soap	Tallow Soap	C. N. O. Soap
0	70.99	70.99	37.57	37.69
1	71.19	71.19	56.44	54.57
2	73.44	70.44	60.32	56.82
3	71.44	71.44	63.82	59.19
4	70.94	70.69	63.52	60.52
5	71.19	71.44	65.19	62.02
6	70.69	70.94	62.86	63.69
7	71.19	71.19	65.52	63.69
8	71.19	71.19	66.19	64.02
9	71.19	70.94	65.69	63.86
10	70.94	71.19	67.52	62.02
11	71.19	71.19	62.69	66.02
12	70.19	70.69	64.52	65.69
13	69.34	69.19	64.19	64.86
14	70.19	70.19	66.86	65.36
17	71.19	70.19	68.52	68.19
20	71.00	70.19	68.02	66.86
23	71.00	70.19	68.90	67.99
28	71.00	70.19	68.36	67.99
33	70.70	70.50	68.86	68.69

FIGURE 8

Since the formation of spots in soaps is analogous to the temperature increase of olein in the Mackey test, both being dependent upon oxidation, it has been suggested that it would be of benefit to introduce the Mackey test into the soap industry for testing the color permanency of soaps and fats or their liquid fatty acids during oxidation. *Seifensieder-Ztg.* 58,291-2 (1931). In this connection it is noteworthy that it has been recently announced that the material and design of the "cage" of the Mackey apparatus affect the results obtained in the apparatus. Nichrome cages have been suggested. *Chimie & Industrie* Special No., 650 (March, 1931).