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Deflocculation and Detergency Not Entirely Correlative

A Report on Detergent Experiments on Cotton Soiled with Carbon Black

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AFTER work presented by the writer[1] on the deflocculation of carbon black, it seemed desirable to perform detergent experiments upon fabrics soiled by the same substance with the object of determining whether deflocculation and detergency are correlative phenomena.

The Washing Machine:—Comparative washing tests should be conducted under uniform conditions of agitation and "rubbing," and so practically demand the use of some sort of machine. Whether a laboratory machine imitates any commercial washer in action seems of slight importance, for the determination of the relative efficiencies of various machines is essentially an independent problem. The machine used was devised to wash and rinse small slips of fabric with vertical agitation in test tubes immersed in a water bath. The slips were held at one end in spring clips suspended from rocker-arms and were weighted at the free ends. Construction drawings are given in Figures 1 and 2. The machine carried four double rocker-arms accommodating eight clips with their suspending shafts. The shafts were equipped with perforated metal discs to cover the test tubes. The supporting frame was made of steel, painted; the pulley of wood; the rest of the apparatus of hard brass.

The motive power was a 1/50 hp. motor equipped with a variable friction gear and further controlled by a slide rheostat. The belt, on its traction side, ran over a small pulley attached to the shaft of a bell revolution counter, so that the speed of the machine, always kept close to 300 r.p.m., could be audibly checked.

The bath was an ordinary enamelled pail, about 11 inches in diameter at the top. On this was fitted a cover of sheet brass, containing

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two rows of holes to accommodate the test tubes, the rows being spaced 3⅞ inches between centers. A hole for a thermometer was also provided. The test tubes were of Pyrex glass, 25 x 200 mm. Each was equipped with a tightly fitting ring of wire drawn through small rubber tubing, the lower edge of the ring being set 6 inches above the inside of the bottom. These rings supported the tubes in position in the bath. When set up the apparatus was adjusted to afford clearances of 1¼ inches between the extremities of the clips at their lowest points of travel and the bottoms of the test tubes.

Preparation of the Fabric:—New fabric, in 18-inch squares, was boiled gently for 1 hour in a liberal volume of a 0.5 to 1.0 per cent solution of neutral, silica-free white soap in a beaker provided with a grating of nichrome gauze to keep the goods off the bottom. After cooling to 40°-50° C. the goods were plunged by hand about 2 minutes, then squeezed strongly and transferred to a similar beaker in which they were simmered 15 minutes in a 1 per cent solution of concentrated ammonia water. After again cooling, plunging and squeezing they were given a second, and then a third similar rinsing with diluted ammonia. During the washing and rinsing the goods were frequently overhauled and punched with a stout glass rod. From the last rinse they were removed dripping wet, dried on clean sheet

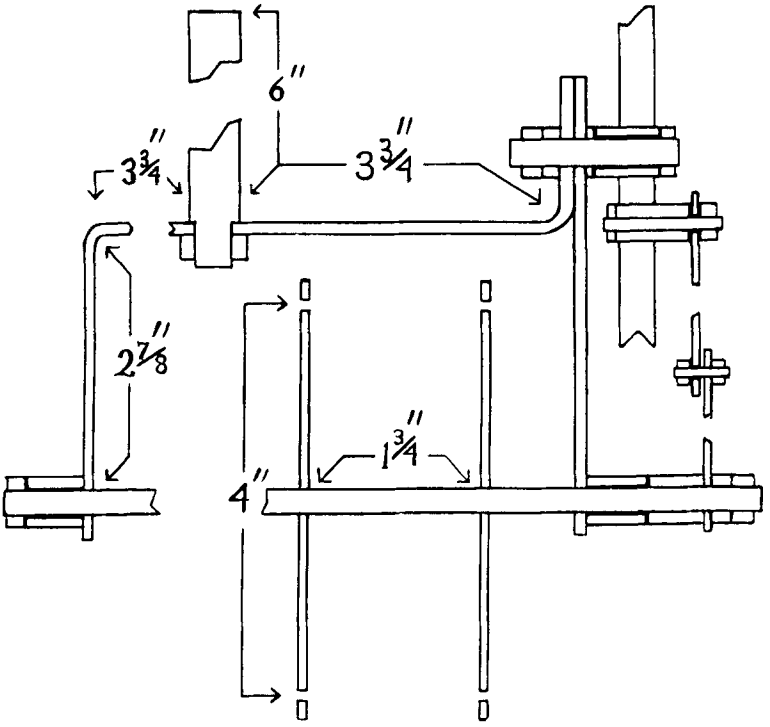

Fig. 1.—*Plan of Washing Machine.*

glass, and cut into slips 2 x ¾ inches for heavy goods or 2 x ⅞ inches for light goods, the longer dimension being parallel to the selvage. Some were then used without further preparation; others were first extracted with ether in a Soxhlet apparatus. All were provided with lead weights before use. Sheet lead, about 1/16 inch thick, was cut into ⅜-inch squares, the pieces averaging about 1.7 g. each. A square was bent into a V with pliers and pinched firmly onto an end of each slip.

To insert a slip into a clip the latter, with its jaws held uppermost, was slipped over the handle of a metal spatula, horizontally clamped to a ring stand. A slight movement of the shaft then sufficed to pry the jaws of the clip sufficiently open to allow the unweighted end of a slip to be evenly inserted for about ⅛ inch.

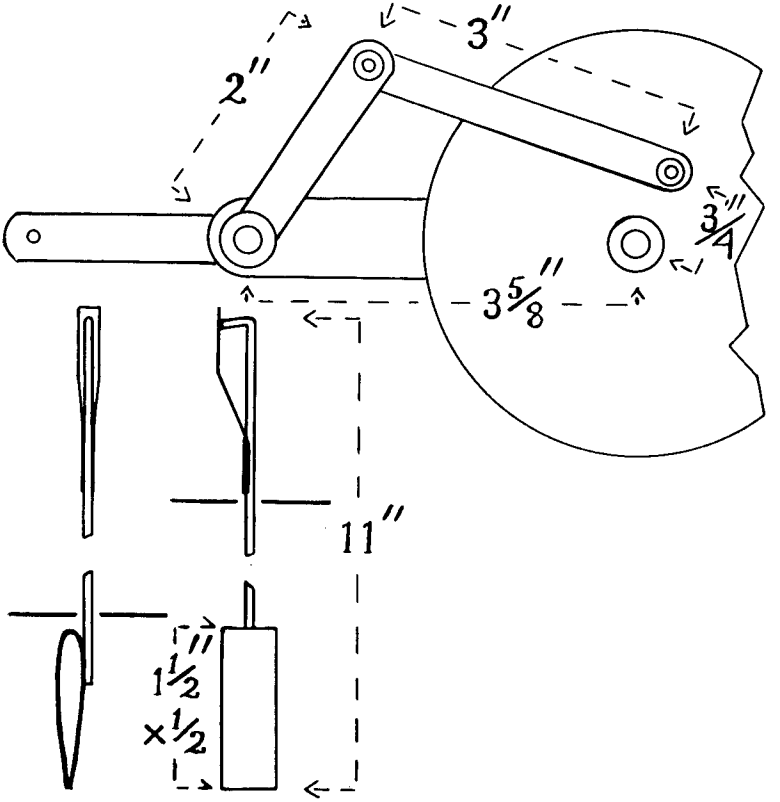

Fig. 2.—End View of Washing Machine.

Evaluation of the Residual Soil: —In order to arrive at a numerical expression for the soil remaining on a piece of washed fabric, a colorimeter was converted into a reflectometer in a manner which the writer has not seen described in the literature. The two mirrors of a Kober-Klett instrument were replaced with a single rectangle of plate glass smoothly covered with dull black woolen cloth. This will be termed the "reflecting table" of

the instrument. Only uniform artificial illumination was employed. First, a slip of the unsoiled fabric was smoothly laid down at each end of the reflecting table so that its half-field in the eyepiece was completely filled. Second, the two cups were charged with a slightly acid and perfectly clear solution containing cobalt, nickel and copper salts in appropriate proportions, and both plungers were set at the same reading, say 30 mm. Third, the instrument was shifted sideways in front of the lamphouse until the half-fields in the eyepiece exactly matched. Fourth, one of the cups, say the right-hand, was emptied, rinsed and charged with distilled water, and the right-hand slip was removed from the reflecting table. The apparatus was then ready for use. A slip carrying soil to be evaluated was laid on the right-hand end of the reflecting table and the left-hand plunger was moved until the half-fields matched, the right-hand plunger being also moved nearly in unison. After the reading of the left-hand plunger had been taken the soiled slip was turned over and the process was repeated. The readings obtained against the two sides of the soiled slip were averaged for the final result.

The appropriate blending and dilution of the standard solution of cobalt, nickel and copper salts had to be determined by repeated trials, and probably would vary with different light-sources. The numerical result for residual soil was therefore directly obtained as the millimeters read on a particular colorimeter against a standard that was of unknown, though probably of permanent, composition. If it should prove worth while, such results could be recalculated so as to make the detergent power of some standard soap solution the ultimate unit for comparison.

Cleansing from Initially Adsorbed Carbon Black

In the first attack upon the problem it was desired to keep the composition of the system as simple as possible. Therefore the slips were soiled by agitation in a mixture of carbon black and water only. The carbon black was the identical lot used in the previously published experiments on deflocculation. It seemed to be strongly adsorbed by the fabric but naturally only upon the surface, being unable, in its coarsely suspended condition, to penetrate deeply into the threads.

The soiling was done at room temperature. Test tubes were charged with 0.3 gram carbon black and 30 cc. distilled water, stoppered, given a brief vigorous shaking, and placed in position in the machine. Slips of weighted fabric in their clips were introduced and the machine was run 8 minutes. Some slips were then given a 2-minute rinse in 30 cc. distilled water; others had received in addition a preliminary 2-minute rinse before entering the carbon black suspension. All were finally laid on glass plates, dried at 100° C. and stored in paper boxes.

Experiment 1.—The first experiment dealt with the effect of duration of washing. Tubes were charged with 30 cc. of 0.03 N pure, neutral, sodium palmitate, heated to incipient boiling, stoppered and held in the bath at 70° C. for 1 hour. Then soiled slips were introduced, washed varying periods, rinsed 4 minutes in 50 cc. water at 70° C. and dried on glass. In Figure 3, Curve I, are shown the

results on a light-weight plain nainsook, not ether-extracted, soiled without either a preliminary or final rinse. Curve II shows the results on a light handkerchief linen,

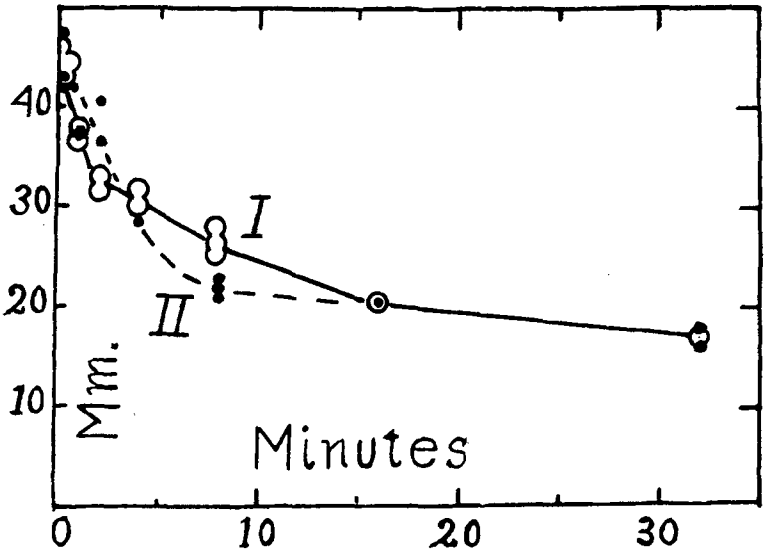

Fig. 3.—Effect of Duration of Washing in Experiment 1. Curve I, Nainsook; Curve II, Linen.

which had been ether-extracted and also given the double rinse when soiled.

Experiment 2.—Sodium stearate, neutral, acid and alkaline, was tested at 70° C. upon nainsook slips, ether-extracted and soiled with the double rinse. The soap solutions were all held 1 hour at 70° C., after incipient boiling and thorough mixing, before the goods were introduced. The wash period was 8 minutes; the rinse 4 minutes. The results are given in Figures 4 and 5.

Experiment 3.—Following Experiment 2, it seemed necessary to test the effect of sodium hydroxide at 70° C. in absence of soap, with the results shown in Curve I of Figure 7.

Experiment 4.—To observe the effect of temperature, tests were run on neutral sodium stearate as in Experiment 2 except that the temperature was 60° C. The results are shown in Curve I of Figure 6. Above 0.04 Normal the soap solutions were too thick to be workable. Results at 25° C. are given in Curve II, Figure 6.

Experiment 5.—Neutral potassium stearate, tested at 25° C. but otherwise according to the technique of Experiment 2, gave the results shown in Curve II of Figure 7.

Experiment 6.—Neutral sodium laurate was tested at 25° C. and at 70° C., but otherwise according to the technique of Experiment 2 with the results shown in Figure 8.

Experiment 7.—Inasmuch as some of the experiments on deflocculation had indicated that sodium laurate might show notably

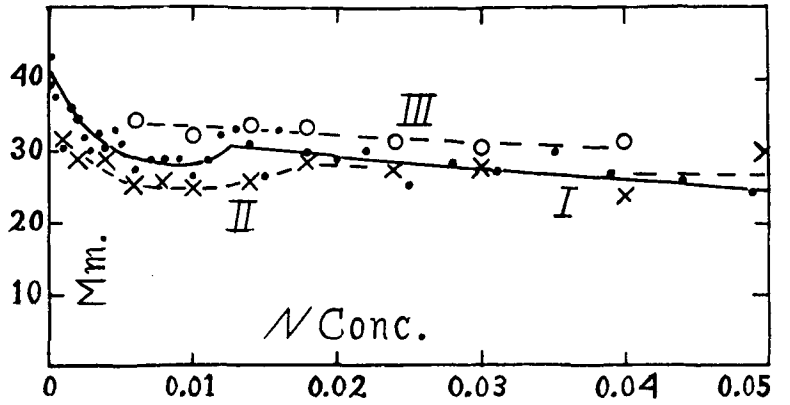

Fig. 4.—Sodium Stearate at 70° C. in Experiment 2. Curve I, Neutral; Curve II. Alkaline; Curve III, Acid.

increased power when crystals of the substance were present, tests were run at 25° C. in which the standard temperature was approached from below. The tubes of prepared soap solution were chilled 1 hour in ice water, then held 1 hour in the bath at 25° C., being stirred with a glass rod toward the end of the period, after which the experiment was completed according to the technique of Experiment 2. Crystals were abundantly present at the time of washing at concentrations of 0.20 and 0.16 Normal, but the results practically coincided with the corresponding results in Experiment 6. They also coincided at concentrations of 0.12 and 0.08 Normal, in which crystals were absent but at 0.06, 0.04 and 0.02 Normal they indicated a loss in detergent power.

Experiment 8.—Neutral sodium oleate from Oleic Acid U.S.P. was tested according to the technique of Experiment 2. In Figure 9 the results at 25° C. are shown as dots, those at 70° C. as circles.

Experiment 9.—A few tests were run on substances other than soap for comparison with data on deflocculation previously secured. The test slips were of ether-extracted

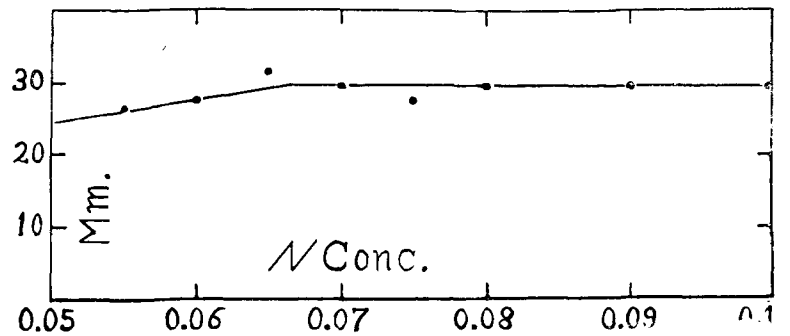

Fig. 5.—Extended Curve of Neutral Sodium Stearate at 70° C. in Experiment 2.

nainsook soiled with the double rinse. The temperature was 27°-28° C. All solutions were left in the bath 1 hour before test. The wash-period was 8 minutes, with a 4-minute rinse. The data are given in Table 1.

Experiment 10.—Similar soiled slips of nainsook were soaked for about 1 hour at room temperature in various liquids, drained briefly and then washed in 0.03 Normal neutral sodium palmitate at 70° C. for 8 minutes with a 4-minute rinse. Preliminary experiments had revealed no difference between sodium palmitate and stearate at this concentration and temperature. The data are given in Table 2.

Experiment 11.—A slip of similarly soiled nainsook from which the lead weight had been removed was sewed by the two ends to the inside of a pair of white duck pants worn in the laboratory, being placed at the back, slightly below the waist-band, and the soiled pants were sent to the laundry as usual. On return the strip was cut off, wet out in hot water and dried on a glass plate to smooth it. It then read at 17 mm. in the colorimeter. A similar experiment at a later date afforded a reading of 13 mm.

Discussion.—The method is decidedly less sensitive to variations in the nature and proportion of soap, and to other influencing factors, than is the previously described method for testing deflocculating power. It is also lacking in precision, largely owing, no doubt, to the initial non-uniformity of the test slips soiled in the manner described. As it stands, it is not a practical routine method for determining the relative detergent powers of competing commercial soaps. However, the results do seem to support the following generalizations respecting the washing of cotton, and probably linen, goods soiled by adsorbed non-oily carbon black:—

(a) There is an optimum temperature for each soap; sodium

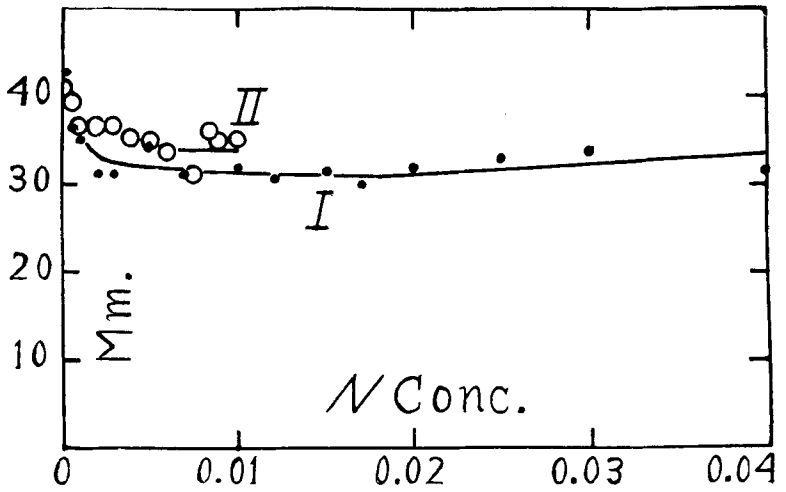

Fig. 6.—*Neutral Sodium Stearate in Experiment* 4. *Curve I, at* 60° *C.; Curve II, at* 25° *C.*

laurate was more powerful at 25° C. than at 70° C., while the reverse was true of sodium stearate. An oleate appears the best soap for use with cold water, while at or above 70° C. a stearate or palmitate appears more powerful.

(b) Alkali, in moderate concentration, appears to possess slight detergent power by itself and it may decidedly enhance the power of soap solutions. Power is diminished by excess of fatty acid.

(c) Some other substances showed significant detergent power but none was found equal to soap at its best.

(d) No addition other than alkali was found to enhance the detergent power of soap.

(e) Detergency and deflocculation were found parallel in the fact that excess alkali enhanced power while excess fatty acid decreased it, but other possible resemblances were vaguely defined at best.

In the course of the work it was observed that the violence of the "rubbing" may considerably affect apparent detergent power. Occasionally ravellings would become entangled across the face of a strip and the friction would produce a pale streak. Also some experiments were made with slips of extra heavy cotton shirting and it was found that the goods were so stiff that the flexions during washing were likely to occur mostly across the middle with consequent production of a transverse pale band.

Prevention of Adsorption of Carbon Black

Inasmuch as the experiments on the removal of initially adsorbed carbon black had been unsatisfactory, the problem was approached from the other direction. It seemed possible that a comparison of the powers of soap solutions to prevent adsorption of carbon black by a fabric might afford a more sensitive and precise method for practical application.

The fabric employed was "Burton's Irish Poplin," a mercerized cotton, washed, ether-extracted, cut into slips and weighted as before described. This material was easier to handle and seemed to work

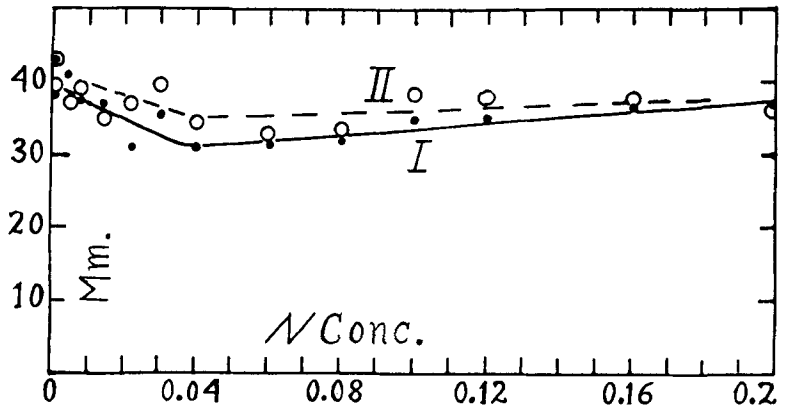

Fig. 7.—Sodium Hydroxide at 70° C. in Experiment 3 (Curve I); Neutral Postassium Stearate at 25° C. in Experiment 5 (Curve II).

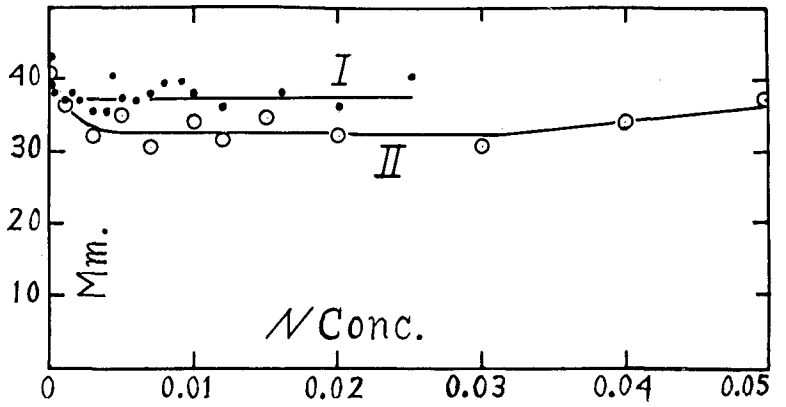

Fig. 8.—Neutral Sodium Laurate in Experiment 6. Curve I, at 25° C.; Curve II, at 70° C.

more uniformly than nainsook. First, the test tubes were charged with 30 cc. soap solution, heated with mixing to incipient boiling, stoppered and left in the bath at the desired temperature for 50 minutes. Second, charges of 0.3 g. of the same carbon black as previously used, already weighed out on celluloid slips, were brushed into the tubes and clips were inserted each of which carried a loop of small brass chain made from a 6-inch length with its ends joined. The machine was now run for 8 minutes. Third, the clips carrying the chains were removed and other clips carrying clean slips were inserted. The machine was now run 8 minutes. Lastly, the slips were given a 4-minute rinse and the residual soil was evaluated as in the previous experiments.

Experiment 12.—The effect of temperature was tried on neutral pure sodium palmitate with the results down in Figure 10. Also the curve at 40° C. was coincident with that at 55° C. so far as it could be carried without undue

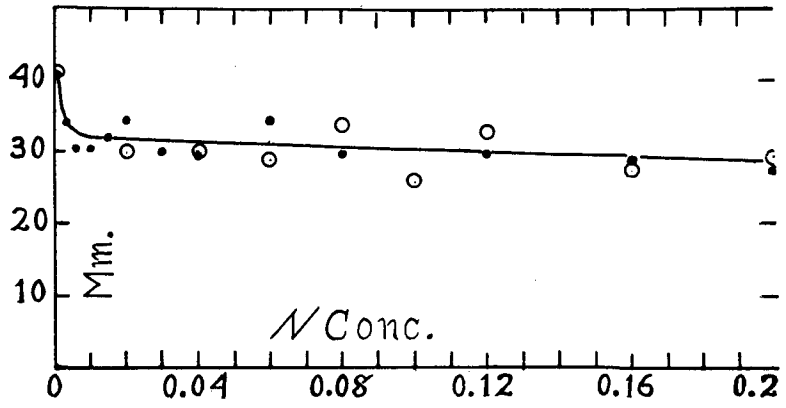

Fig. 9.—Neutral Sodium Oleate in Experiment 8.

thickening of the solution, namely, to 0.01 Normal.

Experiment 13.—Results with neutral sodium laurate at 25° C. are given in Figure 11. The

hibited adsorption of suspended carbon black by the fabric; stearates and palmitates more powerfully than laurate. But sodium stearate was a more powerful in-

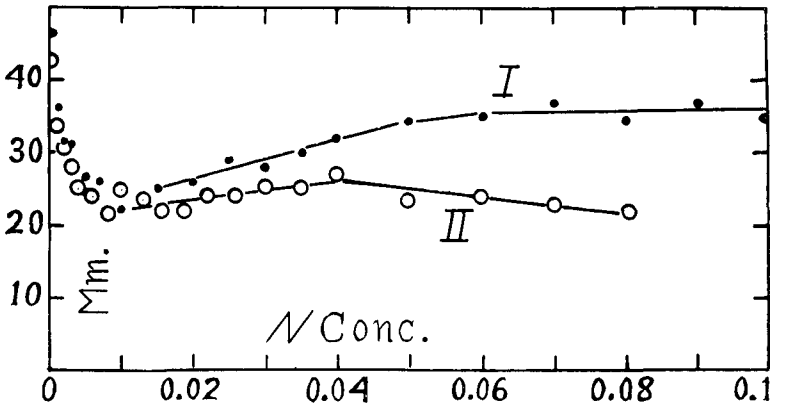

Fig. 10.—*Neutral Sodium Palmitate in Experiment* 12. *Curve I, at* 70° *C.; Curve II, at* 55° *C.*

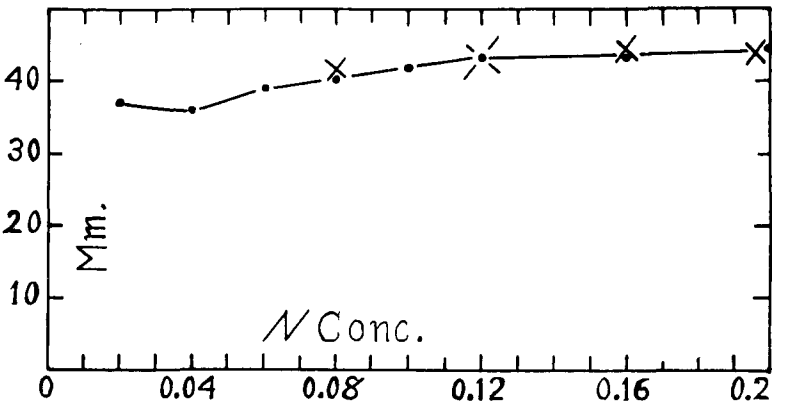

Fig. 11.—*Neutral Sodium Laurate at* 25° *C. in Experiment* 13.

crosses indicate other tests in which the final temperature was approached from below, as in Experiment 7.

Experiment 14.—Acid and alkaline sodium stearate was tested at 70° C. with the results shown in Figure 12.

Discussion.—Soap clearly in-

hibitor in presence of excess fatty acid than in presence of excess alkali, while in the straight detergent experiments the reverse was the case. The most plausible explanation seems to be that the stearic acid is directly adsorbed by the carbon black as an oily coating and thus prevents the ad-

sorptive affinity between black and cotton from coming into full play. On the other hand the detergent experiments seemed to show that neither stearic acid nor other oily substances possessed significant power to dislodge carbon black, once it had been adsorbed by the fabric. Such being the case it is evident that the power to prevent adsorption of carbon black by clean fabric cannot be regarded as a criterion of the power of the soap as a detergent against the same black after adsorption upon the fabric.

These detergent experiments were carried on against adsorbed carbon black for the obvious reasons mentioned in the introduction. But it is doubtful how much they signify from a practical point of view. Fabric in actual service probably seldom becomes soiled with adsorbed non-oily carbon black. It is more likely that such "soot" as may be present carries a distinctly oily film, and accordingly may respond to various detergents in quite a different manner. At all events detergent experiments on fabric soiled with oily carbon black are very desirable.

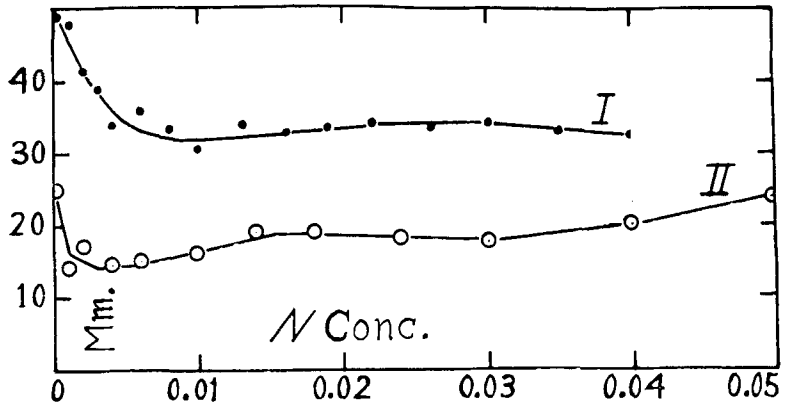

Fig. 12.—*Sodium Stearate at* 70° *C. in Experiment* 14. *Curve I, Alkaline; Curve II, Acid.*

Summary

1. There is described (a) a laboratory washing machine, and (b) the conversion of a colorimeter into a reflectometer for the evaluation of soil on a fabric.

2. Detergent experiments were performed on cotton fabric soiled in simple aqueous suspensions of non-oily carbon black. The most powerful detergent appeared to be an alkaline solution of sodium stearate or palmitate at 70° C. or above. In this effect of alkali deflocculation and detergency are parallel but other possible correlations were but vaguely defined. The method as given will not suffice for selection of the superior among competing commercial soaps.

3. Comparative tests were made on the power of soap solutions to prevent adsorption of suspended carbon black by clean fabric. Acid soaps were the more effective, probably owing to masking of adsorptive affinities by an oily film of fatty acid. Power to prevent ad-

sorption therefore is not correlative with detergent power in the special case of the prevention of absorption of suspended carbon by fabric. This result is based on tests using soap solutions.

TABLE 1. DATA OF EXPERIMENT 9.

Washing Solution		Colorimeter reading[1]
(a)	Hydrochloric Acid; 0.1 Normal	40
(b)	Saponin, "Purified," 2 per cent in distilled water, dissolved at room temperature	34
(c)	Acacia, 5 per cent, in 0.1 Normal HCl. Acacia was dissolved in water at 60°-70° C., cooled and made to volume with addition of HCl.	33
(d)	Casein, "Technical," 3 per cent, in 0.05 Normal HCl, dissolved at 60°-70° C.	31
(e)	Gelatine, edible, 5 per cent, in 0.1 Normal HCl. Gelatine was dissolved in water at 60°-70° C., cooled and made to volume with addition of HCl	29

[1] Average of duplicate slips.

TABLE 2. DATA OF EXPERIMENT 10.

Soaking Solution		Colorimeter reading[1]
(a)	Neat's-foot Oil	45
(b)	Kerosene	34
(c)	Cyclo hexanol	33
(d)	Sodium Silicate, containing 1.76 Normal Na_2O by titration	31
(e)	Cresol, U.S.P.	31
(f)	Sodium Hydroxide; Normal	29
(g)	Aniline	29

[1] On a single slip only.