Comparison of Emulsifying and Deflocculating Powers of Soaps Upon Oil and Carbon Black

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WHEN presenting their carbon black test for the "detergent action" of soaps McBain, Harborne and King[1] surmised that the effect of a soap on carbon black might be to a certain extent specific and not wholly parallel with its effect on oily matter. To settle this question the writer has undertaken comparative experiments involving the filtration of oil emulsions and of carbon black suspended in soap solutions.

With exceptions to be noted, the technic was similar to that previously used[2] in experiments upon carbon black. Quantities of 20 cc. of various dilutions of a stock soap solution in test tubes were heated, after complete solution and mixing, for 0.5 hour at a temperature at least 10° C. higher than the projected temperature of the test. The tubes were transferred to the special water bath, described in the previous paper, in which they were agitated 20 minutes and left at rest 10 minutes. The charges of oil or of carbon black were then added and the tubes were rotated at 20 to 22 r.p.m. for 40 minutes, after which the contents were filtered through standardized filter papers contained in funnels immersed in the same water bath. The temperature of the bath was held constant from the first immersion of the tubes until all the filtrates had been collected. The quantity of oil or of carbon black found in a fixed first portion of each filtrate was taken as a criterion of the emulsifying or deflocculating power of the corresponding soap solution.

[1] Jour. Soc. Chem. Ind., **42**, 373 T (1923).
[2] Ind. Eng. Chem. **18**, 1313 (1926).
[3] Kolloid, Z. 36, Ergänzungsband. Zsigmondy Fest-schrift, p. 196. (1925).

Emulsification of Oil

The oil was taken from a single container of laxative mineral oil which had been found free from acid and to suffer no change in weight at 105° C. The charge employed was the quantity delivered by the same wide-tipped 1 cc. pipet, with its stem wiped dry, in an outflow time of 1 minute. The filter papers were selected to pass 10 cc. water at room temperature within 18 to 23 seconds after 20 cc. had been poured on. The volume of each filtrate was 10 cc. This was rinsed with hot water into a separatory funnel, acidified with hydrochloric acid and cooled. The total oil and fatty acid was extracted by ether, washed free from mineral acid and weighed after drying to constant weight at 105° C. Neutral alcohol and phenolphthalein were next added to the residue and the fatty acid was determined by titration. Thus the weight of the oil was found by difference, a procedure earlier employed by Gurwitsch[3]. Both palmitates and oleates carried so little oil through the filter paper that the work had to be confined to stearates.

Experiment 1. The results af-

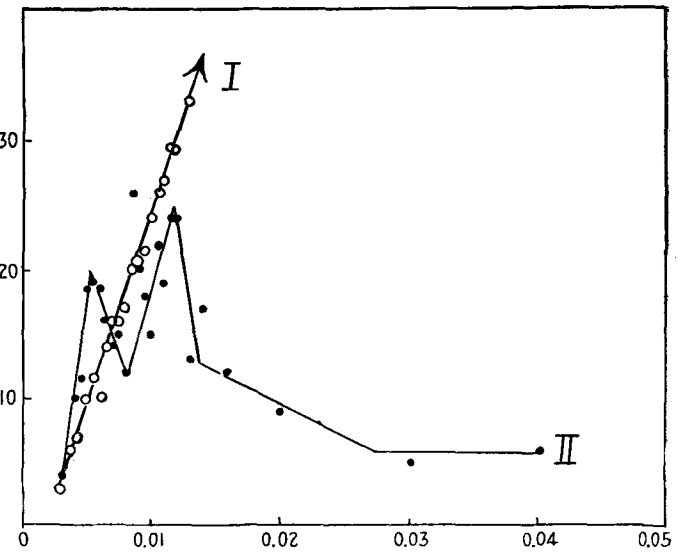


Fig. 1
Oil and Neutral Sodium Stearate at 70° C. in Experiment 1.
Horizontal — Normality of soap.
Vertical—Mg. in 10 cc. filtrate.
Curve I—Stearic acid.
Curve II—Oil.

forded by neutral sodium stearate at 70° C. are given in Figure 1, and those at 60° C. and at 50° C. in Figure 2. At 50° C. no filtrate was found to contain more than 2 milligrams stearic acid.

Experiment 2. Alkaline solutions of sodium stearate were tested at 70° C. by the procedure of Experiment 1. Results are given in Figure 3. The curves for fatty acid in presence of 0.002 and 0.005 N excess sodium hydroxide practically coincided with Curve I, and this, it will be noted, is practically superposable upon Curve I of Figure 1.

Experiment 3. In this experiment the soap solutions contained 0.005 N stearic acid in excess. The tubes were first charged with 5 cc. of a solution of 1.1376 g. stearic acid in 200 cc. alcohol, then the alcohol was expelled by heat, first

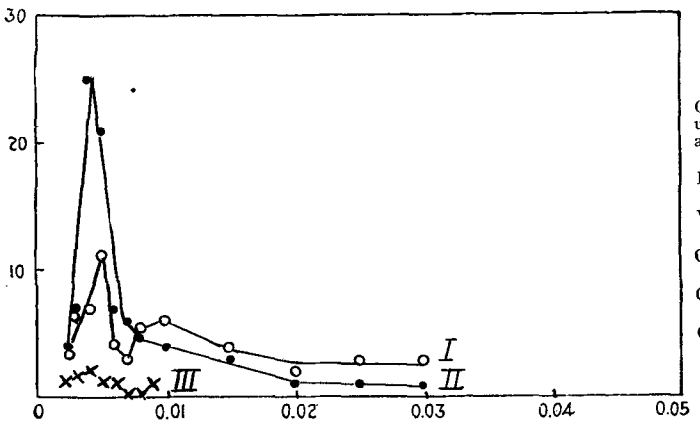


Fig. 2
Oil and Neutral Sodium Stearate at 60° and 50° C. in Experiment. 1.
Horizontal — Normality of soap.
Vertical—Mg. in 10 cc. filtrate.
Curve I—Stearic acid at 60° C.
Curve II—Oil at 60° C.
Curve III—Oil at 50° C.

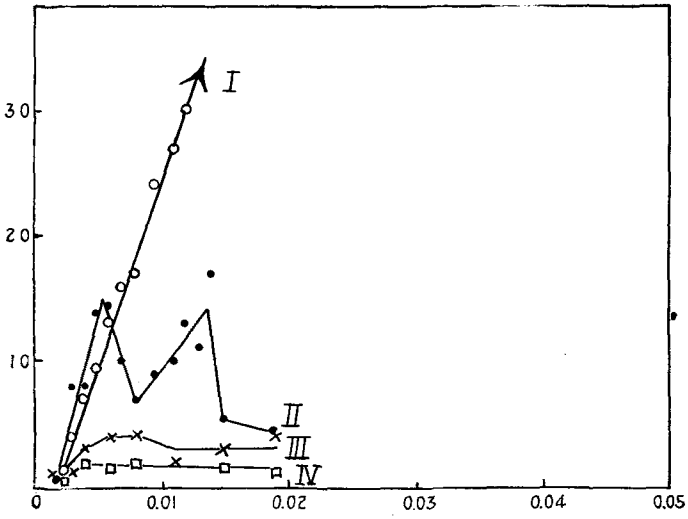


Fig. 3

Oil and Aklaline Sodium Stearate in Experiment 2.

Horizontal — Normality of soap.

Vertical—Mg. in 10 cc. filtrate.

Curve I—Stearic acid in presence of 0.001 N excess NaOH.

Curve II — Oil in presence of 0.001 N excess NaOH.

Curve III—Oil in presence of 0.002 N excess NaOH.

Curve IV—Oil in presence of 0.005 N excess NaOH.

in a water bath and finally in an oven. After being further charged with neutral soap solution the tubes were carried through as in Experiments 1 and 2 except that during the preliminary heat treatment they were vigorously shaken twice to distribute the excess stearic acid. The results are given in Figure 4, in which the scale of the ordinates is only one-fourth the scale in Figures 1, 2, and 3.

In the cited work on carbon black the writer demonstrated that a soap solution may show two peaks of deflocculating power. The anterior peak, at the lower concentration, was attributed to the action of soap anions, the posterior to the action of simple soap molecules. It now appears that soap solutions may show two peaks of emulsifying power also.

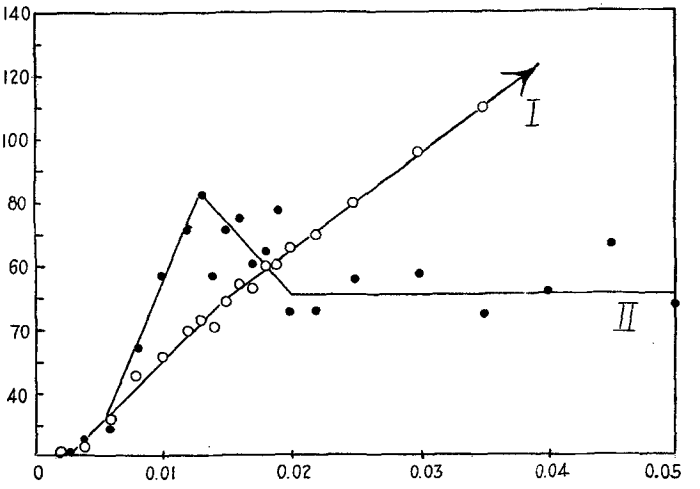


Fig. 4

Oil and Acid Sodium Stearate at 70° C. in Experiment 3.

Horizontal — Normality of soap.

Vertical—Mg. in 10 cc. filtrate.

Curve I—Stearic acid.

Curve II—Oil.

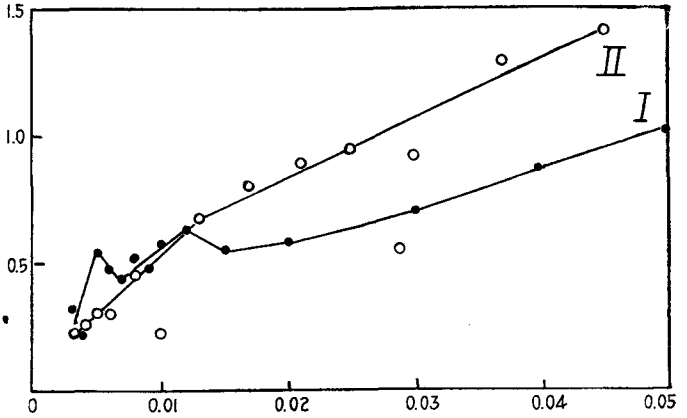


Fig. 5
Colored Oil and Sodium Stearate at 70° C. in Experiment 4.
Horizontal — Normality of soap.
Vertical — Mg. color in 10 cc. filtrate.
Curve I — Neutral stearate.
Curve II—Stearate plus .01N excess NaOH.

The Distribution of a Color

Experiment 4. The foregoing method of arriving at the weight of oil carried through each filter is so tedious that an attempt was made to employ an oil-soluble color as an indicator for the concentrations of oil in the filtrates. A solution of 1 gram of dimethylamidoazobenzene ("butter yellow") in 100 cc. of the mineral oil was used instead of plain oil. After the 10 cc. of each filtrate had been collected and rinsed with hot water into a separatory funnel, 5 cc. concentrated hydrochloric acid was added and after cooling, 25 cc. petroleum ether or ethyl ether. Then the color was completely extracted by successive washings with diluted (1:3) hydrochloric acid, the extracts being received in 100 cc. graduated flasks. The contents of the flasks were made to the mark and filtered through plugs of cotton, with rejection of the first runnings. The quantity of color in each filtrate was determined colorimetrically in either a colorimeter or Nessler tubes against a standard obtained by pipetting 1 cc. of the colored oil directly into a

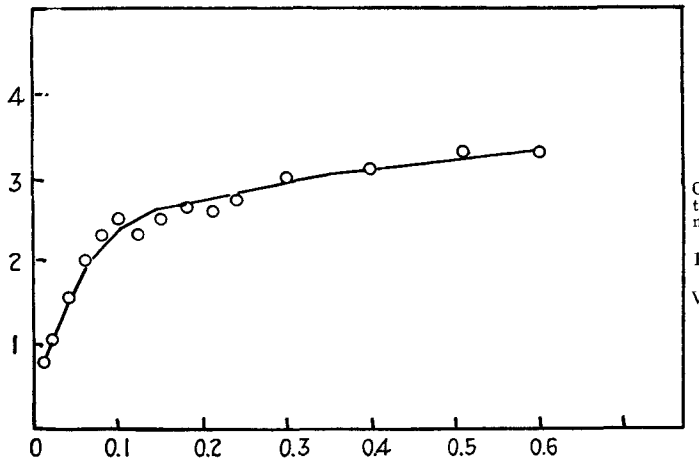


Fig. 6.
Colored Oil and Neutral Potassium Palmitate at 40° C. in Experiment 4.
Horizontal — Normality of soap.
Vertical — Mg. color in 10 cc. filtrate.

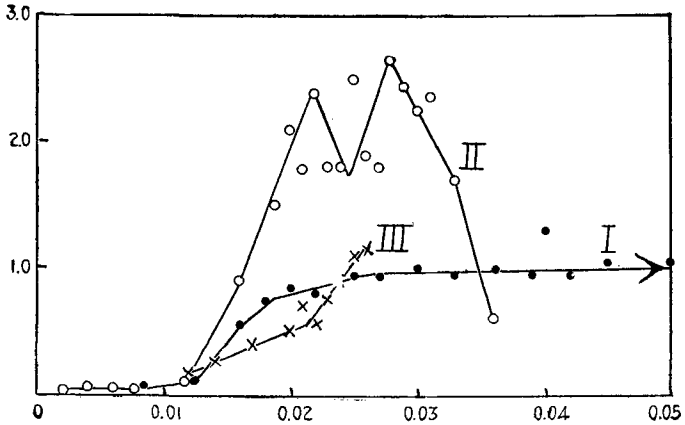


Fig. 7.
Naked Carbon Black and Neutral Sodium Stearate at 70°, 60° and 50° C. in Experiment 5.
Horizontal—Normality of soap.
Vertical—"Color ratio" of filtrate.
Curve I—at 70° C.
Curve II—at 60° C.
Curve III—at 50° C.

separatory funnel, extracting with acid and making to a volume of 200 cc. with the diluted hydrochloric acid. The results obtained on neutral and alkaline sodium stearate at 70° C. are given in Figure 5 and the results on neutral potassium palmitate at 40° C. in Figure 6.

It is evident that with increasing concentration of soap the quantity of color appearing in the filtrate becomes increasingly out of proportion to the oil found to be carried through in Experiments 1 and 3. Apparently colloidal soap in the aqueous phase extracts color from the oil phase. Two important consequences follow. First, a method of this sort offers little promise for the laboratory comparison of the emulsifying powers of different

Fig. 8.
Naked Carbon Black and Acid and Alkaline Sodium Stearate at 70° C. in Exp. 6.
Horizontal — Normality of soap.
Vertical—"Color ratio" of filtrate.
Curve I—In presence of 0.005 N excess NaOH.
Curve II—In presence of 0.002 N excess NaOH.
Curve III — Neutral soap (from Figure 7).
Curve IV—In presence of .005 N excess stearic acid.

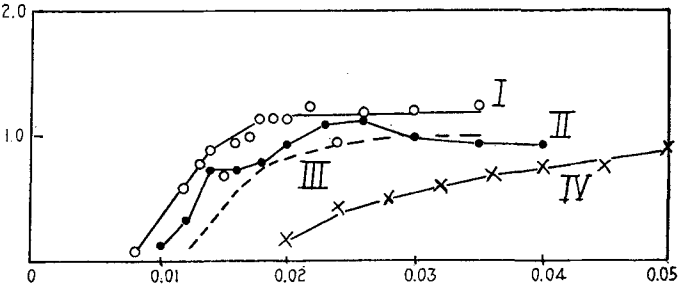
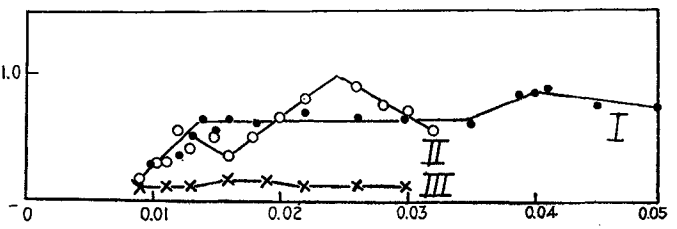


Fig. 9.
Oiled Carbon Black and Neutral Sodium Stearate at 70°, 60° and 50° in Exp. 7.
Horizontal—Normality of soap.
Vertical—"Color ratio of filtrate.
Curve I—at 70° C.
Curve II—at 60° C.
Curve III—at 50° C.



soaps; second, the relative effects of soaps in promoting the fading of certain dyed goods may be far from parallel with their powers to cleanse the goods.

Naked Carbon Black

The carbon black employed was the same as in previous work. Tubes of the soap solutions were prepared exactly as already described in the work on emulsions. Each was charged with 0.5 gram of the black and the contents were filtered on similar standardized papers after 40 minutes agitation. Each filtrate was collected until the top of the meniscus reached the 7 cc. mark on the graduate. Each was appropriately diluted with an alkaline solution of potassium oleate and compared in a colorimeter under artificial light with the cobalt-nickel-copper standard solution described in the first paper. The results were calculated to the "color ratio" for each filtrate made to a standard volume of 100 cc.

Experiment 5. Results on naked carbon black with neutral sodium stearate at 70°, 60° and 50° C. are given in Figure 7. The curve at 70° C. was further found to run on a level from 0.05 N to at least 0.10 N. Evidently the effect of temperature upon the power of neutral sodium stearate to deflocculate naked carbon black does not appear very closely parallel with its effect upon the power of the same soap to emulsify oil as indicated in Figures 1 and 2. As a deflocculant it seemed even more powerful at 50° C. than at 70° C., while as an emulsifier its power at 50° C. was a small fraction of its power at 70° C.

Experiment 6. Results on naked carbon black treated at 70° C. with alkaline or acid sodium stearate are given in Figure 8. The curve for neutral stearate is also transferred from Figure 7. The soap clearly appears a more powerful deflocculant of naked carbon black with increasing alkalinity. This is the direct reverse of the effects noted upon the emulsification of oil at 70° C. in Figures 1, 3, and 4.

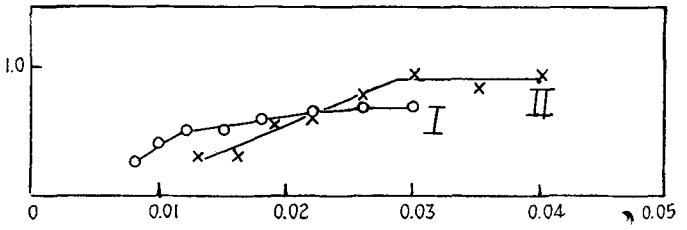


Fig. 10.
Oiled Carbon Black and Acid and Alkaline Sodium Stearate at 70° C. in Experiment 8.
Horizontal—Normality of soap.
Vertical—"Color ratio" of filtrate.
Curve I—In presence of 0.005 N. excess NaOH.
Curve II—In presence of 0.005 N. excess stearic acid.

Experiments with Oiled Carbon Black

Fifty grams of the same carbon black previously used was stirred with a spatula into a solution of 10 grams of the mineral oil in about 250 cc. petroleum ether contained in a stout beaker. The solvent was

cautiously evaporated off below the boiling point and the material was finally well dried at 105° C., with frequent stirring during the whole process. The oiled black was brushed through a 100-mesh sieve and thoroughly mixed. It was employed in exactly the same manner as the naked black, the weight used in each test being 0.6 gram, corresponding to 0.5 gram of the original black.

Experiment 7. Results on the oiled black at 70°, 60° and 50° C. are given in Figure 9. The much lower deflocculating power at 50° C. than at 70° C. is significant when compared with the similar behavior of emulsions (Figures 1 and 2) and the opposite behavior of naked black (Figure 7).

Experiment 8. Results on the oiled black in presence of excess sodium hydroxide or stearic acid are shown in Figure 10. In comparison with the similar curves for naked black (Figure 8), that for the acid soap is significantly higher, while that for alkaline soap is notably depressed, a behavior corresponding in order with the behavior of oil emulsions (Figures 3 and 4).

In conclusion, it therefore appears that the carbon black test, employing naked carbon black, can not afford very useful indications of the relative powers of various soaps to emulsify oil. The employment of oiled carbon black offers more promise. But a grave fault in technic must be first overcome. During filtration the larger particles of black tend to settle upon the filter and to themselves constitute a filtering medium of less porosity than the paper, so that a self-clearing filter will have to be devised. The work on oil emulsions is probably not so subject to this criticism because the larger globules of oil tend to rise and leave the filter clear.

Summary

Comparisons were made of the emulsifying or deflocculating powers of soap solutions as measured by the proportions of (1) mineral oil, (2) oil-soluble color, (3) naked carbon black, and (4) oiled carbon black, carried through filter papers under standard conditions. The results indicate no close parallel between the emulsification of oil, the distribution of oil-soluble color, or the deflocculation of naked carbon black. The use of oiled carbon black as a test object for determining emulsifying power offers some promise provided an appropriate technic can be devised.

L. C. WHITON IN EUROPE

Louis C. Whiton, representing Edouard Bataille in the United States left on January 8th for Europe. Mr. Whiton will make his headquarters at Paris and will spend the next two months inspecting several up to date Vegetable Oil Refining plants which use the Bataille Vacuum Neutralizing and Vacuum Bleaching Systems and also several new plants which are using non-inflammable solvents for the extraction of oil seeds. Another purpose of the trip is to inspect and become familiar with the recent improvements on the Bataille Super-Deodorizer which has added to its high vacuum equipment, means for obtaining high temperatures with the oil, when, as is frequently the case with American Oils, this is found advisable.