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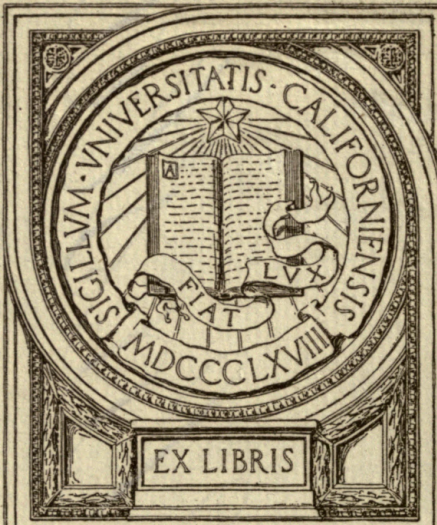


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Studies in Dyeing and Cleaning

A THESIS

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL
OF CORNELL UNIVERSITY FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

By
DYER BARKER LAKE

(Reprinted from the Journal of Physical Chemistry, 20, 761 (1916).)

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STUDIES IN DYEING AND CLEANING

BY D. B. LAKE

Studies on the displacement of adsorbed substances have been made quite recently by Freundlich,¹ and by C. G. Schmidt.² Freundlich studied the adsorption, by charcoal, from a solution containing two dissolved substances. The solutions studied contained the following pairs of acids: oxalic acid and acetic acid; oxalic acid and succinic acid; and oxalic acid and benzoic acid. They found that each acid diminished the adsorption of the other; in other words that a given amount of one acid in the presence of another acid was adsorbed less by charcoal than it was from its own solution. From this it was concluded that each acid of the pairs studied displaced the other from the charcoal. By the same method, Schmidt studied the adsorption by charcoal of iodine and acetic acid dissolved in chloroform and obtained results similar to those of Freundlich. He states in general that if a dissolved substance, A, is adsorbed by charcoal, the addition of a substance, B, soluble in the solvent, will bring about a displacement of A; and *vice versa*. He found that the amount of the two dissolved substances adsorbed was less than the sum of the amounts adsorbed separately.

These experiments seem strongly to confirm the idea of the displacement of one adsorbed substance by another. This displacement, it is evident, is by no means confined to the above examples. Among the many interesting cases where it would seem to apply is that one relating to the adsorption of two dyes, under certain conditions, by a fiber as wool. Thus if a dyed fiber such as wool is treated with another dye of the same class under the same conditions, the second dye seems partially or completely to displace the

¹ Van Bemmelen's Gedenkboek, 88 (1910).

² Zeit. phys. Chem., 74, 731 (1910).

first dye as indicated by the change of color of the dyed fiber, and the mixed color of the final bath.

Preliminary experiments to verify this matter were carried out in the spring of 1915 by Miss R. R. Murray. Miss Murray used a silk-wool flannel cloth, the warp of which is wool, the woof silk. Briefly, the method of procedure was to put a piece of cloth into a cold, dilute solution of the first dye, bring to a boil and keep at that temperature for one-half hour; remove; wash; set aside a piece for comparison, and place the remaining piece in the fresh bath of the second dye, in which the cloth received the same relative treatment as in the first case. The reverse treatment was also carried on at the same time. "Thus a succession of displacements of dyes by each other under similar conditions was obtained." Acid and basic dyes were used. Among the acid dyes used were: acid green BBN, acid violet 3R, crocein orange R, alkali blue, lanafuchsine, cyanole green, and brilliant scarlet; among the basic dyes: safranine, thioflavine T, brilliant green and emerald-green.

Concerning the displacement of one color by another on wool, the work seemed to show that crocein orange could be displaced by acid green and acid violet; acid green by alkali blue; thioflavine T by safranine and brilliant green; and safranine by brilliant green and emerald-green. On silk, also, a color displacement was shown. On it, acid green and crocein orange, acid violet and crocein orange, brilliant scarlet and cyanole green displaced each other in the order named, and in the reverse order. In one direction only, thioflavine T was replaced by safranine; and brilliant green and safranine by emerald-green. The color changes indicated above were clear and sharp. With both the wool and the silk there were, in addition to the above, several cases of a partial displacement of one color by another. On wool, there was the case of the partial displacement of acid violet by crocein orange; on silk that of safranine by thioflavine T.

From the evidence of the fiber, it is seen that in many cases we have complete displacement of one color by another.

From the point of view of the final bath also the work seemed to show that there was a more or less complete displacement of one dye by another. Thus in the final bath from the fiber dyed either in crocein orange or acid violet, and then followed by acid violet or crocein orange, both dyes were present as indicated by the color of the final bath which was a wine-red. As with acid violet and crocein orange, so with the other dyes studied, the final baths always contained some unadsorbed dye and some "apparently displaced dye."

Thus it is seen that Miss Murray's work brought out the interesting question: Does one dye, under the experimental conditions described, displace another as indicated (1) by the change of color of the fiber, (2) by the presence in the second final bath of the two dyes?

In the fall of 1915 additional experiments were carried out along the lines indicated above. The fiber chosen was pure hank wool, and was used as bought. At room temperature, one gram of the wool was placed in the dye bath of definite volume (50 cc) and concentration, brought to the temperature of a boiling water-bath, and kept there for one-half hour. The dyed fiber was then removed, thoroughly washed in distilled water, and placed in a bath (50 cc) of the second dye of definite concentration, and the same treatment repeated.

First, an account will be given of the attempts to bring about color changes on the wool fiber, and then an account of the apparent displacement of one dye by another dye. The dyes used in the greater part of the experiments here recorded were those sent to the Physical Chemical Department through the courtesy of the Schoellkopf, Hartford and Hanna Company of Buffalo, N. Y.

On the wool in the silk-wool flannel acid violet was not displaced completely by crocein orange, the color obtained being a "mixed brown;" accordingly, experiments were first carried out with these two dyes. It was thought that by dyeing the fiber in a comparatively small amount of acid violet and then treating this dyed fiber by varying amounts

of crocein orange, *viz.*, 10, 20, 30, 40 and 50 mg, respectively, a concentration of crocein orange, within reasonable limits, could be found that would completely displace the color of the acid violet. Negative results were obtained; that is, in no case was the final color of the fiber that of pure crocein orange. At the concentrations of 40 mg and 50 mg of crocein orange, however, its color tended to predominate, that is, the color of the acid violet was more or less completely masked. The final color of the fiber at these higher concentrations of crocein orange was on the whole of a light brick-red.

A few experiments were made to ascertain the minimum amount of acid violet with which the fiber could be dyed in order that the color imparted to the fiber would just influence the succeeding crocein-orange color. The concentration of acid violet varied from 5 mg to 0.2 mg per 50 cc, while that of the crocein orange was kept at 25 mg per 50 cc. The minimum concentration of acid violet was found to be 0.25 mg. This experiment brings out strikingly the comparative intensity of the color of the two dyes when adsorbed by the wool.

Results for the wool dyed in a bath of crocein orange followed by acid violet were somewhat different than for the above experiments. In these cases, the crocein-orange color was practically although not completely displaced by acid violet. The concentration of both dyes in 50 cc was 25 mg, respectively. To learn whether by prolonged treatment of the dyed fiber by the second dye, a complete displacement of the first dye could be brought about, the dyed fiber from the crocein orange was left in the acid violet bath at the temperature of the dyeing for four hours. Twenty-five milligrams of each dye per 50 cc were used. On the whole the result was negative; that is, even after this prolonged treatment of the dyed fiber in acid violet, the acid violet did not entirely mask the color of the crocein orange. However, these results are in harmony with those of the preceding experiments where acid violet was followed by crocein orange, since they show that acid violet is by far the stronger of the two colors on wool.

A few other combinations of colors were then tried out according to the same general method. The combinations were: crocein orange and acid green, alkali blue and acid green, acid violet and acid green, brilliant green and safranine. The concentration of each dye with the exception of brilliant green and safranine was 50 mg in 50 cc of water. In the case of the brilliant green and safranine, 25 mg of dye in 50 cc were used. For the above combination for dyes, as for the acid violet and crocein orange, in no instance was the first color replaced by the second color. The resulting color for the first two combinations was practically the same, namely, a brownish black; for the acid violet followed by acid green a greenish black. When the safranine was followed by the brilliant green, the color resulting was a greenish black; when the fiber was dyed in the reverse order, the color resulting was a bluish black, thus showing that the brilliant green tended to displace the safranine more readily than the safranine the brilliant green, that is, the brilliant green is the stronger color on wool. This is analogous to the behavior of acid violet and crocein orange. The acid violet displaced the crocein orange more than the crocein orange did the acid violet.

It is evident from the above data that on wool alone, one color cannot be completely replaced by another in one treatment unless, as in the case of acid violet, the amount of the first dye used is very small in comparison to the amount of the second dye used.

To ascertain whether the color on a fiber could be displaced by successive treatments of the second dye, wool was dyed in the usual manner and then further treated to fresh successive baths of the second dye. As a typical case, the fiber dyed in acid green followed by crocein orange was studied. The concentration of the acid green was 50 mg in 50 cc. Two samples were dyed first in acid green and then each of these in fresh baths of crocein orange (40 mg). The first treatments of the dyed fiber resulted in a brownish black color which color remained after the second treatment. In the third treatment an orange tint of the fiber was noticeable. In the

fifth treatment practically all of the acid-green color had been displaced. Similar experiments were carried out with alkali blue and crocein orange, and acid violet and crocein orange. With respect to alkali blue and crocein orange the fiber was dyed first in 50 mg of alkali blue. This dyed fiber was then treated with four successive amounts of crocein orange, namely, 50, 25, 25 and 25 mg, respectively. The resulting color of the fiber at the end of the fourth treatment was only slightly different from that at the end of the first treatment. However, a slight orange tinge of the fiber was noticeable. Concerning the acid violet and crocein orange two sets of fibers were dyed in 30 mg and 40 mg of acid violet, respectively. These dyed fibers were then treated with five successive amounts of crocein orange, namely, 50, 25, 25, 25 and 25 mg respectively. At the end of the last treatment the color of the fibers did not seem markedly different from that at the end of the first treatment.

From the above experiments the conclusion may be drawn that it is very difficult to mask completely, that is, displace, by a second dye the color of the dye adsorbed by wool fiber. This would seem to show that the influence of the dye in the bath in displacing the adsorbed dye is small, if not negligible. Furthermore, it would seem that where the final color of the dyed fiber tended to become more like that of the second dye it was due, in part at least, to the more or less partial masking of the color of the original, adsorbed dye by the second dye.

From this we should conclude that if it is desired to bring about a rapid complete change of color of a fiber, dyed for example with acid violet, it would first be necessary to remove the dye from the fiber by means of a solution of either Na_2CO_3 or $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ before treating the fiber with the dye for the desired color.¹ There are cases where this method would not be necessary as shown in the experiment with acid green and crocein orange. There it was seen that the acid green was not held so tenaciously as was acid violet or alkali

¹ Knecht, Rawson and Lowenthal: *A Manual of Dyeing*, 1, 217 (1910).

blue; hence by successive treatments of the dyed fiber in fresh baths of crocein orange, the acid-green color should eventually be completely displaced by the crocein-orange color. From preceding experiments we should expect this color displacement to be accompanied by a fairly rapid displacement of the dye, acid green. This displacement of the acid green may be explained as due to the fact that it was either dissolved or peptized by the water, or peptized by the crocein orange. There is no doubt that in the case of alkali blue and acid violet their complete displacement could be brought about eventually and for the same reason.

The idea that the displacement of a dye from a fiber may be accounted for by assuming that the first dye is either dissolved or peptized by the solvent or is peptized by the second dye, leads us to the second point in the investigation, namely, to account for the apparent displacement of one dye by another.

If we go back to the experiments described, we can consider this evidence of the displacement of a dye from a fiber by the appearance of the final baths in each case. In the case of the first experiments with acid violet and crocein orange, where only a small amount of acid violet was used for the first color, it was rather difficult to detect any acid violet in the second final bath. Up to a concentration of 20 mg of crocein orange the final bath was of a dark lemon color. To the naked eye there was no evidence of acid violet present. Beyond a concentration of 20 mg of crocein orange the color of the final bath was that of the original color of the crocein-orange bath. In none of these experiments was there any visible evidence of the displacement of acid violet. This was especially noticeable as the crocein orange was adsorbed to a considerable extent by the dyed fiber.

However, seemingly more positive evidence of the displacement of acid violet by crocein orange was obtained when the wool was dyed in more concentrated solutions of the acid violet. For example, in the case where two sets of the fiber were dyed in 30 and 40 mg, respectively, and then

treated to successive, fresh baths of crocein orange the final baths in every case, even in the last treatment, were of a wine-red color, thus showing that in each final bath there was present unadsorbed crocein orange and some apparently displaced acid violet. As in the case of the acid violet and crocein orange, so in the case of acid green and crocein orange, alkali blue and acid green, and acid violet and acid green where the fiber was dyed in a rather concentrated solution of the first dye, the final baths in all cases showed the presence of the unadsorbed dye and the apparently displaced dye. This was particularly striking in the case of acid green followed by crocein orange. In every treatment of the dyed fiber, even to the last one, the color of the final bath was of a "dirty" green showing that both dyes were present. In all cases, the apparently displaced dye seemed to be present in considerable amounts.

Doubt as to the correctness of the idea of the actual displacement of one dye by another arose when the fact of the bleeding of a fiber dyed at the temperature of a boiling water-bath was taken into consideration. Thus wool dyed with acid violet, crocein orange, alkali blue and acid green, respectively, was practically stripped of each dye by putting the dyed fiber in successive fresh baths of boiling water. The removal of the dye in each case was brought about by either the solvent or peptizing action of the water. In accordance with the law of "reverse adsorption"¹ more dye was removed during the first two or three treatments than during the succeeding treatments. In fact when the amount of dye on the fiber was rather small its removal was very slow and difficult.

Now at the temperature of the water-bath, at which the experiments described were carried out, bleeding of the dyed fiber likewise readily occurred. This was shown for fibers dyed in acid violet, crocein orange, alkali blue, and acid green. Therefore, from these data it is seen that the question to settle was

¹ Hatschek: "An Introduction to the Physics and Chemistry of Colloids," 82 (1916).

whether a dyed fiber would bleed more in the presence of a second dye solution than in pure water at the temperature at which the experiments had been carried out.

Briefly the method used to answer the question was first to treat four samples of the wool in a dye bath of known concentration at the temperature of the boiling water-bath at about 97° for forty-five minutes; remove; wash; test two of the samples for bleeding at the same temperature for twenty-five minutes in the same volume of water and dye the other two dyed samples in a fresh bath of the second dye of the same concentration as the first dye and under the same conditions. Since the idea was to obtain relative information concerning the bleeding of the dye in its relation to displacement, a volume of 250 cc was used instead of 50 cc as in the previous experiments. The final solutions were analyzed colorimetrically by means of a Duboscq colorimeter.

The following data were obtained for wool, silk, and poplin (a cloth made of silk and wool, and used in place of the silk-wool flannel):

TABLE I
I—*Undyed Wool*
1 gram wool, 5 mg dye per 250 cc H₂O
Temperature—about 97° C

Dye	A	B	C
	Dye adsorbed Milligrams	Dye unadsorbed Milligrams	Bleeding test. Am't dye from dyed fiber given up to 250 cc H ₂ O at about 97° after 25 minutes Milligrams
Crocein	4.26	0.74	0.53
orange	4.30	0.70	0.58
Acid	4.20	0.80	0.45
green	4.30	0.70	0.35

II—*Dyed Wool* from A, not tested for bleeding; 5 mg dye per 250 cc H₂O; temp. about 97° C

Dye	D	E	F
	Dye adsorbed by dyed fiber Milligrams	Dye unadsorbed by dyed fiber Milligrams	Dye given up to 250 cc H ₂ O at about 97° by dyed fiber from D during dyeing Milligrams
Crocein	4.35	0.65	(Acid 0.40
orange	4.50	0.50	green) 0.30
Acid	4.25	0.75	(Crocein 0.50
green	4.35	0.65	orange) 0.50

I—*Undyed Silk*

1 gram, 20 mg dye per 250 cc H₂O
Temperature about 97° C

Dye	A	B	C
	Dye adsorbed Milligrams	Dye unadsorbed Milligrams	Bleeding test. Am't dye from dyed fiber given up to 250 cc H ₂ O at about 97° after 25 minutes Milligrams
Crocein	1.8	18.2	0.46
orange	1.8	18.2	0.23
Acid	9.3	10.7	0.88
green	8.7	11.3	0.79

II—*Dyed silk* from A, not treated for bleeding; 20 mg dye per 250 cc H₂O; temp. about 97° C

Dye	D	E	F
	Dye adsorbed by dyed fiber Milligrams	Dye unadsorbed by dyed fiber Milligrams	Dye given up to 25 cc H ₂ O at about 97° by dyed fiber from D during dyeing Milligrams
Crocein	1.8	18.2	(Acid 0.70
orange	2.0	18.0	green) 0.65
Acid	9.0	11.0	(Crocein orange)
green	9.0	11.0	Presence not indicated by method of analysis

I—Undyed Poplin
 1 gram poplin; 20 mg dye per 250 cc H₂O
 Temperature—about 97° C

Dye	A	B	C
	Dye adsorbed	Dye unadsorbed	Bleeding test. Am't dye from dyed fiber given up to 250 cc H ₂ O at about 97° after 25 minutes
Crocein	3.1	16.9	1.1
orange	2.9	17.1	1.1
Acid	5.5	14.5	2.0
green	5.6	14.4	2.0

II—Dyed Poplin from A, not treated for bleeding; 20 mg dye per 250 cc H₂O; temperature about 97° C

Dye	D	E	F
	Dye adsorbed by dyed fiber Milligrams	Dye unadsorbed by dyed fiber Milligrams	Dye given up to 250 cc H ₂ O at about 97° C by dyed fiber from D during dyeing Milligrams
Crocein	3.0	17.0	(Acid 2.0
orange	3.0	17.0	green) 2.1
Acid	5.0	15.0	(Crocein 1.0
green	5.0	15.0	orange) 0.9

Other data for crocein orange and acid violet were obtained with respect to wool but were lost when Morse Hall burned. Since acid violet could not be obtained in the market, experiments with these two dyes were not repeated. The data in all respects, however, agreed with the above for acid green and crocein orange.

The data seem to account for the apparent displacement of one dye by another. In all of the experiments in which the final bath indicated the presence of the two dyes, it is evident that the presence of one dye is due to bleeding,

and the presence of the other dye to incomplete adsorption. It is evident also that the bleeding of the first dye is not increased as a result of the adsorption of the second dye, or is independent of the presence of the second dye. In other words these data seem to bring out the fact that the removal of the dye on the dyed fiber is brought about through peptization by the liquid rather than peptization by the dissolved dye. This is indicated by comparing Columns C and F of the above tables for any fiber. Thus in the case of wool:

Dye	C	F
	Bleeding test. Amount dye given up by dyed fiber to 250 cc H ₂ O at about 97° C after 25 minutes Milligrams	Dye given up by dyed fiber to 250 cc H ₂ O at about 97° C during dyeing Milligrams
Crocein orange	0.53	Crocein orange 0.50
	0.58	
Acid green	0.80	Acid green 0.40
	0.70	

This apparent inactivity of the dissolved dye is probably due to the fact that the set adsorbed dye is "extremely difficult" to peptize even by boiling water. This is shown, for example, in the case of acid violet 3R which on wool bleeds but slightly in boiling water, that is, is peptized only slightly by it. Hence the conclusion that a dye in solution (true or colloidal) possesses apparently far less ability to peptize an adsorbed dye than does water and, therefore, the dye in solution plays little part in the removal of the adsorbed dye.

Concerning the final color of a fiber, especially with regard to wool, complete change takes place only when the amount of the dye adsorbed is rather small and the amount of second dye adsorbed is relatively large; in other words, when the amount of the first dye adsorbed is so small that

the color of the second dye is able to mask it completely. This is illustrated in the case where only 0.25 mg of acid violet, adsorbed as the first dye, was completely masked by crocein orange. In any case where a large amount of the first dye has been adsorbed, the color replacement goes hand in hand with its actual displacement from the fiber, which displacement seems to be entirely independent of the presence of the second dye.

With regard to silk we have a complete replacement of one color by another as for wool. This is illustrated in the displacement of crocein-orange color by acid-green color. The amount of crocein orange adsorbed was comparatively small; and hence when this dyed fiber was treated to a fresh bath of acid green at the temperature of the boiling water-bath, with the result that considerable bleeding of the crocein orange took place, the amount of crocein orange left on the fiber was so small that its color was easily masked by that of the acid green. Thioflavine T on silk followed by safranine affords an instance in which the color of one dye is displaced by another, and yet in which large amounts of the first dye are taken up. A one-gram sample of silk dyed in 25 mg of each dye per 250 cc H₂O at about 97° C adsorbed about 80 percent of each, respectively. Notwithstanding that relatively large amounts of thioflavine T were adsorbed its color was easily masked by the safranine. It is obvious that the amount of thioflavine T given up to the safranine solution was not sufficient to account for the displacement of the thioflavine T color by the safranine color, as in the case of crocein orange followed by acid green. The probable reason for the masking of the thioflavine color is due to the fact that it is of very light shade, thus making its displacement or masking comparatively easy by a darker one as safranine. It should be pointed out that safranine color was not replaced by the thioflavine T color in one treatment.

Summing up then the results of the experiments, we conclude that we may speak of the displacement, or preferably the masking, of one color by another under suitable conditions.

This masking of one color by another is accompanied by a partial displacement of the dye from the fiber. But this displacement does not seem to be brought about by the presence of the second dye but by the solvent or peptizing action of the solvent.

The above experiments were carried on at the temperature of the boiling water-bath. Since, at this temperature under ordinary conditions, there was no complete replacement of one color by another on wool, a few experiments were carried out at room temperature to ascertain whether dyes behaved similarly at that temperature. In all of these experiments the wool, used as bought, was entered in the first dye bath containing 25 mg of dye per 50 cc H₂O for 36 hours; after which it was removed, washed in distilled water, and then entered in the second dye bath of the same concentration, for the same length of time. The following pairs of dyes were studied: acid violet 3R and crocein orange R, cyanol green and brilliant scarlet, safranine and brilliant green, thioflavine T and safranine, cyanol green and lanafuchsine, brilliant green and thioflavine T.

Acid violet at room temperature is adsorbed very slightly by wool. Crocein orange, on the other hand, is adsorbed strongly, hence it readily displaced the acid violet color from the fiber. Crocein orange color, on the other hand, was in no way displaced by acid violet. The color of cyanol green was completely displaced by brilliant scarlet, although brilliant scarlet followed by cyanol green was not so completely displaced. The second final baths in each case contained both dyes. Safranine, followed by brilliant green, gave a dark-colored fiber, the color of the safranine predominating. Brilliant green, followed by safranine, likewise gave a dark-colored fiber, the brilliant green predominating. The fiber dyed in emerald-green followed by safranine took on a slightly greenish tinge, while in the reverse procedure the safranine color predominated on the fiber. In all of these cases the second final baths showed both dyes to be present. Thioflavine T followed by safranine was completely replaced by

the safranine. Thioflavine T was present in the second final bath. Safranine was not replaced at all, so far as the color of the fiber was concerned, by thioflavine T, although in the final bath safranine was present. Cyanol green followed by lanafuchsine gave a slate-blue color to the fiber, as well as did lanafuchsine followed by cyanol green. The final baths in both cases contained the two colors. Brilliant green followed by thioflavine T retained its color on the fiber, while thioflavine T was completely replaced by brilliant green. In this latter case, I could see no evidence of thioflavine T in the final bath.

The results of these experiments at room temperature are similar to those carried on at the higher temperature. They are purely qualitative, although there is no reason for assuming that quantitative data as to the principles involved would not agree with the data obtained for the higher temperature. At the lower temperature there seemed to be, on the whole, a more complete replacement of one color by another, and a more complete apparent removal of the first dye by the second. This latter phenomenon may be accounted for by postulating that at the higher temperature the dye is more completely "set" on the fiber and hence does not bleed so readily even at that temperature. It was very noticeable that the bleeding of fibers dyed at room temperature was far greater at that temperature than fibers dyed at about 100° and tested for bleeding at that temperature. At the lower temperature two cases were brought out where one color practically replaced the other completely; namely, thioflavine T by safranine and thioflavine T by brilliant green. With respect to thioflavine T followed by safranine, both dyes were present in the second final bath. In the case of thioflavine T followed by brilliant green it was rather difficult to detect the presence of thioflavine T in the second final bath. In fact, with the naked eye, no evidence of thioflavine T could be seen.

An interesting experiment showing how one color will predominate at one temperature, and the other at a higher temperature was brought out in the case of acid violet and

crocein orange. A one-gram sample of wool in 5 mg of crocein orange and 45 mg of acid violet per 50 cc H₂O was dyed at room temperature for 72 hours; another sample in a bath of the same concentration of the dyes at the temperature of the boiling water-bath. At room temperature the fiber was dyed a pure crocein-orange color, while at the higher temperature it was dyed largely the color of the acid violet. This experiment illustrated selective adsorption very finely, especially at the lower temperature. As showing more strikingly this selective adsorption at room temperature in the case of these two dyes a one-gram sample of wool was entered in a volume of 50 cc containing 10 mg orange and 1000 mg acid violet and left in this bath 24 hours. At the end of that time the fiber was dyed a fairly pure color of crocein orange. There was no evidence of the adsorption of any acid violet.

In the experiments described there is one fact that stands out quite prominently, namely, that a dyed fiber, under suitable conditions, will bleed; that is, if placed in water under suitable conditions it will lose some of its dye to the water. This bleeding will continue until, for the particular volume of water, equilibrium is reached between the dye in the solution and the dye on the fiber. As has already been pointed out, if one set of fibers is dyed at room temperature, and another set at a higher temperature, for example, the temperature of a boiling water-bath, the fiber dyed at the higher temperature will bleed less, even when tested for bleeding at the higher temperature, than the fiber dyed at room temperature and tested for bleeding at the lower temperature. In fact a fiber dyed at a high temperature as mentioned above will not bleed at all at room temperature. This difference in bleeding, depending on the temperature of dyeing, is probably due to the fact that the dye adsorbed at the higher temperature is coagulated on the fiber, or, as is popularly known "set" on the fiber, with the result that bleeding is more or less prevented. These general observations concerning bleeding led to a study of the conditions involving the dyeing of a fiber, or

the treatment of a dyed fiber, that would lead to a minimum of bleeding when the dyed fiber is exposed to practically boiling water.

The first experiment was concerned with the relation between the length of time of dyeing at high temperature and bleeding. "The real object of heating is to coagulate or agglomerate the dye, thus making it less soluble."¹ Hence the conclusion that prolonged dyeing at a high temperature should practically prevent bleeding. The dyeing was carried on at the temperature of the boiling water-bath. Samples of wool, one gram each, were entered in a dye bath of 40 mg per 250 cc H₂O. The time of dyeing varied from one to three hours. The dye used was acid violet.

The test for bleeding was carried out as follows: The washed dyed fiber was put in a beaker containing 250 cc of water and the whole heated to the temperature of the water-bath for one-half hour.

The dye unadsorbed and bled was determined colorimetrically. The data following are the average of duplicate experiments:

TABLE II

Time	Dye adsorbed	Dye unadsorbed	Bleeding test. Am't dye given up to 250 cc H ₂ O at about 97° C after 30 minutes
1 hour	37 mg	3 mg	about 0.30 mg
1½ hours	39 mg	1 mg	about 0.80 mg
3 hours	38.5 mg	1.5 mg	about 0.60 mg

These data indicate that prolonged dyeing at practically the temperature of boiling water does not cut down the amount of dye that will bleed from a fiber. This may be accounted for by assuming that equilibrium between the adsorbed and unadsorbed dye was reached at the end of one and one-half hours, hence the dyeing beyond that time was of no avail.

¹ Bancroft: Jour. Phys. Chem., 19, 145 (1915).

In practical work, especially with acid dyes, dyeing is carried on in so-called acid baths, that is, baths to which a certain amount of hydrochloric acid or, preferably, sulphuric acid is added. It is generally accepted that the presence of these acids brings about a better "setting" of the dye and hence makes it faster to washing or bleeding. With this idea in mind, experiments were carried out with acid violet in the presence of hydrochloric acid and sulphuric acid. The conditions of dyeing were the same as in the preceding experiment. Forty milligrams of dye were used and the amount of acids 3 percent by weight of the wool.

The data, the average of duplicate experiments, follow:

TABLE III

Time	Acid used 3% by weight of wool	Dye adsorbed Milligrams	Dye unad- sorbed Milligrams	Dye bled. Am't dye given up by dyed fiber to 250 cc H ₂ O at about 97° after 30 minutes Milligrams
1 hour	H ₂ SO ₄	39.83	0.17	0.10
1½ hours	H ₂ SO ₄	39.70	0.30	0.20
3 hours	H ₂ SO ₄	39.70	0.30	0.20
3 hours	HCl	39.70	0.30	0.20

Thus, as indicated above, these data bring out the fact that a fiber such as wool dyed with an acid dye in an acid bath gives up less dye to practically boiling water than it does when dyed with the same dye in a neutral bath. (See immediately preceding table.) The most probable reason for this is that the acid aids in coagulating or setting the dye on the fiber, thus making it less soluble; hence less dye is extracted by hot water, or the dye bleeds less readily.

It was observed in the above experiments that the fiber adsorbed the dye much faster in the acid bath than in the neutral bath. This was to be expected as postulated by Bancroft.¹

Experiments were next carried out in which wool was

¹ Jour. Phys. Chem., 18, 4 (1914).

dyed in neutral and acid baths as usual, but before testing for bleeding it was subjected to heating in a hot-air oven at a temperature of 105° – 110° C for one hour. The acids used were hydrochloric and sulphuric. Negative results were obtained in all cases; that is, after this heating the dyed fiber bled as much as the fiber which had not been subjected to this extra heating.

In the above experiments the temperature of dyeing was about 96° – 97° C.

It was hoped that by dyeing in an atmosphere of "live" steam the dye would be fixed more firmly on the fiber, so that it would be faster to washing. Accordingly, an apparatus was arranged by which live steam was allowed to bubble through a solution of dye contained in an Erlenmeyer flask. The Erlenmeyer flask was partially immersed in boiling water. Before the passage of the steam the fiber was thoroughly wet with the dye solution. The dye used was acid violet and the amount 40 mg per 50 cc of water. The dyeing was carried on for one hour. Duplicate experiments were performed in neutral and acid (HCl) baths.

In the first set of experiments after the dyeing in live steam the fibers were put at once into distilled water and tested for bleeding as usual at 97° . The bleeding was no less than in the case carried on at 96° to 97° . The fibers dyed in the neutral baths bled slightly more than those dyed in the acid bath. An experiment in which the fibers, dyed as above, were subjected to live steam for one-half hour before testing for bleeding in the usual manner likewise gave negative results; that is, the bleeding by this treatment was not cut down any. The fibers dyed in the acid bath bled considerably less than those dyed in the neutral bath. Another set of fibers was subjected to the live steam for $\frac{1}{2}$ hour, and tested for bleeding by immersing in water through which live steam bubbled for one hour. Here profuse bleeding took place. The fibers dyed in the neutral and acid baths bled about equally. The container in both experiments was immersed in boiling water.

At first thought it seems strange that at the temperature of the live steam the dye was not fixed more firmly on the fiber, as shown when tested for bleeding at the temperature of the boiling water-bath. However, the explanation is similar to that advanced to account for the greater bleeding of the fiber dyed in a neutral bath as compared to its bleeding when dyed in an acid bath. At the temperature of the "live" steam the dye was fixed no more firmly on the fiber than at the lower temperature. Hence the fiber gave up as much color to the hot water as to the one dyed at the lower temperature.

With reference to the bleeding of the dyed fiber at the temperature of "live" steam the data brought out the fact that it was profuse. This profuse bleeding can be explained, however, by assuming that at this high temperature the dye on the fiber was quite readily peptized.¹ Hence a larger amount of color was given up to the water than would ordinarily have been the case.

In dyeing at the temperature of live steam it was found that in all cases not so much dye was taken up by the fiber at this temperature, as was taken up at 96°-97° C, which was from 3 to 5 percent less. This is in harmony with data published by Mills and Rennie,² and Brown.³ Mills and Rennie found that wool dyed with rosaniline acetate adsorbed a maximum amount at 31° and practically none at 81°. The experiments were run for one hour at the temperature —1.46° + 1.50, 6.25°, and at successive ten degree intervals to 80.25°, respectively. The amount of dye left in the bath at the end of one hour was determined colorimetrically. Brown's method of experimentation was similar to that of Mills and Rennie. He studied the adsorption of acid and basic dyes by the wool. The figures in the subjoined table are from his data, and are the percentages of the dye left in the solution. The first three dyes are acid dyes, the last three basic dyes.

¹ Bancroft: *Jour. Phys. Chem.*, 20, 85 (1916).

² *Jour. Soc. Chem. Ind.*, 3, 215 (1884).

³ *Jour. Soc. Dyers and Colourists*, 17, 92 (1901).

Dye	20° C	40° C	60° C	80° C	100° C
Acid magenta	79	14	4	4.3	5.6
Acid green	79	28	4	4.6	5.2
Acid violet 4 B W	44	26	20.8	20.8	28.7
Chrysoidine FF	28.2	32	36	46.5	46.0
Methylene blue	29.2	24.4	28.6	33.1	57.1
Methyl violet B	37.0	7.0	5.3	4.7	6.2

With the exception of the data of the methylene blue these data bring out the fact that from 60° onward the amount of dye adsorbed per unit of time decreased with rise of temperature. This can be accounted for by assuming that with the rise in temperature the peptizing action of the water toward the adsorbed dye increased, thus cutting down the amount of dye adsorbed. With the exception of chrysoidine FF it is seen that up to the temperature of 60° with the rise in temperature there is an increase in the amount of dye adsorbed. This increase, however, is more apparent than real for notably under the conditions of Brown's experiments time was not allowed for a complete adsorption of the dye, especially at 20°, that is, time was not allowed for the adsorption equilibrium to be reached. At 60° and higher one hour's time was, to all intents and purposes, sufficient to bring about a practically complete adsorption of the dye; but at the lower temperatures this was not true. Hence it would seem that if at the lower temperatures the wool had been left in the bath till equilibrium had been reached the amount of dye adsorbed probably would have equalled the amount adsorbed at 60°, and even might have exceeded it. This assumption seems to hold for chrysoidine FF where it is seen that the amount of dye adsorbed up to 80° decreased with the rise in temperature. At 20° it is assumed that the adsorption equilibrium was reached at the end of one hour. Experiments carried on in the latter part of October, but with an entirely different object in view, further confirm the idea that at room temperature the amount of dye adsorbed is rather large in many cases. One-gram samples

of wool were left in their respective dye baths for 48 hours. The baths contained 25 mg dye per 50 cc water. The dye left in the bath was determined colorimetrically. The figures in the subjoined table refer to the percentage of dye left in the bath.

Dye	Percentage dye left in bath
Thioflavine T	18
Acid green	36
Brilliant green	20
Emerald-green	20
Lanafuchsine	54
Brilliant scarlet	60

Without doubt had the fibers been allowed to remain in their respective baths for a longer period of time a greater adsorption of dye would have resulted in each case. Especially would this be expected of lanafuchsine and brilliant scarlet.

At this point it was thought advisable to test a few more acid dyes to see how far the general results obtained for acid violet would hold. The other dyes used were: acid green BBN, crocein orange R, and crystal ponceau. The acids used were HCl, H₂SO₄ and H₃PO₄. Two points were kept in view in these experiments; first to show the relation of "bleeding" to the kind of treatment, that is, to ascertain whether in neutral or acid dyeing bleeding was greater or less; and secondly, to study the adsorption of these acid dyes on wool in the presence of these acids. From the point of view of the adsorption of the dye, the data given above for acid violet in which dyeing was done in hydrochloric acid and sulphuric acid baths, when equivalent amounts of the two acids were used, show that the fiber immersed in a sulphuric acid bath adsorbed as much dye as did the fiber immersed in the hydrochloric acid bath. This is not in accordance with the theory of dyeing as postulated by Bancroft, for according to that theory any acid dye in the presence of a readily adsorbed anion, either from an acid or neutral salt,

should be less readily adsorbed than in the presence of an anion not so readily adsorbed by the fiber.¹ In the case of HCl and H₂SO₄, the sulphate ion is much more readily adsorbed by wool than the chloride ion, hence a fiber dyed in the presence of H₂SO₄ should take up less acid dye than a fiber dyed in the presence of an equivalent amount of HCl. The data above do not confirm this.

In this new series of experiments acid violet was included, for the concentration of the dye used and the method of heating were changed, and it was thought desirable to get comparable data for all dyes. The fiber, one gram of wool, was entered in 250 cc of dye solution containing 40 mg of the respective dye. The dyeing was carried on at the boiling temperature for a period of one hour. Preliminary experiments had shown that at the temperature of boiling water practically complete adsorption of the dyes was brought about at the end of 45 minutes. The fibers were then tested for bleeding in a volume of 250 cc H₂O at the same temperature for 20 minutes. The amount of each acid used was 10 cc of *N*/10 strength. The data, the average of duplicate experiments, follow:

These data bring out facts similar to those obtained above for the wool dyed in neutral and acid baths of acid violet. Here as there in the bleeding test fibers dyed in acid baths gave up less color to the water than those dyed in neutral baths. This is as should be expected as pointed out above. The data show also that the fibers dyed in acid baths adsorbed more dye than those dyed in neutral baths. Furthermore, if we compare the data of the acid violet and crystal ponceau as a whole, it is seen that both dyes gave up about the same amount of color to the water in the test for bleeding. This can be accounted for by assuming that during the dyeing both dyes were about equally set. In general this comparison of crystal ponceau and acid violet holds also for crocein orange and acid green where for each dye under the same conditions there was

¹ Bancroft: Jour. Phys. Chem., 18, 4 (1914).

TABLE IV
 Temperature—100° C
 40 mg dye per 250 cc H₂O
 Time—1 hour

Dye	Acid used 10 cc of each N/10 acid	Dye ad- sorbed Milli- grams	Dye un- adsorbed Milli- grams	Bleeding test. Amount dye given up by dyed fiber to 250 cc H ₂ O at boiling tempera- ture for 20 minutes Milligrams
Acid violet	No acid	38.0	2.0	1.0
	HCl	39.2	0.8	0.4
	H ₂ SO ₄	39.2	0.8	0.4
	H ₃ PO ₄	39.1	0.9	0.6
Crocein orange	No acid	32.5	7.5	5.0
	HCl	38.0	2.0	4.4
	H ₂ SO ₄	35.5	4.5	3.1
	H ₃ PO ₄	35.5	4.5	3.7
Acid green	No acid	30.1	9.9	3.9
	HCl	37.5	2.5	2.7
	H ₂ SO ₄	36.3	3.7	2.7
	H ₃ PO ₄	36.0	4.0	3.3
Crystal ponceau	No acid	37.7	2.3	1.3
	HCl	39.8	0.2	0.5
	H ₂ SO ₄	39.4	0.6	0.6
	H ₃ PO ₄	39.4	0.6	0.6

the same amount of bleeding. A comparison of the data of the acid violet with crocein orange or acid green brings out strikingly the relation between the setting and the subsequent bleeding of the dye. According to the theory postulated the acid violet was more firmly set on the wool than the crocein orange as the data show in all cases the amount of acid violet given up to the water during the bleeding test was much less than the amount of crocein orange. Finally a comparison of the effect of the acids, among themselves, on the adsorbed dyes does not seem to bring out any of the above general relationships. There were apparently disturbing factors that entered in that offset the effect of each acid. However, if we turn to Table VI which contains the data for experiments carried on exactly like those whose data are recorded in Table

IV, except that a larger amount of dye was used, it is seen that on the whole an acid dye adsorbed in a hydrochloric acid bath seemed to be more firmly coagulated on the fiber, or made less soluble in water, than a dye adsorbed in a sulphuric acid bath; and that a dye adsorbed in a sulphuric acid bath was more firmly coagulated on the fiber than one adsorbed in a phosphoric acid bath.

Another interesting point concerning these data in addition to those above is that the sulphuric and phosphoric acids are equally efficient in bringing about the adsorption of the dyes. This seems strange for in the case of crystal ponceau data have been published showing¹ that when fibers were dyed in baths containing equivalent amounts of hydrochloric, phosphoric, and sulphuric acids, respectively, the greatest adsorption of dye occurred in the hydrochloric acid bath, a less adsorption in the sulphuric acid bath, and the least adsorption in the phosphoric acid bath. Since, according to the theory of dyeing,¹ a readily adsorbed anion will decrease the amount of acid dye taken up it can be seen why wool dyed in a sulphuric acid bath should adsorb more dye than when dyed in a phosphoric acid bath. In the case of these acids the anions of each are readily adsorbed by the wool, but the phosphate anion is more readily adsorbed than the sulphate anion, hence the wool dyed in a phosphoric acid bath will take up less dye than when dyed in a sulphuric acid bath of equivalent strength. Now it is to be observed from the above data that the concentration of dye used was nearly equal to the amount which in practical language the fiber would "about clean up" even in neutral baths. This fact then leads to the conclusion that when a fiber as wool is dyed, as described above, the "cutting down effect" of the adsorbed anion is practically overcome for probably the capacity of the fiber to adsorb more dye or sulphate and phosphate ions is still very high. Hence under such conditions wool takes up as much acid dye from a phosphoric acid bath as from a sulphuric acid bath.

¹ Bancroft: *Jour. Phys. Chem.*, 18, 4 (1914).

In order to show that the amount of phosphoric acid used is not so efficient as an equivalent amount of sulphuric acid in bringing about adsorption of acid dyes, or what is the same thing, that in the presence of practically equivalent amounts of adsorbed hydrogen ion the adsorbed phosphate ion cuts down the amount of dye adsorbed more than the adsorbed sulphate ion two methods of experimentation are open: (1) to the same concentration of dye and acid as in the previous experiments add a neutral salt with a common anion; (2) to the same amount of acids as above add a larger amount of dye per 250 cc H₂O.

In the first method as mentioned, the same concentration of dye and acid were used as in the above experiments. The method of dyeing also was the same. To the hydrochloric acid bath 10 cc of *N/1* NaCl were added; to the sulphuric acid bath 10 cc *N/1* Na₂SO₄; to the phosphoric acid bath 10 cc *N/1* Na₂HPO₄. The dyes acid violet and crocein orange only were studied. The data are the average of duplicate experiments.

TABLE V
Temperature—100° C
40 mg dye per 250 cc H₂O
Time—1 hour

Acid dye used	Acid used 10 cc. <i>N/10</i> acid	Salt used 10 cc <i>N/1</i> neutral salt	Dye ad- sorbed Milligrams	Dye unad- sorbed Milligrams
Acid violet	HCl	NaCl	39.5	0.5
	H ₂ SO ₄	Na ₂ SO ₄	36.8	3.2
	H ₃ PO ₄	Na ₂ HPO ₄	1.0	39.0
Crocein orange	HCl	NaCl	33.4	6.6
	H ₂ SO ₄	Na ₂ SO ₄	20.0	20.0
	H ₃ PO ₄	Na ₂ HPO ₄	0.1	39.9

These data bring out rather strikingly the fact that the chloride, sulphate, and phosphate ions cut down the adsorption of an acid dye, even when the concentration of dye used is about what the fiber will "easily clean up." The order in which the salts cut down the adsorption of the dye the least, namely, Na₂HPO₄, Na₂SO₄ and NaCl is exactly what one

would expect on the basis that the phosphate ion is adsorbed the most, and the chloride ion the least. These readily adsorbed anions not only offset the effect of the hydrogen ion, but also counterbalanced the still very great saturation capacity of the fiber for the dye.

In the second method the concentration of dye used was 75 mg; the kind and amount of acid used in each case was the same, namely, 10 cc of $N/10$ HCl, H_2SO_4 and H_3PO_4 , respectively. The method and other conditions of dyeing were the same. Acid green, crocein orange, and crystal ponceau were studied. The data, the average of duplicate experiments, follow:

TABLE VI
Temperature— $100^\circ C$
75 mg dye per 25 cc H_2O
Time—1 hour

Dye	Acid used 10 cc of each $N/10$ acid	Dye ad- sorbed Milli- grams	Dye unad- sorbed Milli- grams	Bleeding test. Amount dye given up by dyed fiber to 250 cc H_2O at boiling tempera- ture for 20 minutes Milligrams
Acid green	No acid	57.9	17.1	5.7
	HCl	72.2	2.8	4.5
	H_2SO_4	67.4	7.6	4.9
	H_3PO_4	65.2	9.8	5.3
Crystal ponceau	No acid	59.8	15.2	5.8
	HCl	74.5	0.5	1.8
	H_2SO_4	73.2	1.8	1.6
	H_3PO_4	72.3	2.7	4.1
Crocein orange	No acid	61.8	13.2	7.8
	HCl	72.7	2.3	3.9
	H_2SO_4	69.4	5.6	4.3
	H_3PO_4	69.4	5.6	5.3

In discussing Table V it was suggested that when the capacity of a fiber for an acid dye is as yet high the effect of an adsorbed ion in cutting down the adsorption of the dye is largely overcome. On the other hand, a low capacity of the fiber for a dye should indicate that adsorbed anions

as the above could bring about a decrease in the amount of acid dye adsorbed. To denote this varying adsorbing capacity of a fiber under the conditions indicated above the use of the term saturation capacity is suggested. By the term saturation capacity of the wool then is meant the capacity of the fiber to adsorb a given amount of dye under definite conditions. In other words as suggested by Professor Bancroft: "If the amount of dye that will be taken up from a concentrated solution is 100 and if x is taken up from any given concentration, then $100 - x$ is the saturation capacity of the latter solution." It is evident that when the fiber has adsorbed a large amount of dye its capacity to adsorb more dye (its saturation capacity) is considerably less than when it has adsorbed a much smaller amount of dye. Thus if we

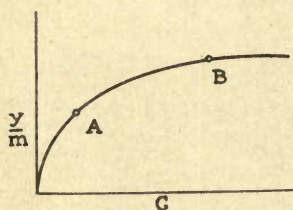


Fig. 1

consider the two points A and B in Fig. 1 on an adsorption isotherm as representing the amounts, respectively, of a dye adsorbed by wool, it is seen that the fiber which had adsorbed an amount corresponding to A has a much larger capacity to adsorb more dye, and its saturation capacity is

much greater than the same fiber which has adsorbed an amount corresponding to B.

If now we compare the data for the adsorbed dye in Table IV (40 mg dye per 250 cc H_2O) with the corresponding data in Table VI, we see strikingly illustrated in the first data as compared with the latter data the marked force of the fiber manifested in cutting down the repelling effect of the adsorbed anion on the adsorption of the dye. In the data of Table VI we see that the cutting down effect of the phosphate ion over the sulphate ion is considerable, with the exception of the crocein orange. It is to be observed that 22.1 mg and 27.8 mg more of crystal ponceau and acid green, respectively, in neutral solutions, were adsorbed by the wool dyed in 75 mg dye per 250 cc H_2O , than were adsorbed in 40 mg of the respective dyes per 25 cc H_2O . This indicates

that the saturation capacity of the fiber for these dyes in the former case has been so nearly reached as to allow the cutting down effect of the adsorbed phosphate ion over the sulphate ion to be manifested.

The table of comparison follows:

TABLE VII

Dye	Acid used	Dye adsorbed from solution 40 mg per 250 cc H ₂ O Milligrams	Dye adsorbed from solution 75 mg per 250 cc H ₂ O Milligrams
Acid green	H ₂ SO ₄	36.3	67.4
	H ₃ PO ₄	36.0	65.2
Crystal ponceau	H ₂ SO ₄	39.4	73.2
	H ₃ PO ₄	39.4	72.3
Crocein orange	H ₂ SO ₄	35.5	69.4
	H ₃ PO ₄	35.5	69.4

As seen in the data, H₂SO₄ and H₃PO₄ are equally efficient in bringing about an adsorption of crocein orange. Experiments with a higher concentration of the dye, 100 mg per 250 cc H₂O, show, however, that the laws of adsorption of an acid dye in an acid solution as postulated by Bancroft hold. The data showing the effects of H₂SO₄ and H₃PO₄ on the adsorption of the dye follow:

TABLE VIII
Temperature—100° C
100 mg dye per 250 cc H₂O
Time—1 hour

Dye	Acid used 10 cc N/10 of each acid	Dye adsorbed Milligrams	Dye unadsorbed Milligrams
Crocein orange	H ₂ SO ₄	92.5	7.5
	H ₃ PO ₄	90.7	9.3

After one of the bleeding tests carried on for wool dyed in a neutral bath of acid violet the dyed fiber was left in the hot solution of the dye that had bled from the fiber, and the whole allowed to cool. As the beaker and contents cooled

it was observed that the dye was quite rapidly reabsorbed. In an hour practically all of the dye had been reabsorbed. This experiment was repeated for acid violet with similar results. Experiments with fibers dyed in crocein orange and acid green and treated as those dyed in acid violet gave similar results, the slight differences being (1) that not quite all of the dye that bled was reabsorbed, (2) that the reabsorption was slower than in the case of acid violet. The results of these experiments seemed to indicate an irreversible adsorption of dyes. That there is also this irreversible adsorption between the adsorbed and unadsorbed dye in direct dyeing was shown in experiments carried out with acid violet, crocein orange, and acid green. One-gram samples of wool were dyed in 60 mg acid violet, crocein orange, and acid green per 250 cc H₂O, respectively, for one hour at the temperature of the boiling water-bath, after which time the beaker and contents (the dyed fiber was left in the solution of unadsorbed dye) were allowed to cool. At the end of ten hours all of the acid violet unadsorbed (about 10 mg) in this direct dyeing was completely adsorbed. The adsorption of the unadsorbed crocein orange and acid green was much slower. To insure complete adsorption of these dyes the dyed fibers were left in the cold dye bath (room temperature) for eight days. At the end of that time about 7 mg of the unadsorbed crocein orange in the direct dyeing and 10 mg of the unadsorbed acid green were adsorbed; or in terms of percentage of the respective unadsorbed dyes 91 percent of the crocein orange was adsorbed, and 90 percent of the acid green.

Various experiments were made to account for this irreversible adsorption of the dye. It was thought, although improbable, that the wool, when heated, was in some way changed so that its specific adsorbing power had increased. Hence an experiment was carried out in which the wool was placed in water heated to the temperature of the boiling water-bath for one hour and then entered while hot in 10 mg of acid violet (room temperature) in 250 cc H₂O. After 24 hours there was no appreciable adsorption of the dye. An experiment in

which the acid violet (10 mg per 250 cc H₂O) was heated at the same temperature for one hour and then the cold wool entered the hot dye bath and the whole allowed to cool, gave scarcely better results although slightly more dye was adsorbed than in the previous case. An experiment in which the wool and dye were heated separately, as in the above, for one hour and then the fiber entered the hot dye bath, gave similar results. A final experiment in which the fiber was dyed in 60 mg of acid violet and then the dyed fiber removed from the bath and entered again when both were cooled to room temperature resulted in an appreciable adsorption of acid violet at the end of six weeks. Experiments of a similar nature with acid green, 11.2 mg dye per 250 cc water, gave negative results in indicating a reason for this irreversibility. The dye, however, in contrast to that of the acid violet, was almost completely adsorbed in all cases at the end of one week.

Although these experiments do not seem to point to any reason for the irreversible adsorption of a dye they do seem to bring out the interesting fact that the more irreversible a dye the less completely and readily that dye is adsorbed at low temperatures. From methods described below it is brought out that of the dyes acid violet and acid green, acid violet is far more irreversible than acid green. From the experiments just described above we see that acid violet, even after a long period of time, is adsorbed very slightly at room (low) temperature. Niagara violet 3R, like acid violet, is a highly irreversible dye. An experiment in which a one-gram sample of wool was left in a bath of 60 mg of the dye per 250 cc water for three weeks at room temperature brought out the fact that the dye was very slightly adsorbed. Acid green in contrast to the above dyes is much more reversible, and hence was much more largely adsorbed at room (low) temperature.

That this apparent irreversible adsorption of dyes is quite general is indicated by the work of Freundlich and Losev.¹ In four cases of the six studied this phenomenon

¹ *Zeit. phys. Chem.*, **59**, 284 (1907).

was exhibited. They found, for example, that on wool patent blue was irreversibly adsorbed; on silk new fuchsin and patent blue, and on cotton new fuchsin. Crystal violet was adsorbed reversibly by wool and silk.

The question now arises: is there any relation between this apparent irreversible adsorption of a dye and its tendency to bleed? If we consider this irreversible adsorption as indicative of the force with which the dye is held by a fiber it would seem that the more irreversible a dye is the less that dye will bleed. Thus, if we consider the experiments described above for acid violet, crocein orange and acid green we see that the irreversibility of the acid violet was complete: the irreversibility of the crocein orange and acid green nearly equal to each other. Therefore, under like conditions of dyeing and testing for bleeding we should expect acid violet to bleed less from a fiber than acid green or crocein orange; and that the two last-named dyes should bleed approximately the same.

To show the relationship between the irreversible adsorption of a dye and its bleeding, two methods of experimentation were carried out: (1) a method suggested by Freundlich, (2) a method suggested by Professor Bancroft. Freundlich's method will be taken up first.¹ One gram of pure wool, used as bought, was entered in 250 cc of water containing 60 mg of dye, and dyed for one hour at the temperature of boiling water-bath. The dye unadsorbed was determined colorimetrically. The dyed fiber was tested for bleeding in a volume of 250 cc H₂O for twenty-five minutes, and the amount of dye bled determined also colorimetrically. Parallel with the above experiment another one was run in which the same weight of wool was entered in just one-half the volume of dye solution containing the same amount of dye, and dyed at the same temperature for one hour. Then the volume of solution was made up to 250 cc and the whole heated at the same temperature for another hour. The amount of unadsorbed dye in

¹ *Zeit. phys. Chem.*, 57, 385 (1906).

this experiment was likewise determined colorimetrically. Thus by these experiments a relation between the irreversibility of a dye and its bleeding was obtained. The data, the average of triplicate experiments, are given in the table below.

Dye	Amount unadsorbed after 1-hour treatment (direct dyeing) Milligrams I	Amount dye unadsorbed on irreversible experiment Milligrams II	Amount dye irreversibly adsorbed Milligrams III	Amount dye bled Milligrams IV
Crocein orange	11.2	8.6	2.6	5.0
Acid green	7.3	6.3	1.0	4.4
Niagara violet 3R	8.9	1.0	7.9	0.1

These data bring out the fact that the more irreversible the dye the less the bleeding. Column I gives the amount of dye unadsorbed by the fiber in the first experiment as outlined above. Column II gives the amount of dye unadsorbed by the fiber which was first entered in just half the volume of dye of double the strength used in the first experiment. After one hour an amount of water was added making the final volume equal to that used in the first experiment. It is seen that in all cases the end concentration in the second column is less than in the first column. This indicates a certain amount of irreversible adsorption on the part of the dye under the conditions of the experiment, for if there had been a definite equilibrium between the adsorbed quantities and the end concentrations, the final concentration in Column II ought to have been the same as in Column I. Column III gives the difference in end concentrations between Columns I and II. Column IV shows the amount of dye given up by the fibers in the bleeding test. In comparing Columns III and IV we see that for the conditions of the experiment the amount of dye irreversibly adsorbed is greater the faster the dye is to the bleeding test as carried out in the experi-

ment. There does not seem to be any quantitative relationship between the quantities given in Columns III and IV.

The other method of showing the irreversible adsorption, as suggested by Professor Bancroft, was as follows: A one-gram sample of wool was dyed in a bath containing 60 mg of the dye for two hours at 90° C or till equilibrium was reached. The fiber was then removed, washed, and the amount of dye left in the bath determined colorimetrically. The data are given in Column I, of the subjoined table. The dyed fiber was put in a beaker containing 250 cc water and the whole heated to the temperature of the water-bath for about 25 minutes. The beaker and contents were at once cooled to 90° C and the fiber then placed in another beaker which contained in 250 cc H₂O an amount of dye that was not adsorbed by the fiber during the dyeing at 90°. The whole was kept at 90° C till equilibrium was reached, or for about two hours. The fibers were then removed, washed, and the amount of dye left in the solution determined as above. The data are recorded in Column II in the table below. The difference between the amount of unadsorbed dye during the direct dyeing, and the amount of dye in the second final dye bath is taken as a measure of the amount of it irreversibly adsorbed. Column III of the table below contains the data. The data, the average of duplicate experiments, follow:

Dye	Dye unadsorbed on direct dyeing Milligrams I	Dye unadsorbed on irreversible experiment Milligrams II	Amount of dye irreversibly adsorbed Milligrams III
Crocein orange	7.3	6.5	0.8
Acid green	9.5	5.7	3.8
Niagara violet 3R	9.5	1.2	8.3

These data bring out the same general relationship that were brought out in the immediately preceding table. Here as there the most irreversible dye is Niagara violet followed by acid green and crocein orange in the order named.

These two sets of experiments point to the general conclusion that the more a dye is irreversibly adsorbed, other factors being the same, the less it will bleed when subjected to such tests. This is brought out rather strikingly in a comparison of the amounts of dye bled for crocein orange and acid green, in Tables IV and VI. In five out of the eight cases compared crocein orange bled more than acid green. This is what one should expect from a knowledge of the comparative irreversibility of the two dyes. The three exceptions noted may be more apparent than real.

FROM TABLE IV

Treatment	Amount dye bled Milligrams	
	Crocein orange	Acid green
Neutral bath	5.0	3.9
HCl bath	4.4	2.7
H ₂ SO ₄ bath	3.1	2.7
H ₃ PO ₄ bath	3.7	3.3

FROM TABLE VI

Neutral bath	7.8	5.7
HCl bath	3.9	4.4
H ₂ SO ₄ bath	4.3	4.8
H ₃ PO ₄ bath	5.3	5.3

To sum up this part of the work:

This irreversible adsorption of a dye, as suggested above (page 792), may be taken as indicative of the force with which a dye is held by a fiber. From this point of view one would conclude that Niagara violet or acid violet is much more firmly held by the wool than is crocein orange or acid green; hence the less bleeding exhibited by the first two named dyes than the last two. This force by which the dye is held by the fiber is of a selective nature; that is, there seems to be no relation between the constitution of a dye, and its irreversibility. It is possible that the more irreversible dyes act as

better mordants toward themselves than the less irreversible ones.

Stains and Their Removal

In an experiment in which acid violet was practically, although not completely, removed from the fiber by boiling water we have a case analogous to the partial removal of a fruit stain from cloth by this same means and method. Thus in the experiment with acid violet we can look upon the dye as the stain upon the wool. Its practical removal from the fiber was due to the fact that the boiling water peptized it, that is, made a colloidal solution of it.

Dyes also can be removed from a fiber by reagents other than water, as, for example, by the use of bleaching agents, aqueous solutions of ammonium acetate or sodium carbonate, and solid reagents such as fullers' earth. The above reagents are used also to remove stains from textiles, and in many instances the methods and principles of removal of the stain by a given reagent is the same as for the dye. This very interesting analogy between some stains and dyes with regard to their behavior towards various reagents led to the following classification of the principles underlying the removal of the greater majority of stains from textiles, and to a brief study to confirm each method in this classification.

The following classification has been proposed by Professor Bancroft:

- I. Mechanical removal.
 - Mud and brush.
- II. Dissolving in a liquid.
 - Grass in alcohol, benzene.
 - Sugar in water; dyes in hot water.
 - Iodine in alcohol.
 - Syrup in warm water.
- III. Peptizing in a liquid.
 - Balsam of Peru with kerosene or alcohol.
 - Dyes in hot water; chocolate with hot water.
 - Machine oil with turpentine.
 - Grease with gasolene.

Glue with warm water.
Milk with cold water.
Paraffine with benzine or kerosene.
Pitch with benzine.
Vaseline with turpentine.
Punch with warm water.
Coffee tannin with boiling water.
Iron rust with kerosene.

IV. Peptizing with a solution.

Dyes with sodium carbonate, ammonium sulphate,
borax.
Blood with ammonia.
Soot with sodium hydroxide (2 percent solution).
Glue with acetic acid.
Paint with sodium carbonate.

V. Peptizing with peptized colloid.

Blood with soap.
Soot, iron rust, with soap.
Cream with soap.
Perspiration with soap.
Old black silk clothes with skimmed milk.
Kerosene with soap.
Meat juice with soap.

VI. Peptizing in two stages.

Tar and oil and soap.
Grease and oil and soap.
Tea and glycerine and soap.
Black shoe polish and oil and soap.
Grass and benzine and soap.
Rosin and oil and soap.
Coffee and glycerine and soap.
Paint and oil and soap.
Paint and oil and casein and soap.

VII. Adsorption by solid.

Grease and fullers' earth or blotting paper.
Wax and French chalk.

Starched white woolen shawls, lace curtains, with rice or potato starch, and treatment with enzymes.

Dyes and freshly prepared alumina.

Charcoal drawings and bread.

Fruit stains and fullers' earth.

Fruit stains and salt.

Wall paper and dough, corn-meal.

Furs and corn-meal.

VIII. Peptizing with a liquid and adsorption by solid.

Grease, alcohol or turpentine, and pipe-clay or fullers' earth.

IX. Change of substance forming the stain.

Fruit stains oxidized by use of "bleaching" agents.

Ink with salt and lemon juice.

Ink with hydrochloric acid, oxalic acid.

Dyes with bleaching agents, as sulphur dioxide.

Dyes with potassium permanganate and oxalic acid.

Iron rust with hydrochloric acid.

Iron rust with citric acid and cream of tartar.

Perspiration with sodium hyposulphite (for silks and wools).

Tobacco with hydrochloric acid and ammonia.

These methods will be taken up in the order given.

Method I involves mechanical manipulation only. The efficiency of the brush depends upon the fact that the material to be removed is generally held loosely by the fiber.

In Method II stains from iodine and the dye safranine were studied.

With respect to iodine a piece of woolen cloth was immersed in an aqueous solution at room temperature for thirty minutes, and another piece at the boiling temperature for ten minutes. The iodine adsorbed by the fiber at room temperature was readily removed by alcohol at the same temperature. The removal of the stain from the boiling solution was not brought about so readily by alcohol at room temperature, a much longer time being required, namely, about twenty-four hours. However, by immersion of a similarly stained

piece of cloth in several fresh, hot portions of boiling alcohol the removal of the stain was brought about in a short time. Woolen cloth was stained by the dye safranine in the same manner as by the iodine. The larger part of the dye adsorbed at room temperature was removed by repeated immersion in fresh portions of water at that temperature. The removal was brought about more completely by immersion in water heated to 60°–70° C. Not all of the dye, however, was removed, even by boiling water—there being a small portion which “set” on the fiber.

The larger part of the dye adsorbed by the fiber at the temperature of boiling water was removed slowly, and only by repeated immersion of the dyed fiber in fresh portions of boiling water. The last traces of the dye could not be removed by this treatment.

The other cases listed in this division of the general classification are removed, as safranine and iodine were, with the formation of a true solution of the stain with the solvent. When fresh these stains are quite readily removed by the particular solvent. A stain, as grass stain, may, however, become “set” on the fiber with the result, as in the case of safranine, that it cannot be removed by the solvent, even by repeated applications. Chemicals as listed in IX are then generally the only reagents capable of bringing about its removal. The sugar and syrup stains, as is obvious, can easily be removed by water for they are not strongly adsorbed by fibers, and also are very easily soluble in the liquid.

The cases studied where the liquid peptized the stain were: the dye crocein orange removed by water; grease (lard) removed by gasolene.

In the case of crocein orange the method of experiment was identical with that of safranine. The results obtained were similar; that is, in no case was the dye completely removed from the fiber. In the case of the fiber dyed hot in a solution of 60 mg of dye per 250 cc H₂O for one hour, repeated immersions of the dyed fiber in fresh boiling water removed the greater part of the dye only after 4½ hours.

Grease was completely removed by gasolene in a very short time at room temperature.

Peptization of substances by a liquid as in the above cases is a very common phenomenon.¹ In the cases of the fiber stained either by the dye or grease we may look upon the combination as one substance. Thus with the dyed fiber it adsorbs the solvent water, and so part of it, *i. e.*, the colored portion, is peptized. Hence we get a water-soluble colloid of the dye. The same holds for the greased fiber. It readily adsorbed the gasolene and hence part of it was peptized, with a formation of a gasolene-soluble colloid of grease. To quote Professor Bancroft, "If we wash out of cloth a dye which forms a colloidal solution² we are peptizing the dye with water. The removal of chocolate by water is another case of the same type because chocolate does not really dissolve in water. The removal of iron rust from iron by means of kerosene is a case of peptization because the iron oxide does not dissolve in kerosene. The removal of grease by benzine, gasolene, naphtha, etc., is another case under this heading because the grease does not form a true solution in these organic liquids. The removal of resin with benzine comes under the same head."

Just as crocein orange was removed from the fiber by water, just as grease was removed from the fiber by gasolene, so the other substances here listed as stains are removed in the same way by the particular peptizing solvent. Colloidal solutions are formed in all cases. Thus with water we have formed the water-soluble colloids of coffee, glue, milk, and punch; with turpentine we have the turpentine-soluble colloids of machine oil and vaseline; with kerosene the kerosene-soluble colloids of paraffine, pitch, and iron.

Many stains can be removed from fibers by means of dissolved substances. This removal is due to the fact that the undissociated dissolved substance, or one of the products of the dissolved substance, is readily adsorbed by the stain

¹ Bancroft: *Jour. Phys. Chem.*, 20, 85 (1916).

² Bancroft: *Journal of Home Economics*, 8, 356 (1916).

and hence peptizes it, thus giving rise to a colloid solution. In aqueous solutions, in general, peptization by undissociated substances, as for example, inorganic salts, is not so well defined as peptization by an ion.¹ Cases of peptization by an ion, however, are numerous and well known. Thus the removal of the stains as listed in IV can be considered as brought about by their peptization by ions. Thus in the case of the blood stains their removal, from this point of view, is due to the peptization of the haemoglobin of the blood by the adsorbed hydroxyl ions from the aqueous solution of ammonia. Acid dyes can readily be removed from wool by a dilute solution of borax. The borax in solution is hydrolyzed giving rise to the formation, among other substances, of sodium hydroxide, which in turn dissociates into sodium and hydroxyl ions. Now the hydroxyl ions are preferentially and readily adsorbed by the stained fiber,² hence they readily peptize the adsorbed acid dye, and its removal in consequence is brought about.

In the laboratory an example studied under this section (IV) was the removal of soot by a dilute solution of sodium hydroxide (2 percent). A piece of cotton cloth was very thoroughly impregnated with soot and then immersed in the slightly warmed alkali solution. In a few minutes the soot was practically removed from the cloth. In this case we have the peptization of the soot by the preferentially adsorbed hydroxyl ions, giving rise to a sodium hydroxide-soluble colloid of soot.

The removal of soot as listed in V was very interesting. Fibers of wool and silk were thoroughly impregnated with soot and then immersed in a dilute "liquid" soap solution which was heated to about 50° C. The removal of the soot from the wool was very rapid and complete. In the case of the silk a longer time was required but the removal was as complete. To quote Professor Bancroft in this connection,³

¹ Bancroft: *Jour. Phys. Chem.*, 20, 102 (1916).

² Bancroft: *Ibid.*, 18, 10 (1914).

³ Bancroft: *Journal of Home Economics*, 8, 356 (1916).

“Under peptization by a peptized colloid we have all the cases in which soap is used. Soap does not dissolve in water but is readily peptized by it. The theory of washing with soap has been put on a satisfactory basis by Spring.¹ It is to him that we owe a very striking and instructive experiment. If we filter a fine suspension of rouge or soot through filter paper, some of the particles stick to the filter paper or, as we say, are adsorbed by it. If the liquid is filtered several times through the same paper, the water will finally run through clear, the particles of rouge or soot adhering to the previously adsorbed particles and finally clogging the pores of the filter paper. If a soap solution be poured on the filter, a red or a black filtrate is obtained at once, almost as though one had punched a hole in the bottom of the filter with a glass rod. The soap forms a film round the rouge or the soot, removing the particles from the paper and thus allowing them to pass through. All the rest of the particles follow just as a log jam breaks when the key log is started. At first sight it seems as though the soap must have broken up the carbon or the rouge into finer particles which then passed through the filter. There are two reasons for rejecting this hypothesis. In the first place the experiment does not succeed if the rouge or the carbon is too coarse, and there is no apparent reason why the soap should not break up coarse particles if it can break up fine ones. In the second place Spring showed that we are dealing with an adsorption of soot by filter paper. If the black filter paper be reversed and washed with water, only the carbon which is not in immediate contact with the paper is removed.

“Soap acts in a similar way in removing dirt or grease from fabrics or from the hands. The soap forms a film round the dirt or the grease removing it from actual contact with the fiber or the skin, thus simplifying the task of washing it away with water.”

Another colloidal solution which acts like soap is ox-gall in water. Owen recommends it for the purpose of cleaning

¹ *Zeit. Kolloidchemie*, 4, 161 (1909); 6, 11, 109, 164 (1910).

wool carpets.¹ He says: "Take them and beat and shake them thoroughly in a good breezy place to get out all dust. Have the floor scoured clean and, when dry, replace the carpet, and, if still much soiled and dingy, go all over the carpet with ox-gall and water. The secret of success is to clean and rinse them thoroughly without soaking them through. A pint of fresh ox-gall is put into a pail of clean soft water and another pail of clean water set handy. With a brush rub up a lather upon about a square yard of the carpet by dipping the brush in the ox-gall and scrubbing, not too hard but with just the movement that raises a lather, but does not remove the fiber from the carpet. Now with a soft cloth or large sponge, not too wet, remove the lather, aiming to do this by frequent wringing out of the sponge in clear fresh water. After all is done, open the windows and the carpet will soon dry out."

It is obvious that the other substances listed in this section are removed in the same way as soot was by the soap. In all cases with the exception of the stains on the black silk clothes, the water-soluble colloid, soap, is the effective detergent. Old black silk clothes can be "renovated"² by immersing them in scalding hot skim milk and water to which a little glue or gelatine has been added. In this case the dirt and dust are readily removed by the peptized colloid casein in the milk and the peptized gelatine.

It would seem that soluble colloids other than water could be used to remove stains. Thus many aniline dyes that are insoluble in benzene "can be peptized by a benzene-soluble colloid such as zinc or magnesium resinate so-called."³

In the method of peptizing in two stages the following cases as listed under VI were studied: grease and oil and soap; rosin and oil and soap; paint and oil and soap; and paint, and oil and casein and soap. The methods suitable for the above cases are practically identical for the other stains listed in this section.

¹ "The Dyeing and Cleaning of Textile Fabrics," 100 (1909).

² Owens: "The Dyeing and Cleaning of Textile Fabrics," 114 (1909).

³ Bancroft: *Jour. Phys. Chem.*, 20, 108 (1916).

To study the removal of grease and rosin according to the outline suggested white woolen cloth was thoroughly impregnated with automobile grease. These stained pieces of cloth were then very thoroughly rubbed with olive oil till the stains were softened. The whole was finally immersed in a warm soap solution. The removal of both stains was thorough and complete.

With regard to paint stains the following procedure was followed: A large piece of white woolen cloth was thoroughly impregnated with a brown paint, which was allowed to dry thoroughly on the fiber by placing in a hot air oven heated to about 100° C. After the paint had completely dried, the stained cloth was thoroughly rubbed with olive oil till the paint was softened. The cloth was then cut into two parts. One piece of the cloth was immersed in a warm soap solution for about five minutes. It was then removed, washed, rubbed with oil, and again immersed in the soap solution. The removal of the paint was fairly complete. The other piece of cloth before the soap treatment was treated with casein by rubbing into it the finely divided powder. Treatment with a warm soap solution then followed for about five minutes as in the preceding case. The treatment with oil and casein was repeated for this piece of cloth. If anything, the paint in this latter case was more completely removed than it was from the other sample.

It might be well in this connection to quote Owens. He says, p. 90: "Grease spots are of the most common occurrence. To remove these from white fabrics is comparatively easy, but to remove them from colored fabrics without at the same time doing injury to the color is often very difficult and sometimes impossible. Very much depends upon the skill and perseverance of the operator. Good soap and water is the most universal solvent for greasy matters, and where there is no reason for not wetting the goods, soap and water should be tried. Grease spots from carriage wheels, sewing machines, or any source containing iron from wear of bearings, or carbon from any source, red lead, or any insoluble colored substance,

should first be rubbed thoroughly with some oil that is itself capable of being washed out with soap and water, such as lard or fresh butter, olive oil, linseed oil, etc.

“Much depends on how this is done. Don't be afraid to use plenty of oil, butter, or lard, and then work with the fingers, bending the cloth back and forth as if you were breaking a wire, until upon holding it up to the light you see that the dark matter of the spot is completely and evenly distributed and worked up with the oil. When sure this result is accomplished, then work in a thick cold, watery, soapy mass obtained by boiling up sliced laundry soap in water and allowing to cool. If on touching the dry soap bar to the tongue, it does not ‘bite,’ it should have some sal-soda added to it in the boiling. Work the prepared soap into the cloth where the spot is, until the oil in its turn is worked up with the soap as thoroughly as the spot was with the oil. Now, and not before, wash out the spot with soapy water. Only with very old spots will any trace remain after this treatment. Grease spots succumb very well if rubbed up with kerosene, the kerosene rubbed up with new milk, and the whole then worked with soap and water.”

In regard to paint, Owens says, p. 103: “Paint, when fresh, washes out as readily as any grease spot. As it ages and oxidizes it becomes more and more difficult to soften and remove it. . . . Oil the spot and rub the oil in patiently, striving to blend the spot with the oil. If the spot is very old, allow to lie with the oil upon it for several days, rubbing occasionally to see if the paint is softening. A few drops of turpentine, kerosene, or any solvent for greasy matters may be added and worked in. Old lead paint is very persistent. Finally, wash out like a fresh grease spot.”

In all of these cases we have as a result of the oil treatment a peptization of the particular stain by the oil. The peptized stain was then finally removed by the peptized colloid, namely, the soap as explained in V. In the case where casein was used we have an adsorption by the casein of the peptized paint followed by a peptization of the casein and its

adsorbed products by the soap, and their consequent removal.

In Method VII we have an interesting procedure for the removal of stains in that advantage is taken of the greater selective adsorptive power of the solid reagent for the particular stain than the cloth or material to be cleaned. The only case studied was the removal of grease by blotting paper. A piece of cloth, thoroughly stained with automobile grease, was placed between two hot pieces of blotting paper. The grease was removed very rapidly from the cloth. Here, of course, the adsorptive power of blotting paper for the grease was greater than the cloth, hence the removal of the grease.

The use of solid reagents, other than the one studied, for removing stains is quite general as the list in VII indicates. Just before using, these solid reagents should be moistened.¹ They should be thoroughly rubbed into the stained cloth. Repeated applications of the solid reagent will often bring about a complete removal of a stain. Koller² states that infusorial earth is especially to be recommended for cleaning glass plates for photographic purposes. Even very greasy plates rapidly become clean when rubbed with infusorial earth moistened with water. A very interesting case to be listed under Method VII is the removal of dirt, etc., from starched curtains. This method was brought to the attention of Professor Bancroft by Mr. C. P. Long of the Globe Soap Company. Starched lace curtains are placed in water with a diastase which converts the starch into soluble starch. When this is peptized by water the dirt comes off with the starch without any rubbing.

In Method VIII we have an example where the stain is first peptized by a liquid and the removal of the whole brought about by selective adsorption. As in Method VII a piece of wool cloth was stained with automobile grease and then thoroughly rubbed with alcohol. Fullers' earth was then rubbed in and the whole washed in cold water. By repeated

¹ Ray Balderston: "Laundering," 47 (1914).

² "The Utilization of Waste Products," 310 (1915).

applications of alcohol and fullers' earth a large percentage of the grease was removed.

Method IX is resorted to among practical cleaners, only with white goods, or where, with dyed goods, it is believed that they can be re-dyed on the spot thus treated. The removal of the stain in this case is brought about by its conversion into other substances which readily can be removed from the goods by washing.

Iodine and safranine stains were studied. In the case of safranine a sample of cloth was taken upon which were traces of the dye which could not be removed by boiling water. The sample was immersed in a dilute solution of bleaching powder. In a short time the cloth was "bleached." Upon washing, no evidence of the dye was visible.

The sample of cloth stained by iodine was immersed in a dilute solution of sodium thiosulphate. The iodine was reduced very rapidly, and on washing the cloth no evidence of the stain was visible.

These two methods are only suggestions of the many cases where "chemicals" may be used for removing stains. In their use proper regard for the kind of cloth, silk, wool, or cotton, the condition of the cloth, as for example whether dyed or not, must be taken into consideration. One of the most frequent uses made of this general method of removal is in the removal of "stubborn" fruit stains as peach, plum, or coffee stains.

Summary

Under the experimental conditions described the color of one dye can be partially or completely masked by another, but one dye cannot be displaced by another. The apparent displacement is brought about by the solvent or peptizing action of the water.

An experiment is described illustrating the selective adsorption by wool of one dye over the other at different temperatures.

With respect to the bleeding of acid dyes, it is shown that the minimum amount of dye is extracted by hot water when

the fiber (wool) is dyed in an acid bath. The most probable reason for this is that the acid aids in coagulating or setting the dye on the fiber, thus making it less soluble.

The laws of adsorption of an acid dye in various acid baths as postulated by Bancroft hold when, as suggested, the saturation capacity of the fiber has been so decreased that the cutting-down effect of the respective anions can be manifested.

Of the dyes studied the more the dye was irreversibly adsorbed the less completely and readily was that dye adsorbed at a low (room) temperature.

Of the dyes studied by Brown the decreasing or increasing adsorption with decreasing temperature below 60° may be accounted for, in view of the immediately preceding statement, by postulating that those dyes are irreversibly adsorbed to a greater or less degree, rather than by postulating that those dyes are adsorbed with an adsorption or evolution of heat.

The more a dye is irreversibly adsorbed, other factors being the same, the less it will bleed when subjected to bleeding tests.

A classification of the methods for the removal of stains is suggested. A study was made of each method in the classification. It is suggested that a very interesting field for research in washing and cleaning is by a study of the method belonging under Class VII.

This thesis was carried out under the direction of Professor Wilder D. Bancroft. It is a pleasant duty to me to express to Professor Bancroft my gratitude for his helpful criticism, his unflinching kindness and courtesy during the progress of the work.

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