CI.—*Experimental Investigation into the Process of Dyeing.*

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NOTWITHSTANDING the great importance of a precise knowledge of the mechanism of the process of dyeing fibrous materials, this subject has not advanced considerably since the classic work of Walter Crum (Trans., 1863, **16**, 404). The main cause of this is perhaps that although many contributions to the question have been made, the experimental data upon which far-reaching conclusions have been based have in too many cases been altogether insufficient. The amount of really accurate quantitative data bearing on the manner in which colouring matters are absorbed by fibrous materials is quite insignificant when compared with the intricacy of the subject; many of the more comprehensive pieces of experimental work concerned are mentioned in the course of the present paper.

A considerable amount of evidence has been accumulated showing that the absorption of colouring matters by fibres is in many cases not due to the formation of definite chemical compounds nor to the formation of solid solutions of the ordinary kind. W. Crum compared the process of dyeing with the absorption of various materials by charcoal; von Georgievics (*Mitt. techn. Gewerbemuseums, Wien*, 1894) also showed that Magenta, &c., are absorbed by porous plate and by glass beads, and that the dyed products are not readily freed from the colouring matter by boiling water. The latter author further made a comparison of the mode in which colouring matters and tannic acid are taken up by cotton, wool, and asbestos in a fibrous and disintegrated or structureless condition; he found that in every instance the fibrous material absorbed larger quantities of dye than did the corresponding material in the structureless or powdered state. He also showed (*Monatsh.*, 1894, **15**, 705, and with Löwy, *ibid.*, 1895, **16**, 345) that the proportions in which such colouring matters as Indigo-carmin and Methylene-blue are absorbed by wool and cotton do not indicate the formation of solid solutions. Schmidt (*Zeitsch. physikal. Chem.*, 1894, **15**, 56) has ascertained that iodine is not absorbed by charcoal from benzene or alcoholic solution in accordance with Henry's law, and the general results of these investigations have been confirmed by Walker and Appleyard (Trans., 1896, **69**, 1334), who examined the equilibrium established between silk and picric acid both in aqueous and alcoholic solutions.

The recent work of H. Freundlich (*Habilitationsschrift*, Leipzig, VOL. XCI.

1906), who measured accurately the absorption of a number of substances by purified charcoal from solution in different solvents, establishes with even greater precision the conclusion to be derived from the previous work.

The chemical theory of the dyeing process has been largely supported by experimental work having for its object the drawing of close analogies between dyeing and actual typical chemical reactions; in view of the obvious weaknesses of the analogies thus derived and the striking nature of the parallels between the processes of dyeing and of physical or mechanical absorption briefly indicated above, it seemed very desirable that this aspect of the subject should be further examined. This further examination should not include simply the determination of the proportions in which colouring matters, &c., are absorbed by various materials, as has been previously done, but should also have for its object a careful comparison of the behaviour of the different types of materials during and after the dyeing operation.

As a preliminary to this extension of the scope of the analogy to be drawn between dyeing and physical or mechanical absorption further exact information was obtained as to the mode in which the absorption of colouring matters by fibrous materials is influenced by the degree of disintegration of the latter; the fibrous nature of the material used was not entirely destroyed in these experiments, but different series of observations were made with material of different mean length of fibre.

It is well known that fibres such as cotton, which have been converted into paper pulp by mechanical treatment in the presence of water, behave differently towards colouring matters than do the fibres in the original state.

A quantity of material was prepared by boiling cotton yarn from American cotton twice under pressure in the usual manner with caustic soda; it was then well washed, and dried in the stove for several days. The cotton was not bleached in order to avoid the possible formation of oxycellulose. The dried material then contained 5·6 per cent. of moisture; part of it was cut into pieces of about 2 inches in length, whilst the remainder was subjected to mechanical disintegration for various periods in the beating engine. The various portions required for use in the absorption experiments were withdrawn from the beater at the expiration of 1·5, 3, 4·5 and 6 hours' treatment respectively. The average length of fibre left in the beaten material at the end of the several periods mentioned was measured in the usual way, and the results are stated in Table I; the speed at which disintegration proceeds obviously diminishes as the time of beating increases.

For each of the absorption experiments the weight of cotton or pulp used corresponded to 20 grams of absolutely dry fibres. The absorption tests were carried out with the basic colour Night-blue, because the amount present in the dye-bath can be readily and accurately ascertained by titration with a solution of Naphthol-yellow S (Rawson, *J. Soc. Dyers and Colourists*, 1888, **4**, 82). In each case 20 grams of the material were immersed in a solution of 0.2 gram of Night-blue in 900 c.c. of water; the experiments were conducted at the ordinary temperature in Jena glass flasks, which were frequently shaken in order to prevent uneven absorption. It was found that equilibrium between dye solution and fibres was established in about 48 hours. Table I shows the actual weight of dye absorbed by the 20 grams of dry material in the various stages of disintegration and after different periods of immersion; it also states (in brackets) the proportion of the dye used which is absorbed by the material.

TABLE I.

		Gram dye absorbed.				
	Time of immersion in hours.	Original fibres.	1.5 hours' beating.	3 hours' beating.	4.5 hours' beating.	6 hours' beating.
Cotton.....						
Average length of fibre in mm. ...		23.0	2.5	1.5	1.1	0.7
	1	0.0289 (0.1445)	0.1044 (0.522)	0.1137 (0.5685)	0.1168 (0.584)	0.1245 (0.6225)
	6	0.049 (0.245)	0.1177 (0.5885)	0.1183 (0.5915)	0.1184 (0.592)	0.1245 (0.6225)
	18	0.0551 (0.2755)	0.1183 (0.5915)	0.1183 (0.5915)	0.122 (0.61)	0.1245 (0.6225)
	72	0.644 (0.322)	0.1214 (0.607)	0.1269 (0.6345)	0.1294 (0.647)	0.1306 (0.653)
Wool						
Average length of fibre in mm. ...		29.0	3.12	2.2	0.7	0.4
	1	0.0305 (0.1525)	0.0351 (0.1755)	0.0382 (0.191)	0.0459 (0.2295)	0.049 (0.245)
	6	0.0366 (0.182)	0.0382 (0.191)	0.0413 (0.2065)	0.0462 (0.231)	0.0521 (0.2605)
	18	0.0413 (0.2065)	0.0428 (0.214)	0.0443 (0.2215)	0.047 (0.235)	0.0521 (0.2605)
	72	0.0521 (0.2605)	0.0521 (0.2605)	0.0521 (0.2605)	0.0521 (0.2605)	0.0521 (0.2605)
Percentage of water retained at 60°		3.24	2.13	2.33	1.47	1.51

It is noteworthy that the unbeaten cotton yarn shows a constantly increasing absorption during the 72 hours of immersion, whilst the most highly disintegrated material absorbs colouring matter very rapidly during the first hour of immersion, and but a very small further amount of dye is taken up during the remaining 71 hours of immersion. It must thus be concluded that in the case of cotton the degree of subdivision of the fibre greatly influences both the

total proportion of dye absorbed and the rate at which absorption occurs. It is remarkable that the most highly disintegrated material was found coloured to about the same depth of shade as the original yarn, although it had absorbed more than twice the proportion of colouring matter. This observation is in accordance with practical experience in the dyeing of basic dyes on paper pulp.

The fact that the wool fibre differs very materially from the cotton fibre as regards its structure and its dyeing properties made it of interest to study this fibre under similar conditions. A quantity of unbleached woollen rags (flannel) was scoured with ammonia, so as to remove any fatty matter, washed free from ammonia, torn to pieces of approximately equal size, and then disintegrated in the beating engine. Whilst no difficulty was experienced in weighing the cotton pulp, in the case of the wool the water separated so quickly from the wool pulp as to render this impracticable; the different grades of pulp were therefore removed from the beating engine, freed as far as possible from water by pressing, and then left for about four days in a large drying stove at a temperature of 60°. After this treatment the retained moisture was in each case determined; the results are stated in Table I, as are also the average lengths of the fibre. In each experiment 10 grams of absolutely dry fibre were immersed at the ordinary temperature in 900 c.c. of liquor containing 0.2 gram of Night-blue. Previous thereto, and for the purpose of evenly wetting out the dry fibres, 200 c.c. of boiling water were added to each batch of fibre and allowed to stand for 24 hours before adding the dye solution; the fibres in the finest state of disintegration were found to felt together during the drying, and for the purpose of preventing uneven penetration and absorption of the dye boiling water was added as described, and the whole shaken for two hours on a mechanical shaking apparatus.

The amount of colouring matter absorbed by 10 grams of wool, in the various degrees of disintegration and after different periods of immersion, is stated also in Table I. The results obtained with disintegrated wool fibres differ very materially from those obtained with cotton. Equilibrium between the dye in solution and the fibres is, as before, established in less than 72 hours; the amount of dye absorbed after 72 hours' immersion is, however, the same, whether the fibres are in the original state or in a very finely disintegrated condition. The original fibres absorb the colouring matter gradually, maximum absorption being obtained after between 18 and 72 hours of immersion; the finely disintegrated fibres (six hours' beating) behave quite differently in that maximum absorption is obtained after between one and six hours of immersion. The depth of shade of the dyed fibres after 72 hours' immersion is uniform

throughout and independent of the degree of disintegration; this contrasts with the results obtained with cotton.

From this set of experiments it must be concluded that the degree of disintegration of the wool fibre influences the speed with which equilibrium is established as between fibre and dye, but does not influence the proportion of colouring matter ultimately absorbed. It might be suggested that the beating of the cotton or wool in contact with water produces some chemical change in the material; it was therefore desirable also to examine some fibrous material of simpler physical character than either cotton or wool, more especially with the view of ascertaining more directly whether the amount of fibrous surface exposed to the action of the dye-bath influences the proportion of dye absorbed. For this purpose artificial silk of two kinds, differing only in that they consisted of fibres of the average diameters 0·0299 mm. and 0·184 mm. respectively was used. Quantities of these two silks were cut into lengths of about 2 inches, and 10 grams of each (dry weight) were immersed for 72 hours in 750 c.c. of solution containing 0·15 gram of Night-blue. The fine silk absorbed 0·0986 gram, and the coarse silk 0·0558 gram of colouring matter. It is thus clear that the finer silk, which exposes the larger surface, absorbs considerably more dye than the coarser material, and a direct indication is obtained that in the absorption of Night-blue by artificial silk the proportion taken up is roughly proportional to the surface exposed by the fibrous material.

Further confirmation of this result was obtained by studying the absorption of Night-blue by a chemically inert substance, namely, emery powder; two samples of levigated emery, the one very fine and the other much coarser, were used. One hundred grams of each kind were immersed for periods of 1, 6, 18, and 72 hours in 750 c.c. of water containing 0·15 gram of Night-blue. The results were as follows:—

TABLE II.

Time of immersion in hours	Gram dye absorbed.			
	1.	6.	18.	72.
Coarse emery.....	0·0081 (0·0587)	0·0167 (0·1113)	0·0263 (0·175)	0·05 (0·333)
Fine emery.....	0·05 (0·3333)	0·0618 (0·412)	0·09 (0·6)	0·09 (0·6)

The behaviour of the fine and coarse emery is clearly very similar in kind to that of the fine and coarse artificial silks, and also to that of the various grades of disintegrated cotton fibre. It is therefore concluded that the amount of surface exposed to the action of the dye solution greatly influences the proportion of dye absorbed,

not only in the case of a material such as emery, which is certainly chemically inert, but also in that of cotton or artificial silk.

In the above series of experiments a distinct analogy is traceable between the action of cotton and artificial silk and of emery powder on dye solutions.

It seemed desirable further to extend the investigation for the purpose of ascertaining whether or not the indicated analogy has a real physical significance or not. Cotton, wool, silk, &c., were therefore dyed with a number of colouring matters typical of the different classes of coal-tar dyes, for the purpose of comparison with parallel trials carried out with such chemically inert substances as graphite, blood charcoal, China clay, &c.

As the quantity of colouring matter absorbed by materials varies widely with the conditions of dyeing, identical methods were adopted in every case; no attempt was made to obtain absolute results concerning the absorption of colouring matter, as for the present purpose the primary object of the work was the obtaining of values which are rigidly comparable among themselves, but in each case the time of immersion, the temperature, the mode of shaking, &c., were identical.

The colouring matter remaining in the dye bath was determined by titration in the cases of Night-blue and Naphthol-yellow S, and by the Dubosq colorimeter in all other cases.

Table III gives the results obtained by immersing the materials named in the first column (10 grams dry weight) in 750 c.c. of water containing 0.25 gram (in the case of charcoal 3.5 grams) of Night-blue; column 2 shows how much colour is absorbed during 72 hours' immersion in the cold; column 3 gives the amount absorbed during 72 hours' immersion in the cold followed by one hour's heating to 95°, the liquor being drawn off at this temperature; column 4 gives results obtained in the same way as those of column 3, with the difference that the solution after heating for an hour at 95° was allowed to cool and to remain in contact with the material for another period of 72 hours before examination. The numbers enclosed in brackets in this and the other tables state the proportions of colouring matter corresponding to the actual weights absorbed.

The graphite used was in the state of very fine powder, and the blood charcoal was the specially purified material supplied by Merck (Darmstadt).

TABLE III.

	Gram dye absorbed.		
	Cold.	Hot.	Cooled.
Cotton	0·036 (0·144)	0·04 (0·16)	0·04 (0·16)
China clay	0·1693 (0·6772)	0·17 (0·68)	0·172 (0·688)
Graphite	0·2449 (0·9796)	0·2474 (0·9896)	0·249 (0·996)
Wool	0·05 (0·2)	0·23 (0·92)	0·2486 (0·994)
Silk	0·236 (0·944)	0·246 (0·984)	0·249 (0·996)
Charcoal	3·123 (0·8923)	3·495 (0·9987)	3·5 (1·0)

Parallel experiments were also made with lamp-black, the filtration of the solutions presented great difficulties and the absorption values were therefore only approximately ascertained. It was, however, found that the lamp-black absorbs basic dyes freely, more when heated than in the cold, and a further quantity of dye is absorbed when the liquor is allowed to cool after heating. It thus behaves similarly to charcoal.

It is concluded from the results given in Table III that the absorption of the basic colouring matter Night-blue proceeds in a similar manner in every instance independently of whether animal or vegetable fibres or inorganic absorbents are used.

After dyeing, all the materials were separated from the bath and washed with distilled water until the wash-water became colourless; this, even with graphite, China clay, and charcoal, resulted after a few washings, the dye thus being retained by the material in such a manner that it does not "bleed" into water. It is generally supposed that after charcoal has absorbed colouring matters from solution, the dye is very loosely held by the absorbent and can be completely removed, although slowly, by repeated washing in distilled water; this assertion has been used to support the contention that a number of dyeing phenomena cannot arise from mere absorption (Freundlich, *loc. cit.*, 91).

Since it is now definitely established that charcoal, graphite, &c., absorb Night-blue just as do textile fibres, the colouring matter not being washed out by subsequent treatment with water, the objection referred to must be regarded as groundless.

The analogy between the absorption of colouring matters by fibrous materials and charcoal, &c., can be further extended by examining the behaviour of the dyed materials towards a neutral soap solution; the dyed cotton, wool, silk, graphite, China clay, and charcoal bleed freely in hot Marseille soap solution.

The very complete analogy of behaviour existing between the dyeing of fibrous materials and inorganic or inert absorbents when the basic dye Night-blue is used having been thus demonstrated, it became desirable to extend the work to the study of the absorption of acid colouring matters towards the same materials. As typical representatives of the three groups of acid colouring matters were selected the nitro-compound Naphthol-yellow S, the azo-colouring matter Ponceau RR, and the sulphonated basic dye Acid-magenta.

TABLE IV.

	Dye used, grams.	Gram dye absorbed.					
		Without acid.			With 4 per cent. H_2SO_4 .		
		Cold.	Hot.	Cooled.	Cold.	Hot.	Cooled.
Cotton	0.08	0.0	0.0	0.0	0.005	0.005	0.005
	—	—	—	—	(0.0625)	(0.0625)	(0.0625)
China clay	0.08	0.0	0.0	0.0	0.0024	0.0035	0.0024
	—	—	—	—	(0.03)	(0.0438)	(0.03)
Graphite	0.08	0.018	0.0067	0.018	0.017	0.013	0.018
	—	(0.0225)	(0.0084)	(0.0225)	(0.2125)	(0.1625)	(0.225)
Wool	0.6	0.063	0.013	0.063	0.5956	0.566	0.5956
	—	(0.105)	(0.0217)	(0.105)	(0.9927)	(0.9433)	(0.9927)
Charcoal ..	5.5	4.35	3.0	4.35	5.437	5.363	5.402
	—	(0.7909)	(0.5455)	(0.7909)	(0.9886)	(0.9751)	(0.9822)

In this table the amounts of Naphthol-yellow S absorbed by 10 grams of (dry) material, dyed both with and without the addition of sulphuric acid to the dye bath, are given; the conditions, without acid, are therefore the same as in the Night-blue experiments.

It is to be noticed that, without acid, cotton and China clay do not absorb Naphthol-yellow S, and that graphite also absorbs little and much less in the hot than in the cold. Wool and charcoal both absorb very strongly, and in each case much less is absorbed in the hot than in the cold. After dyeing the materials were washed with water; the small quantity of colouring matter absorbed by the graphite is very readily and completely removed by a few washings with distilled water. The behaviour of the other dyed materials is conveniently discussed together with the results obtained by the addition of 4 per cent. of sulphuric acid to the dye bath, also contained in Table IV.

Naphthol-yellow S becomes considerably lighter in shade when sulphuric acid is added to its solution. To counteract this in titrating with Night-blue phenolphthalein was added to the solution, which was then made slightly alkaline by *N*/10-caustic soda. A drop of acetic acid was afterwards added so as slightly to acidify the solution.

The quantities of colouring matter absorbed are very small in the case of cotton, graphite, and China clay, as compared with those absorbed by wool; further, the dye is in the former instances com-

pletely removed by a few washings with water. Dyeing of the cotton, graphite, &c., in the proper sense of the word, therefore does not take place. The following results were obtained by the comparative washing with water of wool and charcoal, dyed with and without the addition of acid to the dye bath. In both cases the wash-water apparently became colourless much sooner when acid was used in the dye bath, the dyeings without acid running more freely and the wash-water remaining slightly coloured even after prolonged washing.

With a view to determine whether very slow washing would remove still further quantities of colouring matter, the samples of charcoal dyed with and without the addition of acid were washed by the aid of the pump. When no acid had been used, about three weeks' washing was required for the removal of practically all the colouring matter absorbed by the charcoal. The amount was checked by collecting all the wash-water and titrating it with Night-blue. A much larger amount of water was required to exhaust the colouring matter from charcoal dyed with the addition of acid; but after about eight weeks' washing titration of the wash-water showed that all the dye absorbed had been removed.

The dyed samples of wool were washed for a considerable time by repeated soakings and running off the wash-water, with similar results to those obtained with the corresponding samples of charcoal.

It is important to note that the running of the colouring matter seems to proceed fairly rapidly up to a certain point, after which much water and considerable time are needed for the removal of the remaining portion. Fowler and Gaunt have drawn attention to a very similar fact, namely, that the washing out of ammonium chloride absorbed by gravels proceeds very rapidly until a certain point is reached, but very slowly after this.

Table V. refers to dyeing with Ponceau RR, with and without the addition of acid to the dye bath.

TABLE V.

	Dye used, grams.	Gram Ponceau RR absorbed.					
		Without acid.			With 4 per cent. H_2SO_4 .		
		Cold.	Hot.	Cooled.	Cold.	Hot.	Cooled.
Cotton	0.2	0.0	0.0	0.0	0.0	0.0	0.0
Graphite	0.2	0.0462 (0.231)	0.0 (0.0)	0.0463 (0.2315)	0.0	0.0	0.0
Wool	1.0	0.0889 (0.0889)	0.064 (0.064)	0.12 (0.12)	0.387 (0.387)	0.807 (0.807)	1.0 (1.0)
Silk	1.0	0.19 (0.19)	0.096 (0.096)	0.192 (0.192)	0.264 (0.264)	0.576 (0.576)	0.713 (0.713)
Charcoal	5.5	5.31 (0.9655)	5.438 (0.9887)	5.5 (1.0)	5.428 (0.9869)	5.473 (0.9951)	5.5 (1.0)

(a) Without the addition of acid:—Cotton absorbs no Ponceau either in the cold or hot. Graphite absorbs a small amount in the cold, which, however, is expelled on heating and is re-absorbed on cooling. Washing removes the colouring matter absorbed by the graphite quickly and completely. Wool and silk absorb less colouring matter in the hot than in the cold, whilst charcoal absorbs more in the hot. In every instance the maximum amount of colouring matter is absorbed after cooling.

(b) With the addition of acid:—Cotton and graphite do not absorb colouring matter, either hot or cold. Wool, silk, and charcoal behave analogously in that they absorb more dye in the hot than in the cold, and take up a further quantity on cooling. On washing with water it is distinctly noticeable that the materials dyed with the addition of acid are more quickly freed from the loosely-held colouring matter than those dyed without the acid. More colouring matter is extracted from the charcoal than from either wool or silk, probably because the charcoal has been completely saturated with colouring matter and takes up more than five times as much as the wool; this excess, which is doubtless held superficially, is washed away more readily, whilst the main bulk of the colouring matter is held much more firmly. Wool and charcoal dyed without the addition of acid both lose a little colouring matter with cold water, more with hot water, and still more when soda and soap are applied. The materials dyed with the addition of acid behave similarly on the whole, but no colouring matter is extracted from the wool by cold water.

It was deemed of interest to ascertain whether charcoal containing the same proportion of colouring matter as the wool would hold it in a similar manner. For this purpose 10 grams of (dry) charcoal were allowed to absorb 1 gram of Ponceau RR, with and without the addition of acid, respectively. Charcoal treated in this manner does not allow any of the colouring matter to bleed, either into cold or hot water, and none can be extracted if soda is added to the wash-water; the colouring matter is therefore more firmly held by the charcoal than by the wool. On boiling with neutral soap solution the colouring matter, however, "bleeds" freely. Silk dyed with Ponceau, both with and without the addition of acid, behaves similarly to wool and charcoal, but "runs" more freely than either.

TABLE VI.

	Dye used, grams.	Gram Acid-magenta absorbed.					
		Without acid.			With 4 per cent. H_2SO_4 .		
		Cold.	Hot.	Cooled.	Cold.	Hot.	Cooled.
Cotton	0.1	0.0	0.0	0.0	0.0	0.0	0.0
Graphite	0.1	0.0	0.0	0.0	0.0	0.0	0.0
Wool	0.5	0.0334	0.0212	0.0518	0.386	0.467	0.5
	—	(0.0668)	(0.0424)	(0.1036)	(0.772)	(0.934)	(1.0)
Silk	0.5	0.222	0.067	0.233	0.469	0.371	0.477
	—	(0.444)	(0.134)	(0.466)	(0.938)	(0.742)	(0.954)
Charcoal	3.25	2.905	2.5	2.784	3.2387	2.803	3.2394
	—	(0.8938)	(0.7692)	(0.8566)	(0.9965)	(0.8625)	(0.9967)
Lamp black	1.0	0.317	0.058	0.244	0.5296	0.1874	0.3649
	—	(0.317)	(0.058)	(0.244)	(0.5296)	(0.1874)	(0.3649)

Experiments carried out with Acid-magenta show that no colouring matter is absorbed by cotton or graphite if dyed either with or without the addition of acid to the dye-bath. Wool, silk, and charcoal, dyed without the addition of acid, absorb less colouring matter in the hot than in the cold, but take up more on cooling. Silk and charcoal, dyed with the addition of acid, exhibit parallel behaviour in that they absorb less colouring matter in the hot than in the cold, but take up slightly more on cooling. Wool, under these conditions, absorbs more dye hot than cold, and still more on cooling.

On washing the Acid-magenta dyeings it was in every instance noticed that more colouring matter is removed than in the case of Ponceau RR, the dyeings with the addition of acid being invariably faster than those without acid. The colouring matter is more readily washed out from the silk than from charcoal or wool.

Experiments similar to those carried out with Ponceau (1 gram of colour) were made with charcoal (10 grams), with and without the addition of acid. The colouring matter is much more strongly held by the charcoal when acid has been added to the dye-bath. Soap and soda have a similar action on wool, silk, and charcoal in removing the dye.

It is thus shown that the analogy pointed out between the absorption of basic dyes by fibrous and inert absorbents extends with remarkable precision to the absorption of acid colouring matters; but in the latter case a differentiation is to be observed. Graphite and China clay absorb the acid colouring matters in exactly the same kind of way as do fibres of vegetable origin, like cotton, whilst charcoal and the fibres of animal origin, such as wool and silk, behave similarly; the two classes of behaviour thus distinguished are strikingly different.

It was still necessary to ascertain whether the analogy also extends to the behaviour of the absorbents towards the colouring matters

which dye cotton direct; as one of these Diamine Sky-blue FF was selected, because, whilst being a typical dye of this class, it behaves quite specially towards wool. In a dye-bath containing a small amount of sodium carbonate this colouring matter, whilst dyeing on cotton, does not dye wool. In the first series of experiments no addition was made to the dye-bath, whilst in the second series 15 grams of sodium sulphate, and in the third 0.6 gram of sodium carbonate, was added to the dye-bath.

From Table VII it will be seen that cotton, artificial silk, and graphite absorb less colouring matter in the hot than in the cold, whilst silk, China clay, and charcoal absorb more in the hot than in the cold. Wool absorbs only a trace of colouring matter after heating and cooling; the amount absorbed is, however, too small to be measured accurately.

From the second series of experiments (dyeing with the addition of sodium sulphate) it will be noticed that cotton is the only material which absorbs less colouring matter in the hot than in the cold. Wool, silk, artificial silk, and charcoal take up more in the hot than in the cold, and a further quantity on cooling. Graphite and China clay, although behaving like the latter, yet on cooling absorb less dye than in the hot.

The third series (addition of sodium carbonate to the dye-bath) shows that wool and silk absorb no colouring matter. Cotton and artificial silk take up less in the hot than in the cold, but on cooling after heating a further quantity is absorbed. Graphite takes up practically the same proportion of colouring matter under the several conditions. China clay takes up more in the hot but gives it up on cooling. Charcoal behaves as in the former two instances.

The following classification of the results facilitates their comparison:—

(a) Material dyed without any addition to the dye-bath:—Cotton and graphite both “bleed” distinctly with cold water, cotton rather more freely than graphite. Both “bleed” more freely in hot water and still more colouring matter is removed when sodium carbonate or soap is added to the water. Silk “bleeds” hardly appreciably in the hot, a little more when sodium carbonate is added, and still more with soap.

(b) Material dyed with the addition of sodium sulphate:—Cotton “bleeds” less than in (a), either hot or cold; soda and soap remove the dye more freely. Graphite does not “bleed” appreciably, either hot or cold, and very little with sodium carbonate or soap. It is quite evident that the graphite holds the dye more strongly than does the cotton. The silk “bleeds” comparatively less than in (a), especially when it is considered that a much greater proportion of colouring matter has been absorbed.

TABLE VII.

Material, 10 grams (charcoal, 5 grams). Dye-bath (750 c.c.) containing 0.4 gram (in the case of charcoal, 3.0 grams) of dye.

	No addition.			Gram Diamine Sky-blue FF. absorbed.			With 0.6 gram Na ₂ CO ₃ .		
	Cold.	Hot.	Cooled.	Cold.	Hot.	Cooled.	Cold.	Hot.	Cooled.
Cotton	0.0442 (0.1105)	0.0075 (0.0188)	0.0578 (0.1445)	0.3171 (0.1105)	0.2269 (0.5672)	0.3654 (0.9135)	0.0712 (0.178)	0.0471 (0.1178)	0.121 (0.3025)
Artificial silk	0.0308 (0.077)	0.016 (0.04)	0.08 (0.2)	0.3059 (0.7647)	0.32 (0.8)	0.4 (1.0)	0.0572 (0.143)	0.0308 (0.077)	0.1091 (0.2728)
Graphite	0.3714 (0.9285)	0.1757 (0.4393)	0.3035 (0.7587)	0.1932 (0.483)	0.2378 (0.5945)	0.1333 (0.3333)	0.0757 (0.1892)	0.08 (0.2)	0.0757 (0.1893)
China clay	0.0571 (0.1428)	0.0735 (0.1837)	0.0429 (0.1073)	0.0471 (0.1178)	0.1 (0.25)	0.0364 (0.091)	0.0308 (0.077)	0.1126 (0.2815)	0.016 (0.04)
Wool.....	0.0	0.0	trace	0.0096 (0.024)	0.1042 (0.2605)	0.188 (0.47)	0.0	0.0	0.0
Silk	0.2323 (0.5807)	0.3117 (0.7792)	0.3526 (0.8565)	0.3529 (0.8823)	0.3633 (0.9083)	0.4 (1.0)	0.0	0.0	0.0
Charcoal	1.743 (0.581)	2.9659 (0.9886)	3.0 (1.0)	1.816 (0.6053)	2.8286 (0.9429)	2.9386 (0.9795)	1.7 (0.5666)	2.95 (0.9833)	3.0 (1.0)
Gram Congo-rubine absorbed.									
Cotton	0.1273 (0.3183)	0.0889 (0.2222)	0.1447 (0.3617)	0.2942 (0.7355)	0.2208 (0.552)	0.3045 (0.7612)	0.1778 (0.4445)	0.1436 (0.359)	0.1395 (0.4737)
Graphite	0.3527 (0.8817)	0.2889 (0.7222)	0.3487 (0.8718)	0.3385 (0.8462)	0.2095 (0.5238)	0.3375 (0.8438)	0.1561 (0.3903)	0.1576 (0.394)	0.166 (0.39)
Wool.....	0.1059 (0.2647)	0.1531 (0.3827)	0.1949 (0.4572)	0.2333 (0.5833)	0.2676 (0.669)	0.3692 (0.923)	0.1059 (0.2648)	0.1241 (0.3104)	0.15 (0.375)
Charcoal	2.1304 (0.7101)	2.975 (0.9917)	3.0 (1.0)	2.3846 (0.7949)	2.9385 (0.9795)	2.961 (0.987)	2.3839 (0.798)	2.92 (0.9733)	3.0 (1.0)

Artificial silk, if compared with cotton, "bleeds" distinctly less, either with or without the addition of sodium sulphate. The dyed wool scarcely "bleeds" in hot water, but the addition of soap or sodium carbonate removes the colouring matter very freely. Charcoal, dyed both with or without the addition of sodium sulphate, resists the action of hot or cold water very well. Sodium carbonate does not remove the dye to any appreciable extent, but with soap and sodium carbonate the colour "runs" very freely. It therefore behaves very similarly to wool.

With the exception of a few dyes, such as the Diamine Sky-blue FF, used above, the colouring matters dyeing cotton direct show a great affinity for the wool fibre; it was therefore of importance to study a dye of this class which dyes wool readily, and for this purpose Congo-rubine was selected. The results obtained are also given in Table VII.

It is seen that when dyed with Congo-rubine, without any other addition to the dye-bath, cotton behaves similarly to graphite, whilst wool is dyed like charcoal. When dyed with the addition of sodium sulphate, cotton, as before, behaves analogously to graphite, and wool to charcoal. With the addition of sodium carbonate wool behaves like charcoal, whilst the cotton absorbs slightly less in the hot than in the cold; the absorption of the colouring matter by graphite is practically uninfluenced by the temperature changes. Both the dyed cotton and graphite "bleed" very little with cold water, more distinctly with hot water, and still more freely with the addition of sodium carbonate or soap. The dyed wool and charcoal also behave very similar in that they "bleed" but little with hot water and more freely with sodium carbonate or soap. The dyed charcoal and wool both bleed comparatively less when dyed with the addition of sodium sulphate.

It is well known that both the acid colouring matters and those which dye cotton direct are capable of forming lakes with the basic dyes. C. O. Weber (*J. Soc. Chem. Ind.*, 1894, **13**, 121) states that wool dyed with Scarlet R absorbs Magenta to the same extent as does white wool, and that this is not due to a simple lake formation between the two colouring matters, but to the formation of a compound lake between the two colouring matters and the wool fibre. To prove this he points out that lakes formed between these dyes in the absence of wool are soluble in alcohol, whilst "in treating with alcohol the hank dyed with Scarlet and Magenta, only a very small quantity of Magenta, but not the faintest trace of Scarlet is dissolved."

Having found, as pointed out above, that colouring matters are, in many instances, absorbed similarly by fibres and by substances

such as charcoal, graphite, &c., it seemed of interest to repeat these experiments both with fibres and inorganic absorbents. For this purpose wool was dyed with Scarlet RR, well washed and "topped" with Night-blue, and afterwards thoroughly rinsed. Charcoal was treated in a similar manner. On treating the dyed wool repeatedly with alcohol practically all the Night-blue was extracted, whilst the Scarlet remained unaltered on the wool. Absolute alcohol acts neither so quickly nor so completely as alcohol to which a very small quantity of water has been added. The compound colouring matter resists treatment with cold water very well, but, on heating, the Scarlet dissolves out slowly whilst the blue remains on the fibre.

By repeated washing (soaking) of the wool in hot water practically all the Scarlet may be removed, whilst the Night-blue is hardly affected. On adding a little ammonia to the water used for dissolving out the Scarlet and by boiling for about 30 minutes the Scarlet was removed completely, whilst the Night-blue remained on the fibre. A small quantity of alcohol added to the water used for the washing also accelerates the solution of the Scarlet and by applying water and alcohol in about equal quantities both colouring matters may be removed slowly from the fibres. Each of these experiments was repeated with the substitution of charcoal for the wool; in every case the charcoal dyeings behaved exactly like the wool dyeings.

The behaviour of colouring matters dyeing cotton direct when "topped" with basic dyes was next studied; for this purpose cotton cloth was dyed with Benzopurpurin 4B, thoroughly washed and "topped" with Night-blue, and finally well washed. Graphite and charcoal were treated in a similar manner.

It was observed that the basic dye could be readily extracted with alcohol, and more rapidly still with alcohol to which a small quantity of water had been added, so that finally the red was left practically pure on the cloth. Benzopurpurin is slightly soluble in alcohol, and the shade stripped off the blue is therefore a trace lighter than the original one. On boiling the dyed samples with water the red dissolves out very slowly. To accelerate this operation, white mercerised cloth, which, as is well known, attracts very strongly colouring matters dyeing cotton direct, was boiled with the dyed cloth. By adopting this course the Benzopurpurin was nearly completely removed after prolonged boiling, frequent changes of water and of white mercerised cloth being made. Benzopurpurin can be removed with the aid of mercerised cotton, as just described, but much more rapidly and more completely by boiling water containing a trace of sodium carbonate. During this treatment the shade of the Night-blue is reddened by the action of the sodium

carbonate; after extraction of the red, however, steeping of the cloth in water slightly acidified with acetic acid completely restores the colour. On substituting dyed charcoal and graphite for the dyed cotton in the above set of experiments it was found that they exhibit behaviour closely analogous to that of the cotton.

The colour lakes produced from basic and acid colouring matters or of basic dyes and colouring matters dyeing cotton direct are thus very fast to cold water when dyed on textile fibres and on the inert absorbents mentioned, and the acid or the direct dyeing colouring matter respectively is only slowly removed from either type of absorbents by hot water.

It is impossible to avoid the conclusion from these results that the dyeing operation in these instances also is of a purely mechanical character.

In the foregoing experiments the textile fibres used have been replaced by inert materials, such as charcoal, graphite, &c., and it seemed desirable to make a series of experiments on the absorption of substances other than coal-tar dyes by these materials. The following experiments were undertaken with a view to ascertain whether iodine and colouring matters are absorbed in a similar manner by wool. Ten grams of (dry) wool were immersed in 750 c.c. of potassium iodide solution containing 1.905 grams of free iodine. The time of immersion varied as shown in Table VIII.

TABLE VIII.

Time of immersion in hours	1.	6.	18.	72.
Gram absorbed	1.32 (0.6929)	1.62 (0.8504)	1.767 (0.9276)	1.848 (0.9701)

Inspection of the table shows that the absorption of iodine by wool proceeds similarly to the absorption of Night-blue.

A comparison was next made of the mode in which iodine was absorbed by textile fibres and by inert absorbents. Table IX.

TABLE IX.

10 grams (dry) of material immersed 72 hours in 750 c.c. of potassium iodide solution containing 7.62 grams of free iodine.

	Grams absorbed.		Grams absorbed.
Cotton.....	0.136 (0.0178)	Wool	4.4 (0.5774)
Graphite	0.9 (0.1181)	Charcoal	7.55 (0.9646)
China clay ...	0.56 (0.0735)		

The table shows that cotton and China clay absorb a small amount of iodine, whilst graphite absorbs rather more; wool and charcoal absorb very large quantities. Washing with water alone, removes the iodine very quickly and completely from cotton, China clay and graphite. Wool and charcoal retain the iodine much more firmly, a large amount of iodine remaining on both

materials after washing with water. The colour of the wool containing iodine is a deep brown orange, and the iodine can be removed completely from both wool and charcoal by solvents such as alcohol or potassium iodide.

These results, therefore, still further extend the analogy of the absorption of a substance from solution in water by fibrous materials, such as cotton and wool, and by inert absorbents, such as graphite, China clay, and charcoal. It is also remarkable that iodine behaves towards all these absorbents similarly to acid dyes.

The foregoing absorption experiments prove conclusively that dyeing with basic colouring matters, with the three different types of acid dyes and with the colouring matters dyeing cotton direct, proceeds in a closely analogous manner independently of whether textile fibres or inert substances, such as charcoal, graphite, &c., are employed as absorbents. It may therefore be safely concluded that all these dyeing processes are due to purely physical or mechanical absorption. The correctness of this view is strongly supported by the results obtained on comparing the action of hot and cold water, of sodium carbonate, soap, &c., on the dyed materials, both fibres and inorganic absorbents exhibiting a remarkable degree of analogy of behaviour towards these treatments.

A number of results have also been obtained with other absorbents, such as finely-divided silver and copper, Kieselguhr, &c.; these substantiate the close analogies pointed out above, and their detailed description is therefore unnecessary in the present connexion.

The investigation is being extended so as to embrace the processes involved in other well known dyeing operations.

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