second crystallization melted at 107–109°. This was used in the condensation mentioned above.

***p*-Homosaligenin,** 5-CH_3-2-$HOC_6H_4CH_2OH$.—Homosaligenin is difficult to prepare by any of the methods now described in the literature. The best two are treating *p*-cresol with formaldehyde, and the reduction of homosalicylaldehyde with sodium amalgam. A most satisfactory method was reduction of homosalicylaldehyde with hydrogen and platinum oxide according to the general method described by Carothers and Adams.[5]

A solution of 27.2 g. of *p*-homosalicylaldehyde in 100 cc. of alcohol was treated with 0.23 g. of platinum oxide and 0.1 cc. of *N* ferrous chloride solution. The mixture was reduced in the usual way, the time required being about 40 minutes when the hydrogen was passed in under a pressure of about 1.5 atmospheres. The yield was quantitative. The platinum was filtered off, the solution was evaporated and the product recrystallized. It then melted at 105°.

Summary

1. It has been found that benzaldehyde and substituted benzaldehydes condense with saligenin and substituted saligenins to yield 2-aryl-1,3-benzo-dioxanes.

2. The condensations take place with the greatest ease and generally without the addition of a catalyst. In the case of benzaldehyde and saligenin, and of nitrobenzaldehyde and saligenin the presence of benzoic acid greatly speeded up the reaction and gave the best results.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE COLOR LABORATORY, BUREAU OF CHEMISTRY, UNITED STATES DEPARTMENT OF AGRICULTURE, NO. 81]

PROPERTIES OF DYED MATERIALS

BY H. WALES

RECEIVED JUNE 30, 1923

Absorption Spectrum and Its Relationship to Color

Ever since the discovery of artificial colors, attempts have been made to find some relationship between the color and the chemical constitution. For some classes of dyes theories have been worked out with fair success. In practically every case, however, the "color" has been determined by means of the position of the absorption band or bands as determined with a spectroscope.[1]

The author has been led to believe by some recent observations that this method is incorrect and that the location of the absorption maximum

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[5] Carothers and Adams, THIS JOURNAL, **45**, 1071 (1923).

[1] Ley, "Beziehungen zwischen Farbe und Konstitution," F. Hirzel, Leipsig, **1911**. Watson, "Color in Relation to Chemical Constitution," Longmans, Green and Co., **1918**.

or width of the absorption band as ordinarily determined has only a general influence on the color, that is, it will determine whether the color will be red or blue, but will not indicate the particular shade of red or blue. This fact was first brought out through solutions of Formyl Violet S4B and Acid Violet 4B Extra. The second solution was of a decidedly redder cast than the first, although it actually absorbed more red light, there being a shift in the absorption maximum of about 250 Å. towards the red end of the spectrum. Wool dyeings made from these two dyes showed the same color differences as the solutions.

Solutions of the majority of the dyes show broad absorption bands with indistinct maxima, due probably to isomers and subsidiary dyes. The yellows, browns, and most of the oranges are unsuited for spectroscopic work because their absorption is either in the ultraviolet or too far into the violet to be read with any degree of accuracy. On the other hand, the dyes of the xanthene group show narrow, well-defined bands which fall near the center of the visual spectrum where the accuracy of reading is at the highest. Strangely enough, the one yellow dye of this group, fluoresceine, has its absorption maximum at about 4850 Å. and should therefore, by comparison with other dyes showing similar absorption, be orange-red.[2]

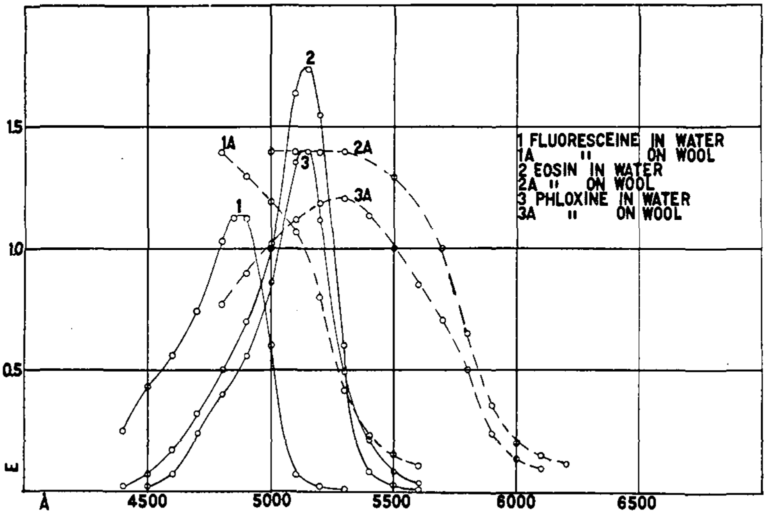

Fig. 1

Since the matching of shades of color is at best subject to large personal errors due to the varying sensitivity of the eye in different individuals, a more absolute method had to be devised. It was found that the ab-

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[2] The absorption maximum for Orange I is at 4750 Å. and for Ponceau 2 G at 4900 Å.

sorption spectra of wool dyed with different colors differed considerably from those determined from the solutions and offered at least a partial explanation for the color of the cloth.

The method used in this work was similar to that used by Meek and Watson.[3] An attachment was fitted to the front of the photometer box of a Hilger spectrometer equipped with a Nutting photometer, to hold the cloth at an angle of 45° with the optical axis of the machine. By means of a suitable source of illumination, light was reflected from the dyed sample[4] into one orifice of the photometer and from an undyed sample into the other orifice. A depth of dyeing sufficient to show an extinction coefficient of 1.0 to 1.5 was used in every case. This gave colorings of almost equal intensity from dyes of different tinctorial strengths. Readings made on dyeings of different depths gave curves which were multiples of one another, although in many cases the samples would appear as entirely different shades to the eye. This is undoubtedly due to the varying sensitivity of the eye towards light of different wave lengths.[5] The large amount of "white" light reflected from the surface of the cloth made it impossible to determine whether Beer's law held in this case.

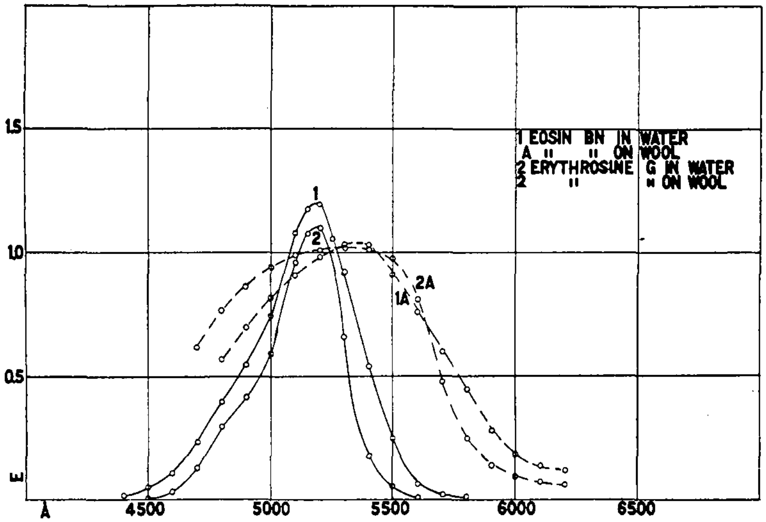

Fig. 2

The 17 dyes used in this work are listed in Table I. The absorption maxima were determined to the nearest 25 Å. for solutions and to the nearest 50 Å. for dyeings.

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[3] Meek and Watson, *J. Chem. Soc.*, **109**, 545 (1916).

[4] All dyes used in this work were carefully purified and dyeings were made from aqueous solutions containing only the dye.

[5] Compare Luckiesh, "Color and Its Applications," D. Van Nostrand Co., **1915**, p. 11, on the effect of illumination.

TABLE I

ABSORPTION MAXIMA OF DYES

Schultz[6] No.	Dye	Absorption maximum of aqueous solution Å.	Absorption maximum of wool dyeing Å.	Schultz[6] No.	Dye	Absorption maximum of aqueous solution Å.	Absorption maximum of wool dyeing Å.
585	Fluoresceine[a]	4875	About 4700	582	Violamine R[e]	5300	5400
596	Phloxine[b]	5150 −	5300	593	Phloxine P[c]	5300	5450
587	Eosin[b]	5150	About 5100	570	Rhodamine S[g]	5400	5400 +
590	Erythrosine G[c]	5200 −	5300	597	Rose Bengal 3 B[c]	5400 +	5600 −
591	Eosine B N[d]	5200	5350	580	Violamine B[e]	5450	5550
583	Violamine G[e]	5225	5350	595	Rose Bengal[a]	5450	5600 −
571	Rhodamine 6 G[c]	5250 −	5300	572	Rhodamine G[a]	5500	5400 +
592	Erythrosine[f]	5250	5375	573	Rhodamine B[a]	5550	5500
574	Rhodamine 3 B[c]	5275	5400				

Makers: [a] Berlin; [b] Schöllkopf; [c] Badische; [d] Heller; [e] Höchst; [f] National aniline; [g] Bayer.

Eight of these dyes, Rhodamine 3B, Rhodamine 6G, Violamine G, Violamine **R**, Eosin BN, Erythrosine, Erythrosine G and Phloxine P, show absorption maxima in aqueous solutions at 5300 to 5200 Å. Disregarding the fluorescence, dilute solutions of 6 of these appear almost identical in color. Rhodamine 6G is slightly more yellow than these 6, while Violamine R, which shows practically the same absorption as Phloxine P, is decidedly purple. When dyeings are made from these 8 compounds, the series shows a gradual change in tint from a yellow-red to a blue-red. Violamine R still has the deepest color, but the yellowest shade is shown not by Rhodamine 6G but by Erythrosine G.

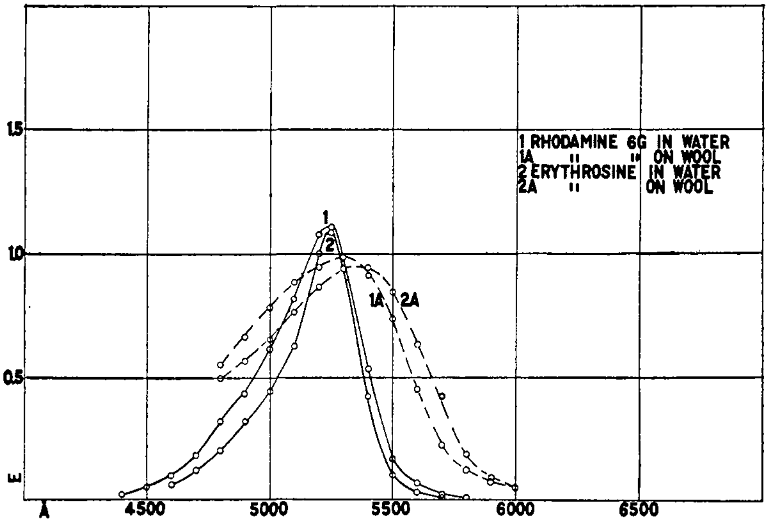

Fig. 3

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[6] Schultz, "Farbstofftabellen," Weidmannsche Buchhandlung, **1914**.

An analysis of the curves for the dyed samples shows that the complete curve and not the maximum determines the color. Erythrosine G and Eosin BN (Fig. 2) show maxima at practically the same point in both their aqueous solutions and wool dyeings, as do also Violamine R and Phloxine P (Fig. 5). The first two show the same red absorption and the latter two the same blue absorption. Eosin BN, however, transmits more

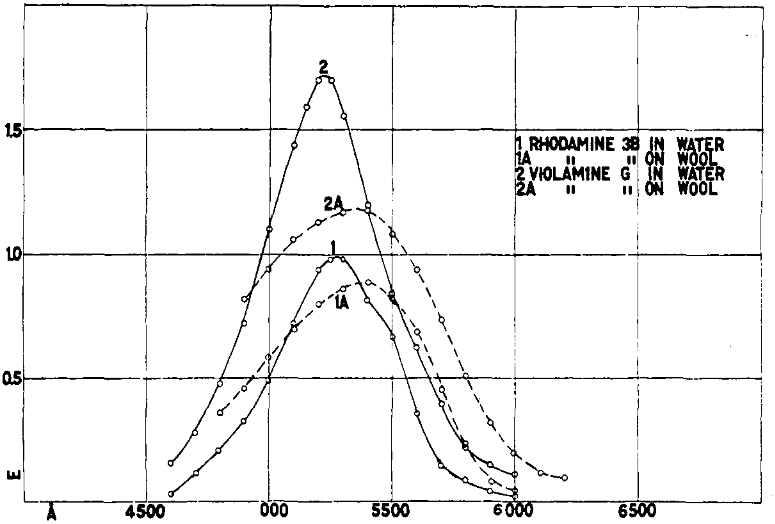

Fig. 4

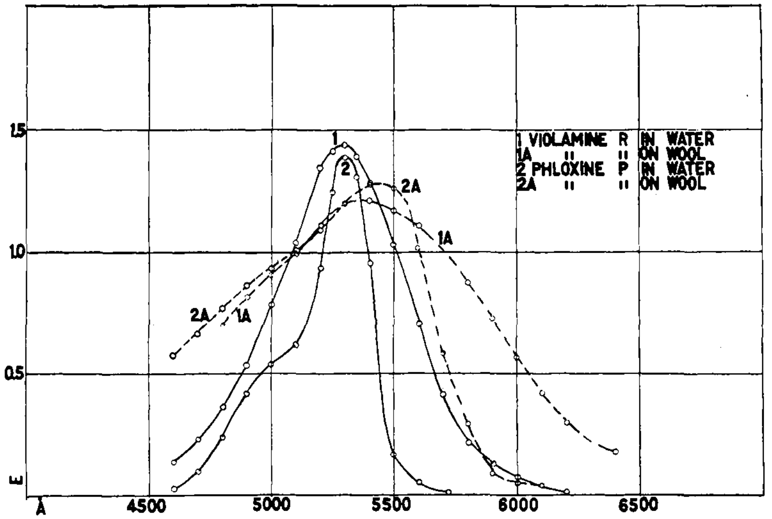

Fig. 5

blue light than Erythrosine G and is therefore bluer. In the same manner, the color of Violamine R is bluer than that of Phloxine P because it absorbs more light towards the red end of the spectrum.[7]

As was mentioned above, Acid Violet 4B extra has a much redder color than Formyl Violet S4B, although it shows a greater absorption in the red region. It also shows slightly more absorption in the blue but not enough to overbalance that in the red. Dyed samples show the same red absorption for both and a greater blue absorption for Acid Violet 4B Extra which is the redder of the two (Fig. 9).

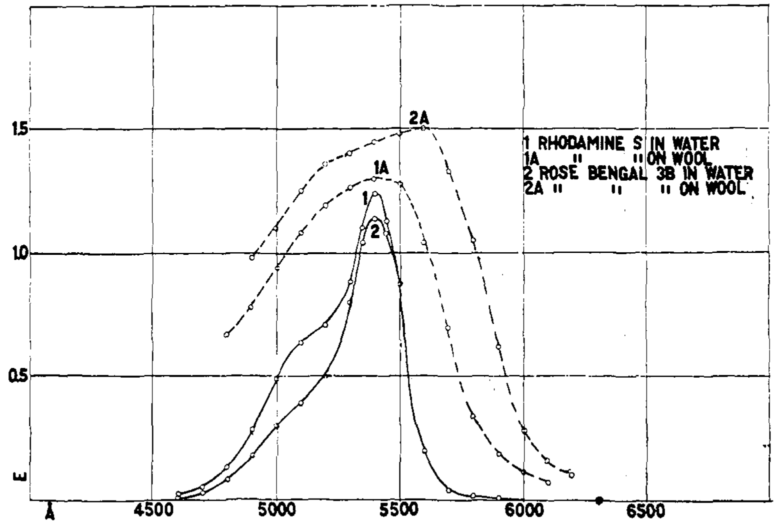

Fig. 6

The curves from the dyed samples show to a certain extent the color of an object. The spectrum of a solution will show only whether a dye should be red or blue. Anyone unfamiliar with the color of this solution would be unable to tell whether the unknown was lighter or darker in hue, by comparing its absorption curve with the spectrum of a known color giving a similar curve. Possibly either the absorption in the ultraviolet or in the infra-red or both may have some influence on the color sensation which is received by the eye. At present there are insufficient data on which to base any definite conclusions. A number of dyes have been studied to a limited extent in the ultraviolet,[8] while only those used for sensitizing photographic plates have been examined for transmission in the infra-red.

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[7] It is of interest to note that wool stained with alcoholic solutions of the color acids of these dyes gave curves identical with samples dyed from the salts.

[8] Uhler and Wood, "Atlas of Absorption Spectra," *Carnegie Inst. Washington*, **1907**.

The Mechanism of Dyeing

The older mechanical, chemical and solution theories of dyeing have of late been largely supplanted by the theory of colloidal adsorption by the fiber.[9] The various methods which have been used to demonstrate these theories are incapable of direct proof. For this reason it was thought that a comparative spectroscopic investigation of dyes, both in solution and on the fiber, might shed some light on the subject.

Many investigators have noted that a dye will not show exactly the same absorption of light in two different solvents. Usually both the position of the maximum and the width of the band are altered with a change in solvent. It has also been claimed[10] that the bands become wider as the dye approaches the colloidal condition. On the other hand, the width of curves obtained from dye lakes[11] may or may not be different from those given by the corresponding dyes in aqueous solutions.

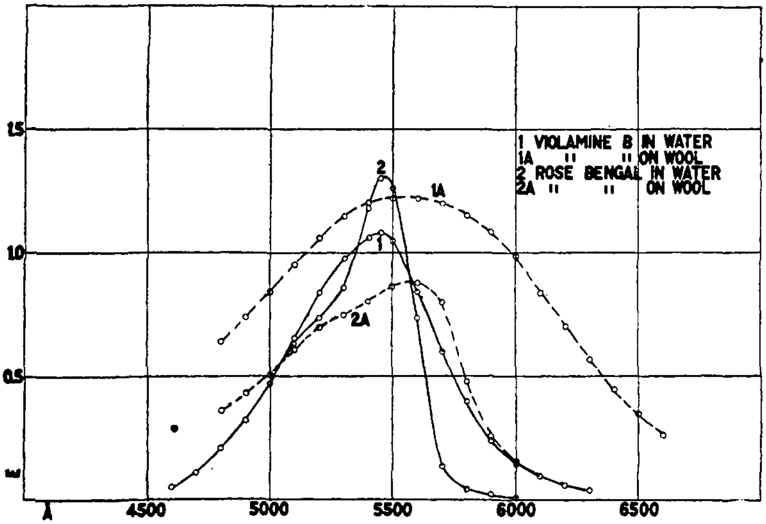

Fig. 7

The spectrophotometric curves obtained from wool dyeings shown above are much broader than those from the aqueous or alcoholic solutions. When filter paper was stained with any of the xanthene dyes and examined by means of the spectroscope, absorption curves which were identical with those from wool dyeings were obtained, showing that the color is present on both fibers in the same state. Further experiments were made by depositing thin gelatin films of Eosin BN and Erythrosine on glass plates and measuring both the transmission and reflection spectra.

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[9] Bancroft, *J. Phys. Chem.*, **18**, 1, 118, 385 (1914); **19**, 50, 145 (1915).

[10] Shephard, *Proc. Roy. Soc. London*, **82A**, 245 (1909).

[11] Holmes, *Color Trade J.*, **13**, 8 (1923).

In both cases the reflection spectra corresponded to those of the wool dyeings and the transmission spectra to those of the aqueous solutions, showing a slight shift in the maxima caused by a change in solvent (Fig. 10). Similar curves were obtained from a film of Erythrosine in cellulose acetate. These results indicate that these dyes are actually dissolved in the wool.

The objections to the solution theory[12] of dyeing are based mainly on the fact that the law of distribution between the solvent and fiber is not followed. Many dyeings are non-reversible.[13] These objections, as well as most of the proofs put forth to substantiate the various theories, are based on the idea that dyes should act like inorganic or simple organic compounds in solutions. Since dyes do not obey the solution laws when dissolved in liquids, there is no reason to expect them to obey these laws when dissolved in solids. For example, many sulfonated azo dyes can be completely extracted from aqueous solution by diluting with an equal volume of hydrochloric acid and shaking out with amyl alcohol.[14] Repeated washings with 1:1 hydrochloric acid will not remove any of the dye from the amyl alcohol although the dye is very soluble in hydrochloric acid. When, however, the acidity of this amyl alcohol solution is reduced to below 0.7 N by washing with dil. acid or with water, these dyes return to the aqueous layer. In this and many similar cases dyes show no distribution between two solvents. Under certain conditions the dye

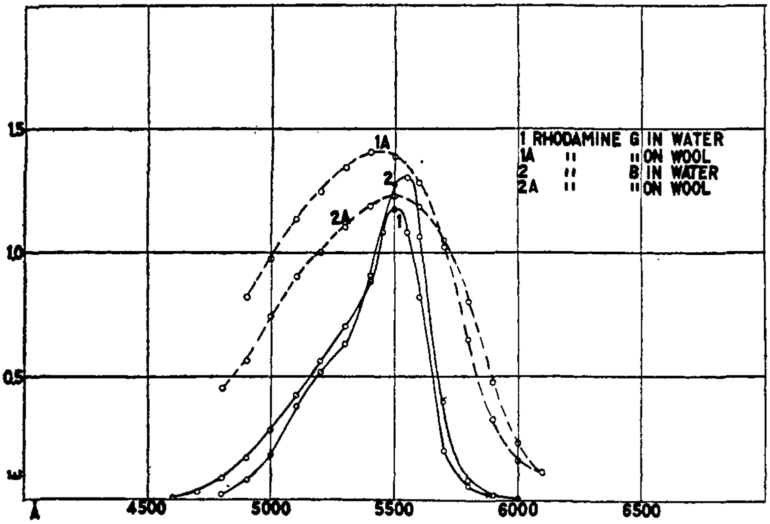

Fig. 8

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[12] Witt, *Färbenztg.*, **1890-1891**, 1.

[13] Von Georgievics, *Mitt. Tech. Gew. Museum Wien*, **4**, 205, 349; *Z. angew. Chem.*, **16**, 574 (1902).

[14] *U. S. Dept. Agr., Bull.*, **448**, 12-13 (1917).

will go completely into one solvent and under slightly changed conditions into the other solvent.

This failure to obey the solution laws may be due to the fact that most dyes are on the border line between the crystalloid and colloid states. This may be shown by some experiments which were conducted on the solubility of pure Tartrazine in water. If Tartrazine and water were placed in a thermostat and solution effected at the desired temperature, good checks on the solubility could be obtained. On the other hand, if solution of an excess of this dye was accomplished at a higher temperature, and then placed in the thermostat, precipitation would not always take place. In fact, many times the solution would continue to dissolve a large additional amount of Tartrazine at this lower temperature until finally some sort of a change in state would take place and an enormous amount of precipitation would occur. An entirely different value for the solubility of Tartrazine in water was given by this method from that found by the method first described. Many unexpected effects, due to the addition of slight amounts of sodium chloride, were also noticed and will be discussed in a later paper.

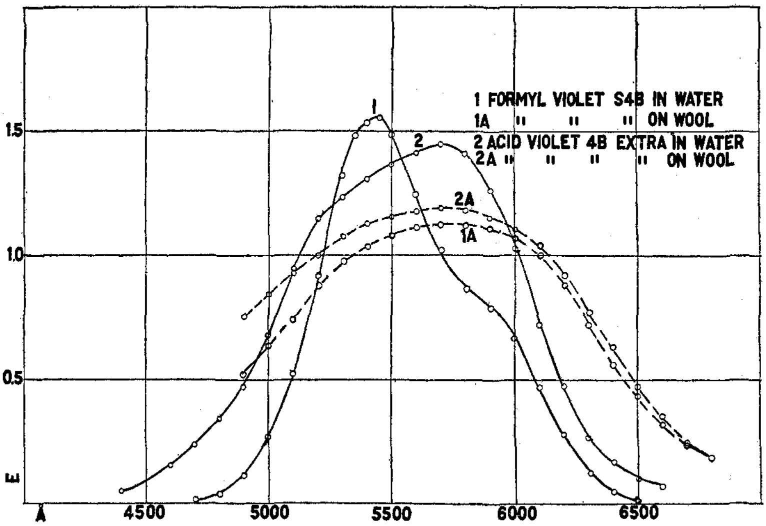

Fig. 9

The properties of the dye and the fiber are such that a large and probably varying amount of dye would be adsorbed on the fiber in addition to that dissolved by it. For this reason it is extremely doubtful whether it will ever be possible to demonstrate the mechanism of dyeing satisfactorily by the methods which have been used in the past. A practice which cannot be too severely condemned in work of this nature is that of dyeing from solutions containing salts, acids or other leveling agents or assistants which may cause secondary reactions on the fiber. Unfortunately, this point has been ignored by most investigators. A study of the literature yields a long record of tests made from solutions containing salt, Glauber's salt, sulfuric acid, soap, etc., and on samples which have been treated with various mordants.[15] Attempts have been made to draw conclusions from the results thus obtained before the process of dyeing from solutions containing only the pure dye has been fully studied. It would seem to be more scientific to investigate first the simple case where dye, fiber and solvent are the only factors concerned. After this has been done, the study of the effect of salt, etc., would follow.

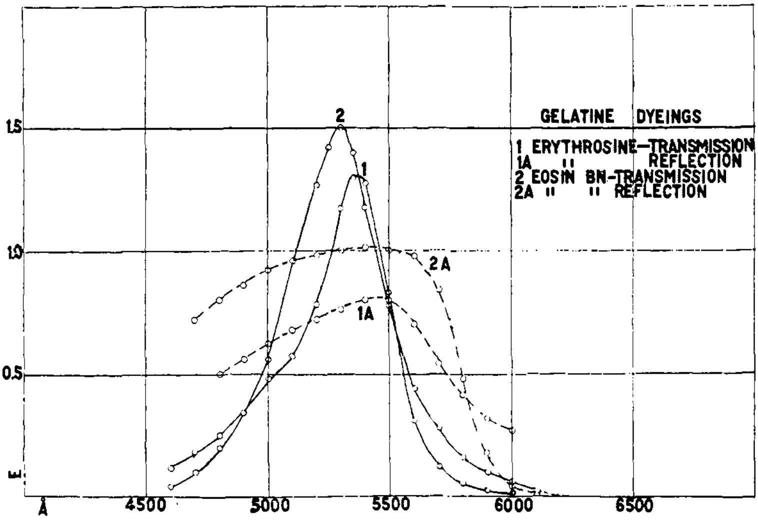

Fig. 10

The colloidal adsorption of dyes by the fiber has been successfully demonstrated by Bancroft[16] and others, but most of the work shows that this cannot be the whole of the dyeing process. Some samples of paper pulp[17] were dyed with Pontamine Sky Blue 3BX with the following results.

Table II

Distribution of Dye

Total volume of solution, 130 cc. Unbleached poplar (soda process), 2.25 g. (bone-dry weight). Time of dyeing, 15 minutes. Temp., 20°.

Dye used G.	Dye in pulp G.	Dye unadsorbed G.	Approximate ratio of dye unadsorbed to dye on fiber
0.0150	0.0128	0.0022	1:6
.0300	.0224	.0076	2:6
.0450	.0291	.0159	3:6

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[15] Dreaper, "The Chemistry and Physics of Dyeing," J. and A. Churchill, London, **1906**.

[16] Bancroft, "Applied Colloid Chemistry," McGraw-Hill Book Co., **1921**.

[17] Pulp obtained through the courtesy of the District of Columbia Paper Mfg. Co.

These results cannot be explained until some method is found of separating the adsorbed and unabsorbed dye on the fiber.

The optical method indicates that there is an actual solution of the dye in the fiber. The next step in explaining the mechanism of dyeing must be to find some method which will separate the dissolved dye from that held on the fiber by adsorption.

Summary

A study of the absorption spectra of light reflected from dyed materials showed that the reflection spectra more nearly explained the variations in color between two dyes than the transmission spectra of the solutions.

Dyeings made on wool, paper and gelatin indicated that the dye was present as a solution in these materials.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY COLLEGE OF SCIENCE OF CALCUTTA]

THE TEMPERATURE OF EXPLOSION FOR ENDOTHERMIC SUBSTANCES. II. TRINITRO-META-CRESOLATES AND THEIR EXPLOSION TEMPERATURES

BY RASIK LAL DATTA, LOKNATH MISRA AND JOGENDRA CHANDRA BARDHAN

RECEIVED JULY 2, 1923

The temperature of explosion has already been studied in the case of a few typical organic compounds, namely, nitro-bodies, picrates, azo compounds, haloid compounds, organic perchlorates, alkaloids, etc.[1] All of these classes of substances are endothermic and hence give explosion temperatures. Previous to our investigations, the explosion temperatures of a very few substances which explode before melting or decomposing were known and for endothermic substances generally such a temperature was never before known to exist. Several of the endothermic substances were, because of their practical use as explosives, known to explode by means of detonators and some of these were shown by Berthellot[2] to explode when thrown into a vessel previously raised to a high temperature.

The object of these investigations is to show that endothermic substances in general give an explosion temperature, and how the temperature varies according to the endothermic properties and molecular grouping. The reason why such an important constant has previously escaped detection is that substances which either melt or decompose at temperatures below the explosion temperature could not at all attain that temperature in the ordinary course of heating. The temperature is known only for those substances which explode before they are decomposed or volatilized.

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[1] Datta and Chatterjee, *J. Chem. Soc.*, **115**, 1006 (1919). Previous communication on the subject.

[2] Berthellot, *Compt. rend.*, **105**, 1159 (1887); **129**, 926 (1899).