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## An Investigation of Known Blue, Red, and Black Dyes Used in the Coloration of Cotton Fibers

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**ABSTRACT:** Previous work on blue, red, and black cotton samples dyed with unknown dyes showed that, within a color class, the use of microspectrophotometry can give a significantly higher degree of discrimination than is possible using microscopy alone. The present study was undertaken (1) to assess the frequency of matching spectra being produced from dyes known to be different; (2) to show what extra level of discrimination, if any, is obtained when thin-layer chromatography (TLC) can be carried out on the extracted dyes; and (3) to examine the extent of intrasample spectral variation.

Spectra were recorded from 77 blue, 32 red, and 26 black cotton samples dyed with known examples of sulfur, leucosulfur, direct, reactive, and vat dyes. TLC was attempted on all spectrally matching samples. Spectral variations (shifts of peak maxima and peak reversals) were noted for each sample.

The occurrence of matching spectra from different dyes in each color class was very small (0.2% for blue dyes, 1.5% for red dyes, and 1.5% for black dyes). TLC was only effective in separating 5 out of 21 spectrally matching sample pairs. All color classes showed occasional examples of peak reversal, especially in pale blue and pale black samples. Shifts of absorption maxima were sometimes considerable. The casework implications of these results are discussed.

**KEYWORDS:** forensic science, fibers, dyes, spectroscopic analysis, microspectrophotometry, thin-layer chromatography, cotton fibers, absorption spectra

The range of dyes and dye mixtures that may be applied to cotton fibers is considerable. Some of the more common examples of the ranges used in Europe are:

Direct dyes—Suprexcel<sup>®</sup>, Paramine<sup>®</sup> (Holliday), Solophenyl<sup>®</sup>, and Cuprophenyl<sup>®</sup> (Ciba-Geigy).

Reactive—Procion<sup>®</sup> (ICI), Remazol<sup>®</sup> (Hoechst), Cibacron<sup>®</sup> E, and Cibacron F (CIBA-Geigy).

Sulfur—Sulphol<sup>®</sup>, Sulphol Liquid, and Sulphosol<sup>®</sup> (J. Robinson).

Vat—Indanthren<sup>®</sup> (BASF, Hoechst and Bayer) and Indigo (BASF and ICI).

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Each class contains many dyes which normally cover a wide color range. The individual dyes can be a single color component or a mixture of two or more color components of the same class. Brown and black dyes, for example, are often mixtures of red, yellow, and blue [1]. Dyes in the various classes will be produced by different manufacturers and may be chemically identical products. Most single components are listed alphabetically in the *Colour Index Volume 5* [2] according to usage class, generic name, *Colour Index* number, commercial name, and manufacturer, for example:

Direct Dyes—Direct Blue 86, CI 74180. Solophenyl Turquoise Blue GL; CIBA Geigy.

Chemically identical dyes have the same *Colour Index* number. The *Colour Index* lists 86 alternative dyes produced by other manufacturers (not necessarily current) which also have the *Colour Index* (CI) Number 74180. There is no CI number for dye mixtures.

It is not always correct to assume that because the products of different manufacturers are listed in the *Colour Index* under the same generic name or CI number or both that they are identical in chemical structure. Differences caused by manufacturing processes, for example, may be related to the number or position of halogen atoms [3]. In addition to the colorant, cutting agents, dyeing assistants, and dispersing agents may be present. These may vary in nature and amount and may not be evenly distributed within drums of dye [4].

The number of manufacturers of a dye with a particular generic name is an indication of its popularity and the quantities in demand. Since dye spectra are not identifiable, this does not help the forensic scientist with any attempts at frequency estimates. The actual number of dyes in each usage class is considerably smaller than suggested by the *Colour Index* as some dyes have more than one generic name, representing alternative uses, while other examples of generic names are no longer manufactured [4]. The mixtures of different ingredients in dyes in addition to the colorant often influence important dye properties such as solubility and dyeing behavior [3]. It is not possible to estimate the frequency of dye usage. Dyeing is fashion dependent, and the choice of dyestuff will also depend on the degree of fastness required.

### Why Spectra Cannot Be Used To Identify Dyes

Different spectral curves may be produced from the same dye by the use of different additives, pH changes caused by the addition of salt to the dye bath, or dye solvent interaction [3]. Peak reversal in spectra from the same dye may be caused by agglomeration of the dye molecules causing alteration of Van der Waals forces and affecting the absorption of light. The result will be a shift in the position of maximum absorption. Dyers in different countries can produce different colors from the same dye; and a dyer in a particular dyehouse can produce color variation by accentuating the effect of, for example, the red or blue component of a dye mixture by using a change of pH.

The absorption curve of a mixture of dyes is normally expected to be the sum of the absorption curves of the individual dyes assuming each dye in the mixture acts independently. In some cases, however, interaction may produce a totally unpredictable mixture curve [5]. Absorption/transmission curves only allow determination of color. Superimposable curves are only produced from identical dyestuffs which also agree in shade (hue) and depth and which are used under the same conditions. An identification of the separate dyes used to produce this color is not possible by this method.<sup>3</sup>

Spectra cannot be used to identify dyes in the absence of information on the dye class and the number of dye components. The choice of solvent required to extract the dye will give information on the former and the number of components can be investigated

<sup>3</sup>BASF, Ludwigshafen, West Germany, personal communication, 1986.

by thin-layer chromatography (TLC), which supports the use of this technique as a complimentary step to microspectrophotometry. This is particularly well illustrated in the recent paper by Wiggins and Cook [6].

Dye manufacturers can identify their own products and possibly those of rival companies by using TLC, but it usually requires about a centimetre square of material plus a lot of experience. Interpretation of spectra in relation to the dye used is almost always impossible because of the difficulty of establishing whether or not a mixture is present. It is not easy to identify the individual components of a mixture from a reflectance curve especially for fashion shades like browns and grays. Dyes with widely different dyeing characteristics and chemical structure may have very similar reflectance curves. Dyeings with different dye combinations can also have very similar reflectance curves. For example, a mixture of Solophenyl Gray NGL and Solophenyl Red GBL with three different Solophenyl Yellow dyes allow three brown dyeings which all have indistinguishable reflectance curves.<sup>4</sup> In addition, as already stated, the same dyes will give different curves under different dyeing conditions, and different dyes or mixtures can give very similar spectra.

Spectra with only one peak may or may not be a mixture, but spectra with two distinct peaks are not necessarily from a mixture of dyes, although this feature appears to be infrequent in single dyes (blue—six examples; red—three examples). The curve from the red dye Cibanon Red 6B is shown in Fig. 1. Variation in the ratio of the two main peaks is apparent.

The spectra from mixtures do not always reflect the spectra from individual dyes, and the small shoulders caused by dye mixing are more readily apparent from reflectance spectra, but much more material is required than is generally available for forensic science purposes.

Variation within a control fiber sample (Fig. 2) may occur for a variety of reasons: uneven dye uptake (caused by fiber structure or dye molecule variation), the presence of dye precursor residue which is reactive and which will color the fiber, faulty dye bath

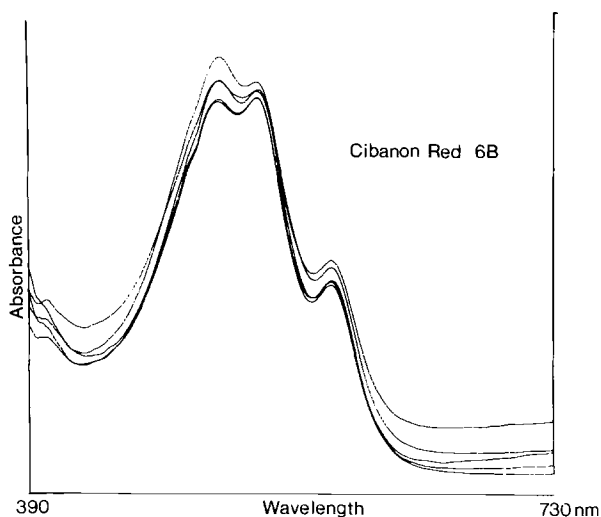


FIG. 1—A red dye, Cibanon Red 6B, where the absorption spectrum shows three distinct peaks. Note the variation in ratio of the two main peak heights.

<sup>4</sup>Ciba-Geigy, Basel, Switzerland, personal communication, 1985.

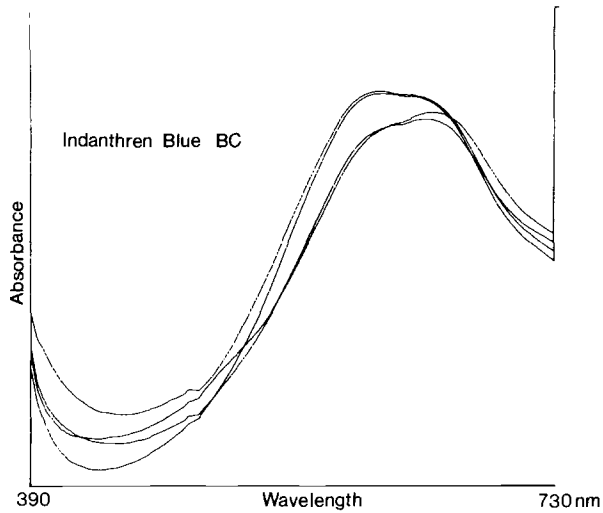


FIG. 2—Variation in the spectra recorded from cotton fibers taken from one sample of cloth dyed with Indanthren Blue BC showing peak reversal and shifting of absorption maxima.

cleaning, dye bath topping up or changing the dye bath conditions (temperature, pH, salt added, and so forth), or the presence of “dead” fibers in a bale.

### Materials and Methods

Cotton dye shade cards were provided by BASF (Germany), CIBA-Geigy (Switzerland), and from Holliday Dyes and Chemicals and James Robinson & Co. Ltd. in the United Kingdom. Samples from all red, blue, and black cottons contained therein were made into microscope slide preparations by teasing out fibers into XAM Neutral Improved White<sup>®</sup> mountant supplied by Searle Diagnostic.

Ten replicate absorption spectra were recorded from each sample taking care to include the full range of concentration and color variations. The instrument used was a Nanospec 10S microspectrophotometer fitted to a Leitz Ortholux microscope. Spectra were recorded over the range 390 to 730 nm at a 200-nm/min scanning rate. The slit aperture used was 5 by 40  $\mu\text{m}$ . Care was taken to avoid positioning the slit over twists and irregularities. Absorbance values recorded at 10-nm intervals were transferred by an analog-to-digital converter (Anaspec Data Systems) to a Commodore PET microcomputer for computation of Complementary Chromaticity Coordinates (CCC values) as described by Laing et al. [7]. Lists of the dyes examined are presented in Tables 1 to 3. Complementary Chromaticity Coordinates for all dyes examined are presented in Table 4.

Note that fibers from different sources may be of the same color in numerical terms using the complementary system, although they may not match visually (because of concentration differences) or spectrally (because of differences in the dye or in dyeing conditions). This has the disadvantage that, when using a data bank, the number of “hits” associated with particular CCC values may exceed those that are true matches both visually and spectrally.)

Within each color, all ten spectra from each individual dye sample were visually compared with those from all other samples. In any instance in which a spectrum in one sample matched a spectrum in another sample this was recorded as a positive pairing.

TABLE 1—Blue cotton dye samples.<sup>a</sup>

Dye	Commercial Name	Generic Name	CI Number	
1	Indanthren	Navy Blue TRR	Vat Blue 22	59820
2		Dark Blue BOA	Vat Blue 20	59800
3		Navy Blue BF	Vat Blue 19	59805
4		Dark Blue DB	not listed	...
5		Navy Blue G	Vat Blue 16	71200
6		Brilliant Blue RCL	Vat Blue 6:1	...
7		Blue RS	Vat Blue 4	69800
8		Blue GC	Vat Blue 14	69810
9		Blue BC	Vat Blue 6	69825
10		Blue CLF	Vat Blue 66	...
11		Blue 3G-N	Vat Blue 12:1	69840
12		Blue CLB	Vat Blue 30	67110
13	Cyanine B		Pigment Blue 15	74160
14	Basilen-E	Blue E-R	Reactive Blue 39	...
15		Blue E-RN	Reactive Blue	...
16		Blue E-3G	Reactive Blue 2	...
17	Basilen M	Blue M-R	not listed	...
18		Blue M-4GD	not listed	...
19		Navy Blue M-D	not listed	...
20	Suprexcel	Blue 2RL	Direct Blue 67	...
21	Paramine	Sky Blue FF	Direct Blue 1	24410
24	Suprexcel	Blue 2FL	Direct Blue 71	...
26		Brilliant Blue BL	not listed	...
27		Blue 4GL	Direct Blue 78	34200
28		Blue 7GL	Direct Blue 76	...
29		Blue RL	Direct Blue 74	34146
30	Cibanon	Blue RS	Vat Blue 4	69800
31		Blue GF	Vat Blue 6	69825
32		Marine Blue DB	not listed	...
33		Dark Blue MBN	Vat Blue 19	59805
34		Dark Blue BOA	Vat Blue 20	59800
35		Marine Blue RA	not listed	...
36	Sulphol	Green B	Sulfur Blue 15	53540
37		Brilliant Blue 6BS	Sulfur Blue 13	53450
38		Direct Blue JRL	Sulfur Blue 4	53235
39	Sulphol	Dark Blue L	Sulfur Blue 5	53235
40		Blue D	not listed	...
41		Navy Blue VS	Sulfur Blue 1	53235
42	Indone B	...	Sulfur Blue 7	53440
43	Sulphol	Direct Blue RLS	Sulfur Blue 11	53235
44	Sulphol Liq.	Blue QB	Leucosulfur Blue 13	53450
45		Navy QGE	Leucosulfur Blue 19	...
46		Navy QLG	not listed	...
47		Dark Blue QL	Leucosulfur Blue 5	53235
48		Navy Blue QR	Leucosulfur Blue 4	53235
50	Sulphosol	Fast Blue SBN	not listed	...
51		Dark Blue SL	Sol. Sulfur Blue 5	53236
52		Navy Blue SR	Sol. Sulfur Blue 4	53236
53	Cibacron-E	Blue 7GR-E	not listed	...
54		Blue TR-E	Reactive Blue 52	...
55		Brilliant Blue G-E	not listed	...
56		Turquoise Blue 2G-E	Reactive Blue 41	...
57		Turquoise Blue 3G-E	not listed	...
58		Navy Blue R-E	Reactive Blue 40	...
59		Navy Blue GR-E	not listed	...
60		Navy Blue 2G-E	not listed	...
61	Solophenyl	Navy Blue RL	not listed	...
62		Navy Blue BL	not listed	...
63		Blue 3RL	Direct Blue 67	27925
64		Blue 2RL	Direct Blue 80	24315

TABLE 1—Continued.

Dye	Commercial Name	Generic Name	CI Number
65	Blue GL	Direct Blue 71	34140
66	Blue FGL	Direct Blue 85	...
67	Blue AGFL	Direct Blue 212	...
68	Blue 2BL	Direct Blue 207	...
69	Brilliant Blue BL	Direct Blue 106	51300
70	Blue 4GL	Direct Blue 78	34200
71	Blue 7GL	Direct Blue 218	24401
72	Turquoise Blue GRL	Direct Blue 189	...
73	Turquoise Blue BRL	Direct Blue 199	...
74	Turquoise Blue GLC	not listed	...
75	Cuprophenyl Brilliant Blue 2BL	Direct Blue 158:1	...
76	Blue 3GL	Direct Blue 211	...
77	Navy Blue RL	Direct Blue 156	...
78	Cibacron F Blue F-GF	not listed	...
79	Blue FR	Reactive Blue 182	...
80	Marine F-2R	not listed	...
81	Marine F-G	not listed	...

\*Origin: Samples 1-19, BASF, Germany.

Samples 20-25, Holliday Dyes & Chemicals, United Kingdom.

Samples 30-35, CIBA-Geigy, Switzerland.

53-81,

Samples 36-52, James Robinson & Co. Ltd., United Kingdom.

Samples 22, 23, 25, and 49 were not used as they were too pale.

The fiber samples constituting these pairs were then compared under a Leitz Ortholux comparison microscope to confirm that they were, as expected, visual matches (that is, that any of the fibers in one sample matched any of the fibers in the opposing sample).

Attempts were then made to extract the dye from these sample pairs to see whether they could be differentiated by thin-layer chromatography. Solvents were chosen after consulting the paper produced by Home and Dudley [8] and the suggestions from Venkataraman [9]. For reactive dyes, 1.5% sodium hydroxide at 100°C was used with an extraction time of 3 to 4 min. Longer immersion was found to cause bleaching. Dimethylformamide at 130°C was found to give the best results—although often only partial extraction—with sulphur and leucosulphur dyes. In some cases, 25% pyridine was tried as an alternative at 100°C for 15 min. Despite attempts with both these reagents, extraction of vat dyes remained totally unsuccessful. To obtain as concentrated a dye extract as possible, a piece of thread 1 cm long was placed in a 2.5-cm length of Kimax 51 capillary tubing and sealed after just covering the fibers with the appropriate extractant.

In cases in which the extraction under the conditions described was successful, the dye was spotted onto a Merck 5- by 7.5-cm aluminum TLC plate precoated with silica gel 60 F254 using a double-drawn volumetric pipette (Corning Glass Works, New York). A Camag twin trough tank 25155 which allows equilibration of the plate with the eluent vapor before development<sup>5</sup> was used and the following eluent systems [8] were used as those likely to give the best results:

- A. Butanol:ethyl alcohol:25% ammonia:pyridine:water—8:3:4:4:3.
- B. Chloroform:water:methanol:25% ammonia—11:1:7:1
- C. *n*-Propanol:methanol:water:25% ammonia—8:6:2:1.

<sup>5</sup>D. K. Laing and L. Boughy, personal communication, 1981.

TABLE 2—Red cotton dye samples.<sup>a</sup>

Dye	Commercial Name	Generic Name	CI Number	
1	Paramine	Fast Scarlet 4BS	Direct Red 23	29160
2	Suprexcel	Red 8 BL	Direct Red 81	28160
3		Red BR 150%	not listed	...
4		Scarlet BNLL 200%	Direct Red 89	...
5		Scarlet 2GL	Direct	...
6	Sulphol	Liquid Red QRB	Leucosulfur Red 14	...
7	Indanthren	Brilliant Red LGC	Vat	...
8		Red GG	Vat Red 23	71130
9		Red FBB	Vat Red 10	67000
10		Rubine GR	Vat Red 27	61670
11	Basilen-M	Red M-5B	reactive	...
12	Basilen-E	Scarlet E-2G	Reactive Red 43	...
13		Red E-B	Reactive Red 120	...
14		Red E-7B	reactive	...
15	Cibanon	Red 2B	Vat Red 10	67000
16		Red 6B	Vat Red 13	70320
17	Cibacron-E	Scarlet 2G-E	Reactive Red 43	...
18		Brilliant Red 4G-E	Reactive Red 120	...
19		Brilliant Red G-E	reactive	...
20		Rubine TBR-E	Reactive Red 55	...
21	Solophenyl	Scarlet BNL 200	Direct Red 89	...
22		Red 3BL	Direct Red 80	35780
23		Red 6BL	Direct Red 79	29065
24		Bordeaux A2BL 160	Direct Red 92	...
25		Rubine RNL 150	Direct Red 107	...
26		Violet A2R1 220	Direct Red 83	...
27	Cuprophenyl	Red FGL	Direct Red 221	...
28		Red BL	Direct Red 173	29290
29		Rubine RL	Direct Red 233	...
30		Violet 3RL	Direct Violet 93	...
31	Cibacron F	Scarlet F-3G	Reactive Red 183	...
32		Red F-B	Reactive Red 184	...

<sup>a</sup>Origin: Samples 1-5, Holliday Dyes & Chemicals, United Kingdom.  
Sample 6, James Robinson & Co. Ltd., United Kingdom.  
Samples 7-14, BASF, Germany.  
Samples 15-32, Ciba-Geigy, Switzerland.

The first two systems, A and B, were used for sulfur and leucosulfur dyes, the third one for reactive dyes. System C was chosen in preference to methanol:amyl alcohol:water—5:5:2, also suggested by Home and Dudley for reactive dyes, as it gave better results on initial trials. All results are presented in the following section.

Finally, the ten replicate spectra from each of the standard dye samples were examined. The incidence of peak reversal and of wavelength shifts for peak maxima were recorded to provide information on spectral variability within control samples.

## Results and Discussion

### Blue Dyes

The 77 samples (see Table 1) were made up of 25 direct, 18 reactive, 18 vat, 15 sulphur, and 1 pigment dyes. From these, 7 pairs, all of which were sulfur or leucosulfur dyes, were found to have matching spectra. Details are given in Table 5. In all cases, the fibers

TABLE 3—Black cotton dye samples.\*

Dye	Commercial Name	Generic Name	CI Number	
1	Suprexcel	Black L 135%	Direct Black 51	27720
2	Paramine	Black GF 200%	Direct Black 22	23850
3		Black E 230%	not listed	...
4	Viscose	Black NG 200%	not listed	...
5	Sulphosol	Black SG	Sol. Sulfur Black 1	53186
6	Sulphol	Black BS 5%	Sulfur Black 1	53185
7		Liquid Black QG	Leucosulfur Black 1	53185
8		Liquid Black QR	Leucosulfur Black 2	53195
9		Liquid Black QLC	not listed	...
10	Indanthren	Grey GG	Vat Black 20	...
11		Grey CL	Vat Black 31	...
12		Direct Black RBS	Vat Black 9	65230
13		Direct Black RB	Vat Black 9	65230
14		Direct Black R	not listed	...
15		Direct Black BB	not listed	...
19	Cibanon	Black DRB	Vat Black 9	65230
20		Black R	not listed	...
21		Black 2Ba	Vat Black 7	59850
22	Cibacron E	Grey G-E	Reactive Black 13	...
23	Solophenyl	Grey RL 280%	not listed	...
24		Grey NGL 250%	Direct Black 113	...
25		Grey 4GL	Direct Black 62	...
26	Cuprophenyl	Grey 2BL	Direct Black 97	35870
27		Grey GRL	Direct Black 112	36250
28		Black GWL	not listed	...
29		Black RI	not listed	...

\*Origin: Samples 1–4, Holliday Dyes & Chemicals, United Kingdom.  
 Samples 5–9, James Robinson & Co. Ltd., United Kingdom.  
 Samples 10–15, BASF, Germany.  
 Samples 19–29, CIBA-Geigy, Switzerland.  
 Samples 16 to 18 were too pale to be used.

in these pairs matched visually. Only one pair, Samples 48 and 52, could be differentiated by TLC by running them in eluent System A. These dyes have different CI numbers. No separation was obtained using System B. None of the dyes with the CI number 53235 could be separated in either system, as presumably their chemical composition is the same.

The list of blue dyes showed that 10 pairs of blue dyes (3 direct, 3 sulfur, and 4 vat) representing alternative dye ranges produced by different manufacturers have the same generic name and CI number. A further 15 pairs share the same CI number but have different generic names. All of these are sulfur dyes. Despite this, only two pairs, 38 and 48 and 38 and 43, produced spectral matches.

#### Sample Discrimination

The following conclusions were made for blue dyes.

Only a very low percentage (7 pairs from a total of 2926 possible pairings) showed the same absorption spectrum. All instances were sulfur or leucosulfur dyes, and it therefore seems that this is most likely to occur within these classes. Dyes with a different CI number may have the same spectrum although presumably because they differ slightly in chemical composition they can be separated by TLC (for example, Samples 48 and 52).



Pairs of dyes with the same CI number and generic name made by different manufacturers generally show different absorption spectra (23 from 25 pairs).

Dyes with the same CI number, for example, Samples 38 and 48 and 38 and 43 may however produce matching spectra, although this appears to be unusual (2 from 25 pairs). Many sulfur blue dyes have the same CI number; 14 pairs of those examined by us had the CI number 53235.

*Red Dyes*—From 32 samples examined (14 direct, 6 vat, 11 reactive, and 1 leucosulfur) which gave 496 possible pairings, 8 pairs were spectral matches. All these pairs were visual matches. As shown in Table 6, 7 pairs were reactive dyes and 1 pair was vat dyes. The dye could not be extracted from the latter pair (Samples 9 and 15). In four of the remaining pairs (Samples 17 and 31, 19 and 32, 14 and 32, and 11 and 18), the dyes were separable by TLC. The dyes in each pair were from different ranges, that is, they were chemically different and probably have different generic names and CI numbers although this could only be confirmed in the case of Samples 17 and 31. Eluent C was used. Those pairs that were nonseparable had the same generic names and CI numbers although they were the products of different manufacturers.

The following conclusions were made in respect of the red dyes. There is more chance of red dyes having the same spectrum than blue dyes. This is in line with our earlier findings [1]. The chances of red dye separation by TLC appear to be greater than for blue dyes as only four pairs had the same generic name and CI number. All of these pairs were visual matches and the spectra only differed in one case (Samples 4 and 21). Red cotton dyes are less likely to be sulfur or leucosulfur dyes than their blue counterparts.

*Black Dyes*—The 26 samples were made up of 10 direct, 5 sulfur, 9 vat, 1 reactive, and 1 unlisted dye, giving a total of 325 possible pairings. Six pairs had matching spectra (Table 7). These pairs were also visual matches. Attempts at separation were very unsuccessful. The two vat dyes (Samples 12 and 13) could not be extracted and Samples 5 to 8 would only extract partially and would not run in any of the eluent systems without severe streaking. It is probable that since pairs 6 and 7 and 12 and 13 have the same generic name and CI number that they would be inseparable anyway. Our conclusions were that spectral discrimination was not as good as with the blue or red dyes (again in line with the findings in Ref 1), and that separation of black dyes by TLC may be difficult.

### *Spectral Variation*

Only one blue dye (Sample 9) showed an example of peak reversal (Fig. 2). Eight examples (10%) exhibited shifts of position of maximum absorption greater than 17 nm (1 cm on the chart) in their ten replicate spectra. These were made up of three vat, three sulphur, one leucosulphur, and one direct dye. The least variance was noted in the spectra from the reactive dyes.

In the red dyes three examples of peak reversal were noted (Samples 16, 19, and 21). In two cases, shifts of peak maxima greater than 17 nm were noted. Both were in direct dyes in which the greatest degree of spectral variation was apparent. As with the blue samples, the reactive dyes were the least variable.

The black dyes showed the greatest number of peak maxima shifts greater than 17 nm—6 out of the 26 samples. The shifts were the largest noted in any of the dyes. There were 3 instances of peak reversal among the black dyes. There was only 1 reactive dye but again the spectra from that were very constant. The spectra from the vat, sulfur, and direct dyes all showed variation, with it being greatest in the latter. Some examples of spectral variation are shown in Figs. 3 and 4. To understand the causes of these variations it is necessary to appreciate that color has three independent variables, namely, hue, chroma, and brightness [10, 11]. The hue refers to the position of the color in the spectrum, that is, where the peak maxima occur. The values  $x'$  and  $y'$  measure "chromaticness"—

TABLE 4—Complementary Chromaticity Coordinate values for all dye samples.

Dye	$x'$	$y'$	Dye	$x'$	$y'$	Dye	$x'$	$y'$	Dye	$x'$	$y'$
1	0.394	0.417	21	0.418	0.380	41	0.364	0.376	61	0.369	0.393
2	0.372	0.408	22	not recorded	not recorded	42	0.383	0.410	62	0.390	0.388
3	0.386	0.408	23	not recorded	not recorded	43	0.367	0.398	63	0.379	0.414
4	0.394	0.389	24	0.411	0.398	44	0.429	0.392	64	0.403	0.410
5	0.385	0.386	25	not recorded	not recorded	45	0.393	0.403	65	0.400	0.400
6	0.438	0.415	26	0.432	0.373	46	0.398	0.412	66	0.388	0.388
7	0.438	0.406	27	0.424	0.384	47	0.385	0.410	67	0.417	0.402
8	0.459	0.402	28	0.390	0.346	48	0.368	0.408	68	0.409	0.395
9	0.456	0.410	29	0.393	0.389	49	not recorded	not recorded	69	0.438	0.414
10	0.431	0.407	30	0.436	0.420	50	0.388	0.408	70	0.423	0.400
11	0.427	0.392	31	0.456	0.421	51	0.374	0.393	71	0.415	0.368
12	0.414	0.384	32	0.376	0.400	52	0.363	0.404	72	0.540	0.370
13	0.397	0.377	33	0.370	0.429	53	0.432	0.407	73	0.532	0.380
14	0.404	0.399	34	0.351	0.409	54	0.435	0.401	74	0.498	0.369
15	0.431	0.408	35	0.390	0.429	55	0.507	0.415	75	0.423	0.420
16	0.398	0.348	36	0.428	0.392	56	0.514	0.359	76	0.393	0.363
17	0.427	0.385	37	0.407	0.388	57	0.531	0.353	77	0.375	0.393
18	0.410	0.363	38	0.368	0.403	58	0.378	0.406	78	0.477	0.415
19	0.421	0.388	39	0.370	0.384	59	0.399	0.377	79	0.440	0.405
20	0.419	0.386	40	0.367	0.384	60	0.424	0.375	80	0.393	0.410
									81	0.388	0.385

		BLACK DYES										RED DYES									
1	0.358	0.364	11	0.342	0.340	21	0.337	0.330													
2	0.322	0.327	12	0.340	0.334	22	0.340	0.341													
3	0.324	0.318	13	0.332	0.337	23	0.329	0.338													
4	0.325	0.316	14	0.331	0.327	24	0.327	0.325													
5	0.320	0.331	15	0.347	0.329	25	0.324	0.313													
6	0.319	0.322	16	not recorded	not recorded	26	0.360	0.358													
7	0.323	0.329	17	not recorded	not recorded	27	0.328	0.334													
8	0.322	0.330	18	not recorded	not recorded	28	0.317	0.326													
9	0.336	0.364	19	0.334	0.338	29	0.327	0.348													
10	0.344	0.323	20	0.323	0.340																
1	0.189	0.333	11	0.232	0.481	21	0.199	0.322													
2	0.239	0.394	12	0.188	0.338	22	0.228	0.382													
3	0.250	0.403	13	0.231	0.472	23	0.244	0.342													
4	0.200	0.348	14	0.256	0.492	24	0.258	0.388													
5	0.209	0.271	15	0.215	0.373	25	0.262	0.408													
6	0.191	0.333	16	0.252	0.403	26	0.272	0.414													
7	0.200	0.304	17	0.181	0.347	27	0.208	0.319													
8	0.200	0.273	18	0.221	0.478	28	0.183	0.319													
9	0.222	0.386	19	0.263	0.472	29	0.262	0.391													
10	0.234	0.377	20	0.240	0.449	30	0.285	0.436													
											31	0.178	0.332								
											32	0.267	0.461								

TABLE 5—*Details of spectrally matching pairs of blue cotton dyes.*

	Commercial Name	Class	Generic Name	CI Number
38	Sulphol Direct Blue JRL	sulfur	Sulfur Blue 4	53235
43	Sulphol Direct Blue RLS	sulfur	Sulfur Blue 11	53235
39	Sulphol Dark Blue L	sulfur	Sulfur Blue 5	53235
40	Sulphol Dark Blue D	sulfur	...	...
48	Sulphol Liquid Navy Blue QR	sulfur	Leucosulfur Blue 4	53235
52 <sup>a</sup>	Sulphosol Navy Blue SR	sulfur	Sol. Sulfur Blue 4	53236
42	Sulphol Indone RB	sulfur	Sulfur Blue 7	53440
46	Sulphol Navy QLG	sulfur	...	...
40	Sulphol Dark Blue D	sulfur	...	...
41	Sulphol Navy Blue VS	sulfur	Sulfur Blue 1	53235
38	Sulphol Direct Blue JRL	sulfur	Sulfur Blue 4	53235
48	Sulphol Liquid Navy Blue QR	sulfur	Leucosulfur Blue 4	43235
38	Sulphol Direct Blue JRL	sulfur	Sulfur Blue 4	53235
52	Sulphosol Navy Blue 5R	sulfur	Sol. Sulfur Blue 4	53236

<sup>a</sup>Separable by thin-layer chromatography.

TABLE 6—*Details of spectrally matching pairs of red cotton dyes.*

	Commercial Name	Class	Generic Name	CI Number
9	Indanthren Red FBB	vat	Vat Red 10	67000
15	Cibanon Red 2B	vat	Vat Red 10	67000
11	Basilen Red M-5B	reactive	...	...
18 <sup>a</sup>	Cibacron Brill. Red 4G-E	reactive	Reactive Red 120	...
12	Basilen E Scarlet E-2G	reactive	Reactive Red 43	...
17	Cibacron E Scarlet 2G-E	reactive	Reactive Red 43	...
13	Basilen E Red E-B	reactive	Reactive Red 120	...
18	Cibacron Brill. Red 4G-E	reactive	Reactive Red 120	...
19	Cibacron E Brill. Red G-E	reactive	...	...
14	Basilen E Red E-B	reactive	...	...
14	Basilen E Red E-B	reactive	...	...
32 <sup>a</sup>	Cibacron F Red F-B	reactive	Reactive Red 184	...
17	Cibacron E Scarlet 2G-E	reactive	Reactive Red 43	...
31 <sup>a</sup>	Cibacron F Scarlet F-3G	reactive	Reactive Red 183	...
19	Cibacron E Brill. Red G-E	reactive	...	...
32 <sup>a</sup>	Cibacron F Red F-B	reactive	Reactive Red 184	...

<sup>a</sup>Separable by thin-layer chromatography.

a combination of hue and chroma. Chroma represents the depth of dyeing or "saturation," that is, differences in the amount of dye(s) on a single fiber. A saturated red means red light that is not diluted with light of any other color. The greater the degree of saturation, the sharper the spectral peak will be. If the color is less pure the curve will be flattened.

If two dyeings have the same hue and the same depth they will not necessarily match, for the third variable, the brightness or "lightness" may vary between light gray and dark gray (complementary color measurement). The higher the brightness, the more clear and "alive" the color will become. A value of  $Y = 1.000$  would represent a very dark color in complementary work; higher "full scale" values will coincide with higher  $Y$  values.

In the curves from the black cotton dye, Paramine Black GF, shown in Fig. 3, Fiber "a" had a bluish hue reflected by its peak maximum at 650 nm. It was the lightest fiber with the lowest full scale and brightness value ( $Y$ ) of the three fibers (see Table 8). The

TABLE 7—Details of spectrally matching pairs of black cotton dyes.

Dye	Commercial Name	Class	Generic Name	CI Number
12	Indanthren Dir. Black RBS	vat	Vat Black 9	65230
13	Indanthren Dir. Black RB	vat	Vat Black 9	65230
8	Sulphol Liq. Black QR	l-sulfur	Leucosulfur Black 2	53195
6	Sulphol Black BS 5%	sulfur	Sulfur Black 1	53185
8	Sulphol Liq. Black QR	l-sulfur	Leucosulfur Black 2	53195
5	Sulphosol Black SG	sulfur	Sol. Sulfur Black 1	53186
7	Sulphol Liq. Black QG	sulfur	Leucosulfur Black 1	53185
6	Sulphol Black BS 5%	sulfur	Sulfur Black 1	53185
7	Sulphol Liq. Black QG	sulfur	Leucosulfur Black 1	53185
5	Sulphosol Black SG	sulfur	Sol. Sulfur Black 1	53186
5	Sulphosol Black SG	sulfur	Sol. Sulfur Black 1	53186
6	Sulphol Black BS 5%	sulfur	Sulfur Black 1	53185

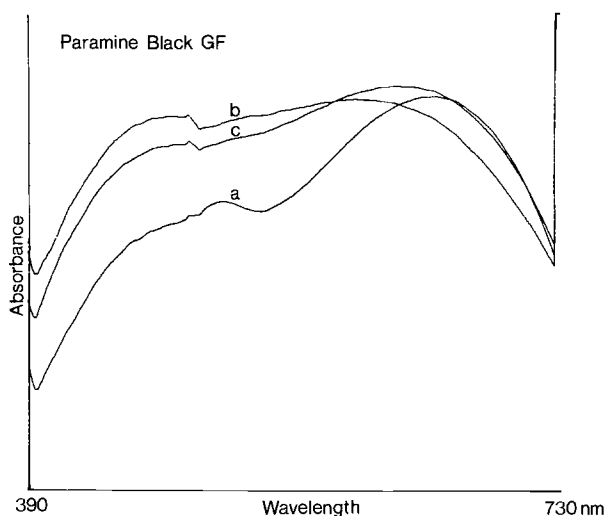


FIG. 3—Variation in the spectra from cotton fibers taken from one sample of cloth dyed with Paramine Black GF. The explanation of the symbols is given in the text.

hue of Fibers “b” and “c” were similar (close  $x'$  and  $y'$  values), but “b,” having a flatter curve, is a less saturated dyeing than “c.” Fiber “b” appeared to be a darker gray than Fiber “c,” which is reflected by it having a higher  $Y$  value. In the curves shown from the red cotton dye Solophenyl Scarlet BNL, Fibers “a” and “b” show a difference in hue represented by a peak shift of 22 nm (Fig. 4). This illustrates a differential uptake of the dye since these spectra were recorded from different areas along the length of the same fiber. The curve from a second fiber, “c,” is flatter showing less saturation than at points “a” or “b.” The highest brightness value as expected relates to curve “a.”

### Casework Applications

This study has illustrated the following practical points.

1. The occurrence of matching spectra from different dyes in each color class was very small (0.2% for blue dyes and 1.5% each for red and black dyes).
2. The TLC results suggest that no general conclusion can be drawn because the extra

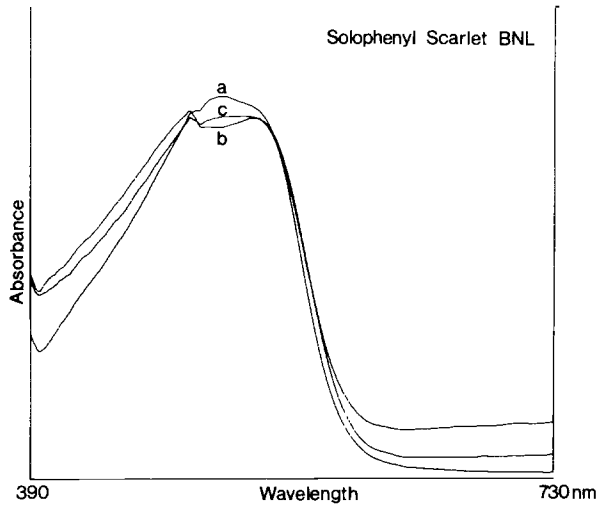


FIG. 4—Variation in the absorption spectra recorded from cotton fibers taken from one sample of cloth dyed with Solophenyl Scarlet BNL. The explanation of the symbols is given in the text.

TABLE 8—Details of variation in spectral curves within one dye sample.

Curve	$x'$	$y'$	$Y$	Full Scale
PARAMINE BLACK GF				
a	0.3475	0.3421	0.3818	58
b	0.3174	0.3263	0.4981	62
c	0.3284	0.3320	0.4702	60
SOLOPHENYL SCARLET BNL				
a	0.1970	0.3386	0.2717	54
b	0.2040	0.3209	0.2209	44
c	0.2161	0.3295	0.2362	46

level of discrimination possible using this technique varied among the color and dye classes examined. Black sulfur and vat dyes appear to be very difficult to differentiate by this method, whereas half of the spectrally matching red dyes, all of which were reactive, were found to be further separated by TLC. The technique is severely limited by the difficulty in extracting the dyes of certain classes from single fibers. Our results suggest that in instances in which TLC would be useful in separate spectral matches, the dyes involved may well be from a class that will pose extraction problems.

3. To avoid possible false exclusions when making spectral comparisons of cotton fibers, it is essential to record an adequate number of spectra (at least ten) including the full range of variation seen in the control or standard. It is common for considerable spectral variation to occur between fibers taken from one sample of cloth dyed with a known dye.

4. More accurate comparisons can be made if spectra from the control/standard sample are run on the same fibers matched in the visual comparisons with recovered fibers under the comparison microscope. The position of these fibers can be identified quickly and easily by using an "England Finder," a microscope slide marked with a reference grid (W. Plannet, GmbH, Marburg, West Germany).

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