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The Evaluation and Selection of Uncorrelated Paired Solvent Systems for Use in the Comparison of Textile Dyes by Thin-Layer Chromatography

ABSTRACT: This paper describes a systematic approach to the evaluation and selection of paired solvent systems for the comparison of dyes extracted from textile fibers by thin-layer chromatography (TLC). The use of two solvent systems, unless relatively uncorrelated, may offer little if any more information than a single solvent system. Ten paired solvent systems are evaluated mathematically (correlation coefficients) and graphically (R_f values of the major dye components). The ability of the individual solvent systems to separate minor colored dye components in "pure" commercial dyes (resolving power) is also considered. Fifty-six commercial acid and basic solid dye samples are used. In addition, acid and basic dyes extracted from 30 black nylon and acrylic fiber samples containing different lots of "identical" dye mixtures are separated. A comparison of the theoretical and actual discriminating power of the solvent systems is then presented. The method is general and may be applied in the selection of paired solvent systems for use in TLC of any usage class of textile dye.

KEYWORDS: criminalistics, dyes, chromatographic analysis

The analysis of textile fibers has become increasingly complex because of the development and general use of man-made fibers and dyes. The evidential value of this type of physical evidence has increased accordingly, as has the need to develop more sensitive and specific methods for the identification and comparison of textile fibers. Microscopic examination will continue to be the first step in fiber comparisons, and an experienced criminalist may save many hours of work through the process of elimination at this stage of the analysis. Fiber samples that exhibit similarities in gross and microscopic characteristics may then be generically identified through their optical properties [1-3] or by a variety of chemical and instrumental methods [4-8].

Although these methods are suitable for the generic identification and comparison of textile fibers, they offer little information as to the dye content of the fibers in question. Textile fibers that are generically alike may contain dyes, or a mixture of dyes, that are structurally similar and appear to be the same color in reflected and transmitted light. In addition, the dye content of most textile fibers is less than 1% of the total sample weight and is therefore not likely to be resolved by many instrumental methods employing whole fiber samples. Sample size may also be a limiting factor in the choice of analytical methods. Destructive

methods such as chemical solubilities and pyrolysis-gas chromatography would certainly be unsuitable for use on small fiber samples. Spectrophotometric methods have proven to be valuable tools in the comparison of extracted textile dyes, but they also have certain drawbacks. Absorbance methods are better suited for the analysis of relatively pure compounds, whereas most textile fibers contain a mixture of dyes, and small sample size may require the application of specialized equipment that is not commonly available to many forensic science laboratories.

There is little uniformity in the naming of textile dyes and most are listed by their commercial or brand name. The Society of Dyers and Colourists of Great Britain and the American Association of Textile Chemists and Colorists have, for the purpose of reference, classified textile dyes according to their usage class, color, and chemical index (CI) number [9]. This is the terminology that will be used in this study.

Commercial textile dyes are not homogeneous compounds, and rigid standards of purity are not commonly specified; for example, thin-layer chromatography (TLC) of Orange 1 (CI Acid Orange 20) yielded six colored bands in addition to the major dye component [10]. The presence of these minor colored bands in "pure" textile dyes is most likely due to the formation of structurally similar colored compounds during the manufacturing process and to the presence of small amounts of shading dyes added by the manufacturer to meet standard colors. It becomes obvious that the resolution of these minor colored components must be taken into consideration when a method of analysis is chosen for the comparison of extracted textile dyes.

Macrae et al [11] recently reported the results of a study comparing microscopical examination and microspectrophotometry of whole fiber samples as well as solution spectrophotometry and TLC of dyes extracted from wool fibers. Their results show TLC of the extracted dyes to be at least equal in discriminating power to the spectrographic methods and far superior to microscopic examination of whole fiber samples. Accordingly, TLC would seem to be the natural choice of method when colored compounds are involved in that it is somewhat quantitative as well as qualitative. Spotting questioned and known extracted dye samples on the same plate allows the criminalist to make a side-by-side comparison of the relative position, color, and intensity of the separated dyes.

Procedures for the extraction and separation of dyes from textile fibers by TLC that have been published by researchers in the textile industry [12-15] have only recently been adapted to the particular needs of the forensic science community [11,16,17]. These studies have given the criminalist some new and sensitive methods for the comparison of textile dyes in case work. Additional research is needed in evaluating the discriminating power of paired solvent systems commonly used in TLC in order to obtain the maximum amount of information from these methods. Smalldon [18] points out the necessity of using solvent systems for TLC that give a combination of random R_f frequency distributions within paired solvent systems and low correlation coefficients between solvent systems. While there can be no doubt that these criteria are important in gaining maximum information from separation techniques, the nature of textile dyes necessitates another consideration when paired solvent systems are developed and used—resolving power. Individual solvent systems should be evaluated for their ability to resolve any minor colored bands in addition to the major dye component in TLC of extracted dyes. The use of individual solvent systems that afford maximum resolution and of paired solvent systems that result in random R_f frequency distributions and low correlation coefficients should result in gaining the maximum amount of information (discriminating power) from the method.

The purpose of this study is to present a method for the evaluation and selection of uncorrelated paired solvent systems for use in the comparison of extracted dyes by TLC. The frequency of minor colored bands in pure textile dyes and the ability of individual solvent systems to resolve those bands (resolving power) are also considered. The approach selected for evaluating resolving power involves detailed observation of the separations obtained on a

series of commercial textile dyes with each of the five differnt solvent systems. In addition, series of generically identical dyes made by different manufacturers and of different lots of generically identical dyes made by the same manufacturer are also separated by TLC to determine if there is any detectable variance between these samples as a result of manufacturing conditions. Dyes extracted from black acrylic and nylon fibers, dyed with different lots of identical dye mixtures, are separated in each of the solvent systems. A comparison of the theoretical and actual discriminating power of the paired solvent systems is then presented graphically.

There are many solvent systems in the forensic science and commercial literature for TLC of acid and basic dyes. A number of solvent systems were initially evaluated, and those in which 32 out of 34 generically different solid dye samples migrated and could be assigned R_f values are used in this study.

It is not the purpose of this paper to offer a method for the identification of textile dyes because there are hundreds of dyes in use today and the rigorous identification of dye components is possible only in laboratories with considerable experience in dye analysis.[3] The method offered is a comparative one. A careful selection of relatively uncorrelated solvent systems for use in TLC of dyes extracted from textile fibers may produce very complex dye patterns, thus adding weight to determinations of similarity or dissimilarity.

Methods and Materials

E. Merck & Co. 10- by 20-cm silica gel 60 F-254 TLC plates were used. The extraction solvents were pyridine/water (57:43 v/v) and dimethylformamide/water (3:1 v/v). Five TLC development solvents were used:

 (I)   chloroform/methanol/acetic acid (70:20:10 v/v),
 (II) benzene/n-butanol/methanol/ammonium hydroxide (6M) (60:10:30:2 v/v),
 (III) chloroform/methanol/ammonium hydroxide/water (50:25:3:2 v/v),
 (IV) n-butanol/95% ethanol/water (40:20:20 v/v), and
 (V) n-butanol/95% ethanol/water/acetic acid (80:8:8:8 v/v).

The TLC developing tanks (Kontes) were 216 mm long, 102 mm wide, and 229 mm high (8½ by 4 by 9 in.). The capillary tubes (Kimble Products) were 1.6 to 1.8 by 100 mm, and the "Microcaps" (Drummond) had a volume of 10 μL (10 lambda).

Sample Distribution

Acid and basic solid dye samples were selected from available samples acquired from three manufacturers from 1977 through 1979 (Table 1). Black nylon and acrylic fibers, dyed with acid and basic dyes, respectively, were obtained from a commercial source[4] and are listed in Table 2.

Sample Preparation

A fiber sample is placed in the center of a capillary tube and the extraction solvent is drawn into the tube by capillary action to a height of approximately 40 mm. The average fiber sample is approximately 2.0 cm long and 0.2 cm in diameter. Both ends of the capillary tube are sealed with an alcohol lamp, and the tubes are placed in an oven at 100°C for ½ h. The

[3]Personal communication, E. I. du Pont de Nemours & Co., Dye Identification Laboratory, Deepwater, N.J.
[4]Burlington Socks/Adler, Division of Burlington Industries, Asheboro, N.C.

TABLE 1—*A tabulation of solid acid and basic dye samples
used in determining correlation coefficients, R_f frequency distributions,
and resolving power for selected solvent systems.*

Sample	Commerical Name	Chemical Index Name	
1	Intracid Pure Blue L[a]	Acid Blue	9
2	Merpacyl Blue SW[b]	Acid Blue	25
3	Merpacyl Blue 2GA[b]	Acid Blue	40
4	Amacid Milling Blue 5R[c]	Acid Blue	113
5	Amasol Blue 2G 200%[c]	Acid Blue	158
6	Intralan Blue GL[a]	Acid Blue	183
7	Stylacyl Blue RP[b]	Acid Blue	298
8	Amalon Red BY[c]	Acid Red	151
9	Intralan Bordeaux BLB[a]	Acid Red	182
10	Nylantherene Red B2BSA[a]	Acid Red	266
11	Stylacyl Red RB[b]	Acid Red	364
12	Stylacyl Red RY[b]	Acid Red	384
13	Merpacyl Yellow 9G[b]	Acid Yellow	49
14	Capracyl Yellow NW[b]	Acid Yellow	151
15	Merpacyl Yellow SL[b]	Acid Yellow	198
16	Stylacyl Yellow RG[b]	Acid Yellow	200
17	Amalan Orange RL[c]	Acid Orange	60
18	Merpacyl Orange R[b]	Acid Orange	128
19	Anthraquinone Green GNN[b]	Acid Green	25
20	Sevron Blue 5GNF[b]	Basic Blue	3
21	Sevron Blue B[b]	Basic Blue	21
22	Sevron Blue ER[b]	Basic Blue	77
23	Sevron Blue ACN[b]	Basic Blue	94
24	Sevron Yellow R[b]	Basic Yellow	11
25	Sevron Yellow L[b]	Basic Yellow	13
26	Sevron Yellow 6DL[b]	Basic Yellow	29
27	Sevron Yellow 8GMF[b]	Basic Yellow	53
28	Sevron Golden Yellow RL[b]	Basic Yellow	79
29	Sevron Orange G[b]	Basic Orange	21
30	Intradene Brillian Red 4G[a]	Basic Red	14
31	Sevron Brilliant Red B[b]	Basic Red	15
32	Sevron Red GL[b]	Basic Red	18
33	Sevron Brilliant Red 3B[b]	Basic Violet	15
34	Sevron Brilliant Red 4G[b]	Basic Violet	16
35	Sevron Blue 5GNF;[b] Lot 08905; 1/8/79	Basic Blue	3
36	Sevron Blue 5GNF;[b] 2/14/78	Basic Blue	3
37	Sevron Blue 5GNF;[b] Lot 04764; 1/7/77	Basic Blue	3
38	Sevron Blue 5GNF;[b] Lot 06891; 11/12/77	Basic Blue	3
39	Intradene Blue 5G;[a] Lot 3773-1; 4/6/79	Basic Blue	3
40	Intradene Blue 5G;[a] 1/3/79	Basic Blue	3
41	Merpacyl Blue SW;[b] 6/15/79	Acid Blue	25
42	Merpacyl Blue SW;[b] Lot 08986; 1/23/79	Acid Blue	25
43	Merpacyl Blue SW;[b] Lot 09565; 8/22/77	Acid Blue	25
44	Merpacyl Blue SW;[b] Lot 27641; 9/18/75	Acid Blue	25
45	Alizarine F Blue CL;[a] Lot 3463-2; 2/22/79	Acid Blue	25
46	Alizarine F Blue CL;[a] Lot SL8642; 2/26/79	Acid Blue	25
47	Alizarine F Blue CL;[a] Lot 8188; 4/5/79	Acid Blue	25
48	Alizarine F Blue CL;[a] Lot SL7604; 8/14/78	Acid Blue	25
49	Alizarine F Blue CL;[a] Lot SL7815; 10/31/78	Acid Blue	25
50	Merpacyl Orange R;[b] Lot 08993; 1/29/79	Acid Orange	128
51	Merpacyl Orange R;[b] Lot 142; 2/13/78	Acid Orange	128
52	Merpacyl Orange P;[b] Lot 07573; 3/21/78	Acid Orange	128
53	Merpacyl Orange R;[b] Lot 06666; 3/28/77	Acid Orange	128
54	Intralan Orange;[a] BL1-100%	Acid Orange	128
55	Intralan Orange;[a] BL1-200%	Acid Orange	128
56	Intralan Orange;[a] BL2; 4/18/79	Acid Orange	128

[a]Crompton & Knowles Co.
[b]E. I. du Pont de Nemours & Co.
[c]American Color and Chemical Corp.

TABLE 2—*A tabulation of black acrylic and nylon*
fiber samples dyed with different lots of otherwise identical
basic and acid dye mixtures.[a]

Sample Number	Fiber Content	Usage Class of Dye Mixture
57A	acrylic	basic
57B	nylon	acid
58A	acrylic	basic
58B	nylon	acid
59A	acrylic	basic
59B	nylon	acid
60A	acrylic	basic
60B	nylon	acid
61A	acrylic	basic
61B	nylon	acid
62A	acrylic	basic
62B	nylon	acid
63A	acrylic	basic
63B	nylon	acid
64A	acrylic	basic
64B	nylon	acid
65A	acrylic	basic
65B	nylon	acid
66A	acrylic	basic
66B	nylon	acid
67A	acrylic	basic
67B	nylon	acid
68A	acrylic	basic
68B	nylon	acid
69A	acrylic	basic
69B	nylon	acid
70A	acrylic	basic
70B	nylon	acid
71A	acrylic	basic
71B	nylon	acid

[a]Each set of fiber samples was taken from a single black sock containing a blend of acrylic/nylon fibers dyed with different lots of identical dye mixtures. They are not identified by lot numbers because that information was considered proprietary.

capillary tubes are then removed from the oven and examined under a low-power microscope to confirm the extraction of the dyes from the fiber. Most of the dye has been extracted from the fiber at this point, although the fiber may not be completely colorless. The dyes in the black nylon fibers are extracted with the pyridine/water solvent, while the dyes in the black acrylic fibers are extracted with the dimethylformamide/water solvent.

A 0.1% solution of each solid dye sample in the pyridine/water extraction solvent is made up for spotting as a known reference.

Separation

The solutions containing the extracted and dissolved dyes are spotted with 10-μL (10-lambda) microcapillary pipettes onto silica gel plates that have been activated in an oven for 30 min at 100°C. A total volume of approximately 5 μL (5 lambda) is spotted for the darker colors and 10 lambda for the lighter colors. Drying is facilitated by using a hand-held hair dryer. After the spotting, the plates are returned to the oven for 15 min, allowed to cool in a desiccator, and developed until the solvent front reaches a 5-cm mark. Five plates, each developed in a separate solvent system, are prepared for each run. Development takes from

15 to 30 min depending on the solvent system. Plates are "read" against a bright light to visualize minor colored bands that might not be seen under ordinary light. Reported R_f values are average values from a minimum of two runs.

Results

Correlation Coefficients

The R_f values of the major and minor dye components from each generically different solid dye sample were recorded after the separation in each solvent system. The R_f values of major dye components, from which correlation coefficients were calculated, are listed in Table 3. Correlation coefficients r for the ten paired solvent systems are shown in Table 4 and were calculated by using the following equation [19]:

$$r = \frac{\Sigma XY - n\bar{X}\,\bar{Y}}{[(\Sigma X^2 - n\bar{X}^2)(\Sigma Y^2 - n\bar{Y}^2)]^{1/2}}$$

where

$X = R_f$ value in first solvent system,
$Y = R_f$ value in second solvent system,
$\bar{X} =$ mean R_f value in first solvent system,
$\bar{Y} =$ mean R_f value in second solvent system, and
$n =$ number of results.

Frequency Distributions

Frequency distributions, plotted for each of the ten paired solvent systems, are shown graphically in Figs. 1 through 10. The R_f values of the major dye components from solid dye Samples 1 through 34 were used in plotting points in Figs. 1 through 10. Figure 11 illustrates a hypothetical situation in which the association between paired solvent systems is not linear but curvilinear.

Resolving Power

The resolving power of the individual solvent systems was evaluated by determining the number of major and minor colored components resolved after the separation of the solid dye samples in each solvent system. The total number of colored components resolved for Samples 1 through 34 in each solvent system is shown in Fig. 12.

Samples 35 through 56, representing three sets of generically identical dyes, were also separated in solvent systems I through V. Within each set of dyes, there are different lots from the same manufacturer and generically identical dyes made by different manufacturers. The ability of the individual solvent systems to discriminate between these samples is shown in Table 5.

Graphic Representation

Extracted dyes from acrylic and nylon fiber samples 57A and B through 71A and B are shown graphically, after separation in solvent systems I through V, in Figs. 13 to 17. Individual major and minor dye components are depicted through a series of standard symbols representing the three primary colors—red, yellow, and blue—to simplify the illustrations. Separated dye components may be represented by a side-by-side combination of standard

TABLE 3—R_f values of major dye components of 34 acid and basic dyes in various solvent systems.

Sample Number	Chemical Index Name	System I	System II	System III	System IV	System V
1	Acid Blue 9	0.04	0.20	0.22	0.50	0.08
2	Acid Blue 25	0.60	0.66	0.68	0.86	0.70
3	Acid Blue 40	0.38	0.60	0.60	0.76	0.56
4	Acid Blue 113	0.20	0.50	0.38	0.70	0.46
5	Acid Blue 158	0.14	0.00	0.00	0.52	0.22
6	Acid Blue 183	0.52	0.66	0.06	0.32	0.04
7	Acid Blue 298	0.14	0.30	0.28	0.62	0.30
8	Acid Red 151	0.56	0.64	0.56	0.70	0.54
9	Acid Red 182	0.40	0.68	0.60	0.98	0.94
10	Acid Red 266	0.36	0.58	0.30	0.76	0.54
11	Acid Red 264	0.04	0.10	0.18	0.62	0.28
12	Acid Red 384	0.00	0.10	0.16	0.62	0.30
13	Acid Yellow 49	0.54	0.52	0.54	0.70	0.64
14	Acid Yellow 151	0.36	0.38	0.64	0.98	0.98
15	Acid Yellow 198	0.56	0.64	0.60	0.80	0.60
16	Acid Yellow 200	0.26	0.30	0.38	0.66	0.42
17	Acid Orange 60	0.40	0.70	0.66	0.98	0.96
18	Acid Orange 128	0.44	0.60	0.28	0.80	0.62
19	Acid Green 25	0.84	0.56	0.76	0.84	0.70
20	Basic Blue 3	0.60	0.44	0.60	0.26	0.18
21	Basic Blue 21	0.04	0.72	0.06	0.04	0.04
22	Basic Blue 77	0.52	0.52	0.64	0.58	0.54
23	Basic Blue 94	0.00	0.00	0.00	0.00	0.00
24	Basic Yellow 11	0.70	0.98	0.64	0.58	0.46
25	Basic Yellow 13	0.90	0.98	0.98	0.58	0.50
26	Basic Yellow 29	0.34	0.30	0.50	0.30	0.16
27	Basic Yellow 53	0.84	0.40	0.64	0.34	0.22
28	Basic Yellow 79	0.60	0.38	0.56	0.34	0.16
29	Basic Orange 21	0.64	0.72	0.86	0.68	0.50
30	Basic Red 14	0.44	0.22	0.58	0.30	0.20
31	Basic Red 15	0.52	0.60	0.60	0.36	0.28
32	Basic Red 18	0.06	0.02	0.04	0.10	0.06
33	Basic Violet 15	0.98	0.42	0.70	0.46	0.48
34	Basic Violet 16	0.72	0.28	0.64	0.44	0.44

TABLE 4—Correlation coefficients for selected paired solvent systems.

	II	III	IV	V
I	0.66	0.80	0.13	0.30
II	. . .	0.59	0.39	0.49
III	. . .	. . .	0.33	0.59
IV	. . .	. . .	. . .	0.92

symbols in cases where discrimination between similar colors or shades is essential. In most cases it is preferable to depict identical shades as one of the primary colors.

Discussion

The sample correlation coefficient is one statistical approach that may be used to measure the degree of relationship between paired solvent systems. Correlation coefficients measure
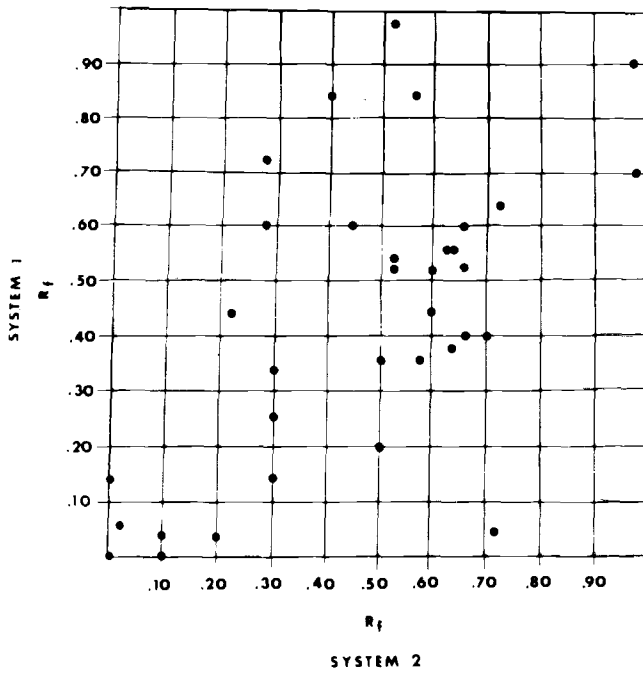
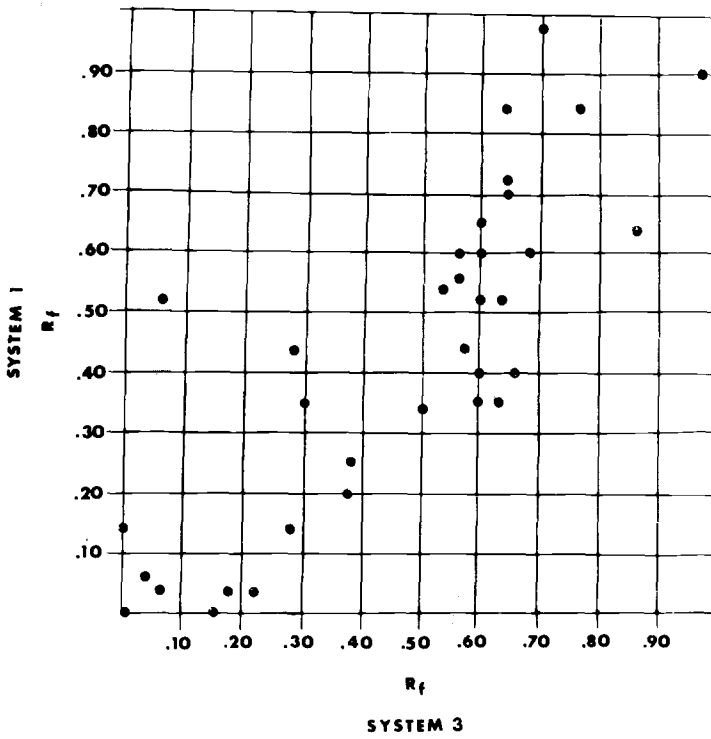FIG. 1—*Coordinates (R_f) of acid and basic dyes developed in solvent systems I and II.*

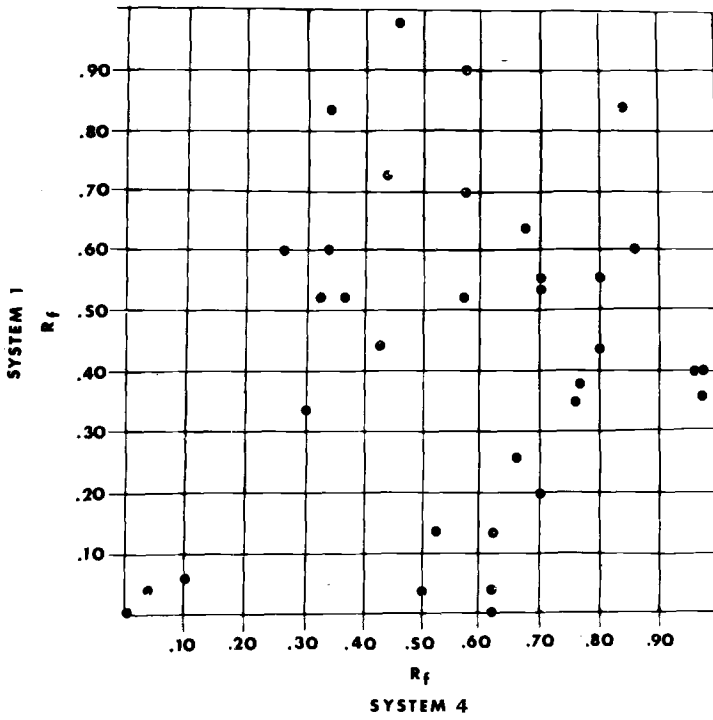FIG. 2—*Coordinates (R_f) of acid and basic dyes developed in solvent systems I and III.*

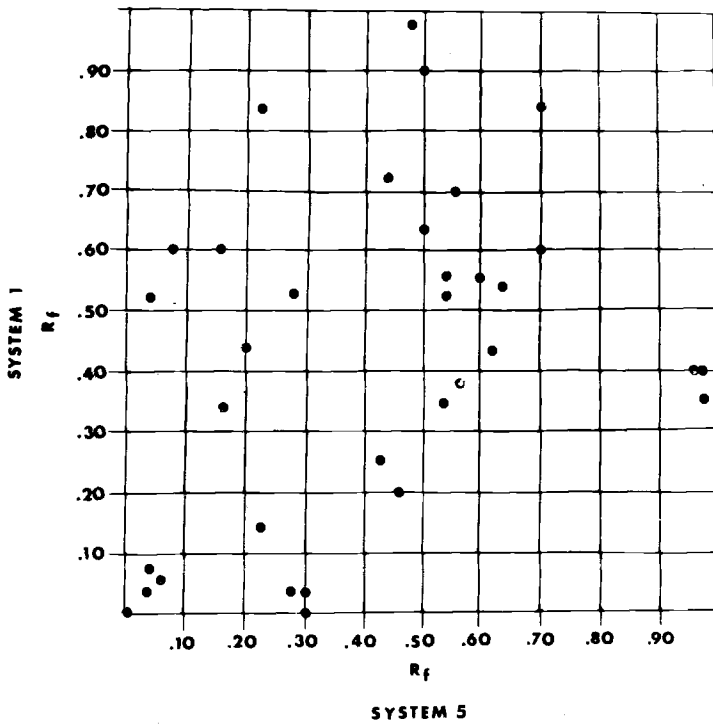FIG. 3—*Coordinates (R_f) of acid and basic dyes developed in solvent systems I and IV.*

FIG. 4—*Coordinates (R_f) of acid and basic dyes developed in solvent systems I and V.*
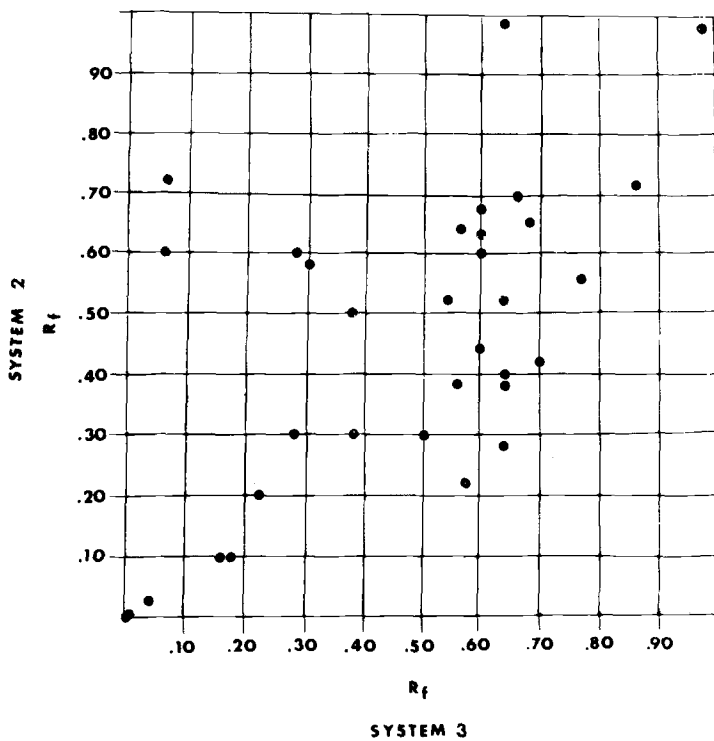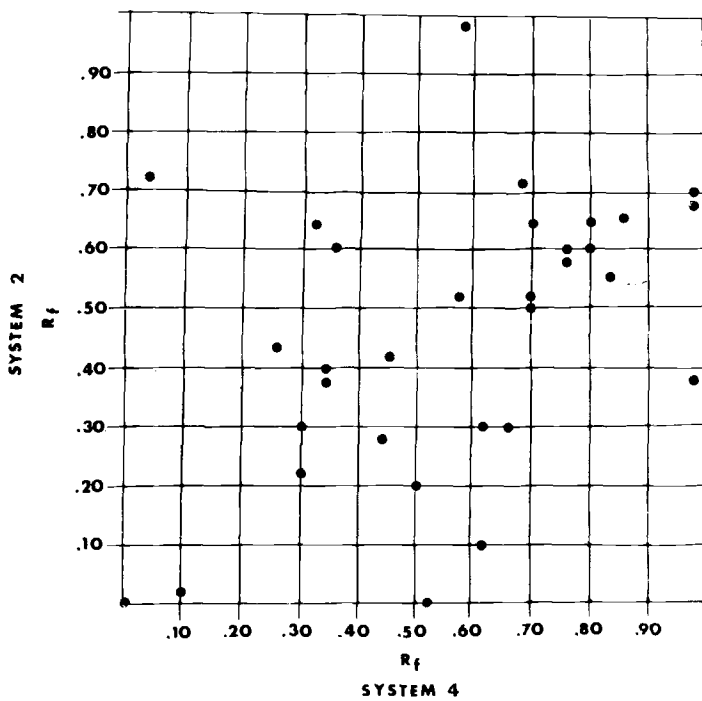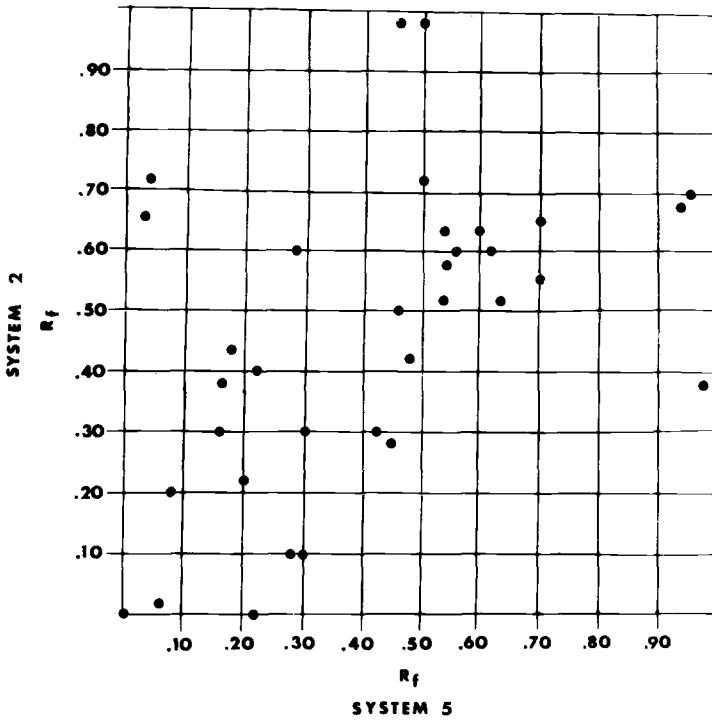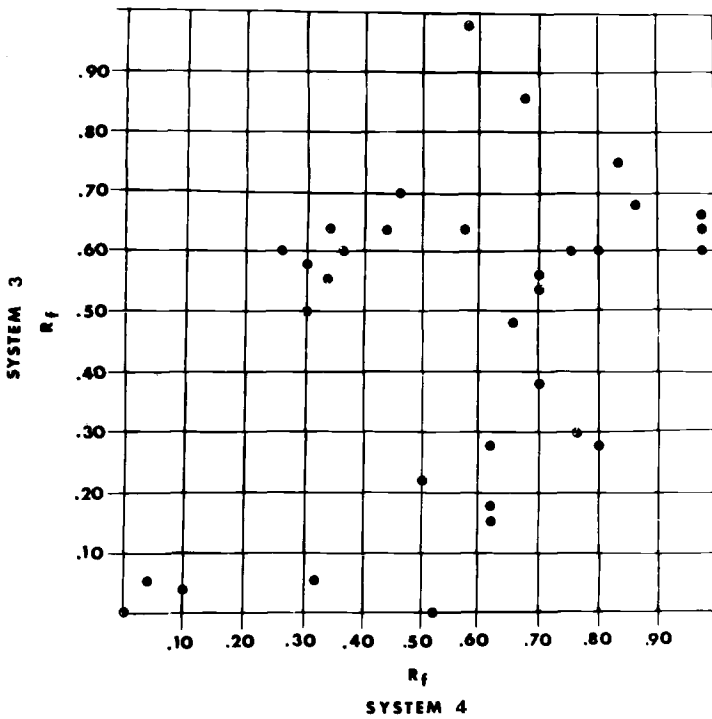
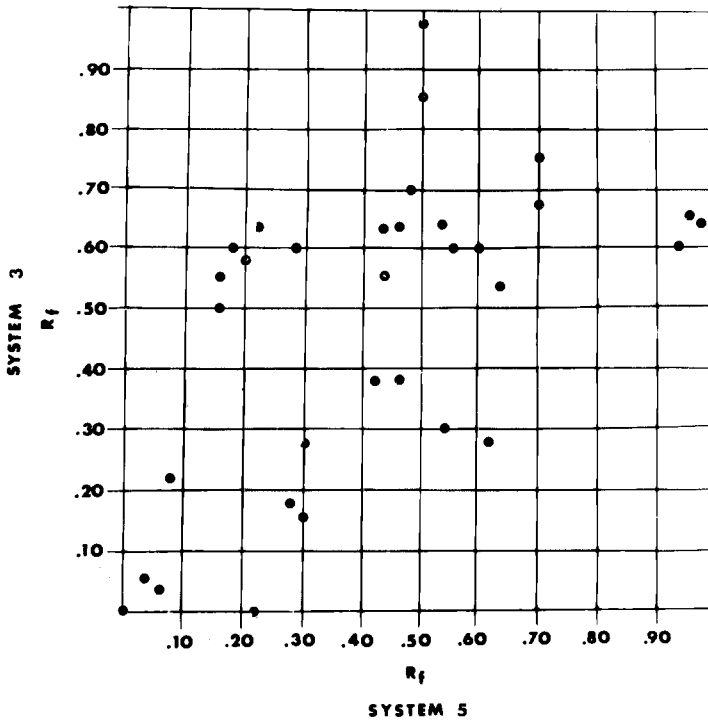FIG. 5—*Coordinates (R$_f$) of acid and basic dyes developed in solvent systems II and III.*

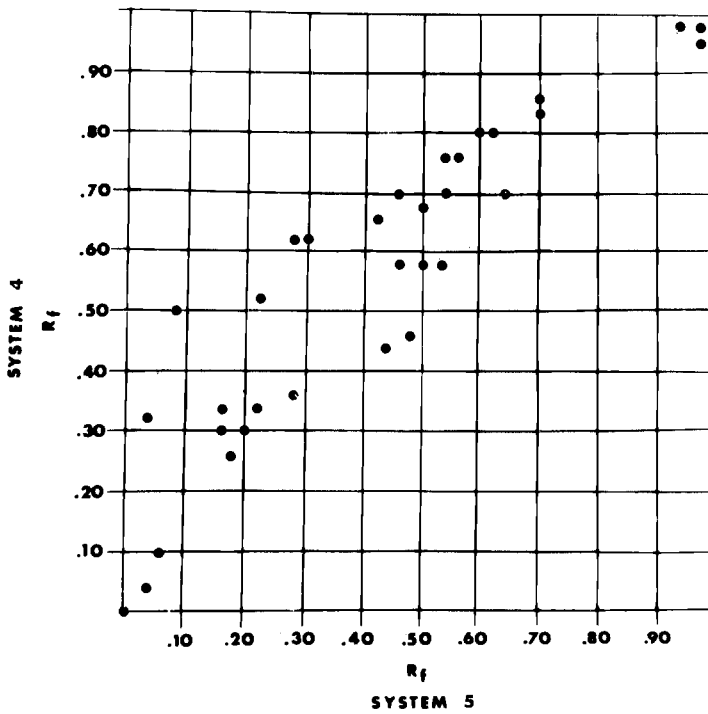FIG. 6—*Coordinates (R$_f$) of acid and basic dyes developed in solvent systems II and IV.*

FIG. 7—*Coordinates (R$_f$) of acid and basic dyes developed in solvent systems II and V.*

FIG. 8—*Coordinates (R$_f$) of acid and basic dyes developed in solvent systems III and IV.*

FIG. 9—Coordinates (R_f) of acid and basic dyes developed in solvent systems III and V.

FIG. 10—Coordinates (R_f) of acid and basic dyes developed in solvent systems IV and V.
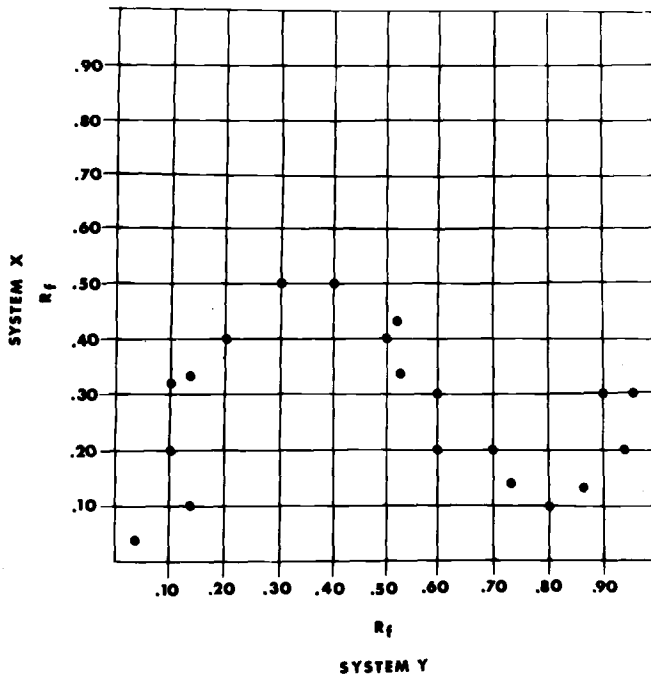
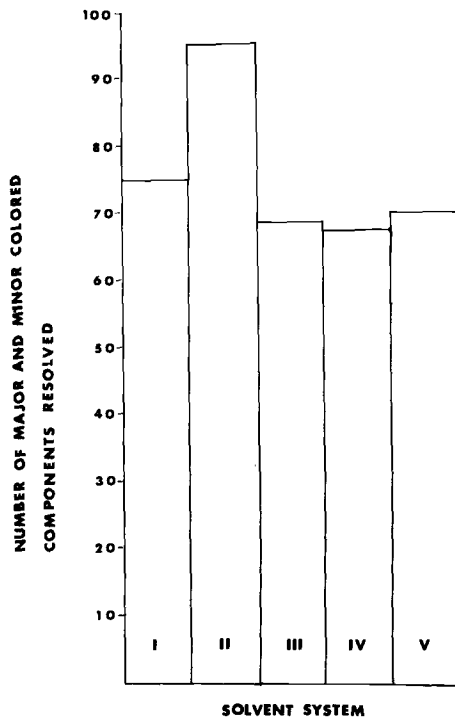FIG. 11—*Coordinates (R_f) illustrating a curvilinear relationship among solvent systems.*

FIG. 12—*Resolving power of solvent systems I through V for 34 solid dye samples.*

TABLE 5—*Number of major and minor colored components resolved in three sets of generically identical solid dye samples.*

Sample Number	Solvent System				
	I	II	III	IV	V
BASIC BLUE 3					
35[a]	6[b]	5[b]	3[b]	3[b]	5[b]
36[a]	6[b]	5[b]	3[b]	3[b]	5[b]
37[a]	6[b]	5[b]	3[b]	3[b]	5[b]
38[a]	6[b]	5[b]	4[c]	3[b]	5[b]
39[d]	6[b]	5[b]	4[c]	3[b]	5[b]
40[d]	6[b]	5[b]	2	3[b]	5[b]
ACID BLUE 25					
41[a]	2[b]	1	1	1	1
42[a]	3	2	2	2	2[b]
43[a]	2[b]	1	1	1	1
44[a]	2[b]	1	1	1	1
45[d]	2[b]	1	1	1	2[b]
46[d]	2[b]	1	1	1	2[b]
47[d]	2[b]	1	1	1	2[b]
48[d]	2[b]	1	1	1	2[b]
49[d]	2[b]	1	1	1	2[b]
ACID ORANGE 128					
50[a]	2[b]	4[b]	3[b]	4[b]	3[b]
51[a]	2[b]	4[b]	3[b]	4[b]	3[b]
52[a]	2[b]	4[b]	3[b]	5[c]	3[b]
53[a]	2[b]	4[b]	3[b]	5[c]	3[b]
54[d]	2[b]	3[c]	3[b]	4[b]	3[b]
55[d]	2[b]	3[c]	3[b]	4[b]	3[b]
56[d]	2[b]	3[c]	3[b]	4[b]	3[b]

[a]E. I. du Pont de Nemours & Co.
[b,c]Chromatographed identically.
[d]Crompton & Knowles Co.

the strength of association between two variables in instances where the relationship between X and Y is believed to be linear [19]. The correlation coefficient of a series of dyes chromatographed in two solvent systems will approach zero when there is little statistical relationship between the R_f distribution of individual dye components in the combination of solvent systems employed. A correlation coefficient approaching 1.0 would indicate a very strong linear relationship between the solvent systems. Obviously, paired solvent systems that give high correlation coefficients would offer little, if any, more information than a single solvent system.

To justify the use of paired solvent systems, one would want to demonstrate a relatively random distribution of R_f values in and between paired solvent systems, resulting in a low correlation coefficient. A combination of a broad, random distribution of coordinates when R_f values of individual dye components separated in two solvent systems are plotted and a low correlation coefficient for paired solvent systems should result in generating a maximum amount of information for the comparison of extracted textile dyes.

The use of scatter diagrams to illustrate frequency distributions for paired solvent systems may best be explained by the following example. The scatter diagram in Fig. 11 shows a definite curvilinear relationship between plotted R_f coordinates in hypothetical solvent systems X and Y. Although solvent systems X and Y are highly correlated, they have a correlation coefficient of -0.21 (negative slope), which erroneously indicates a low degree of correlation. Because a correlation coefficient is not a suitable statistic for calculating the
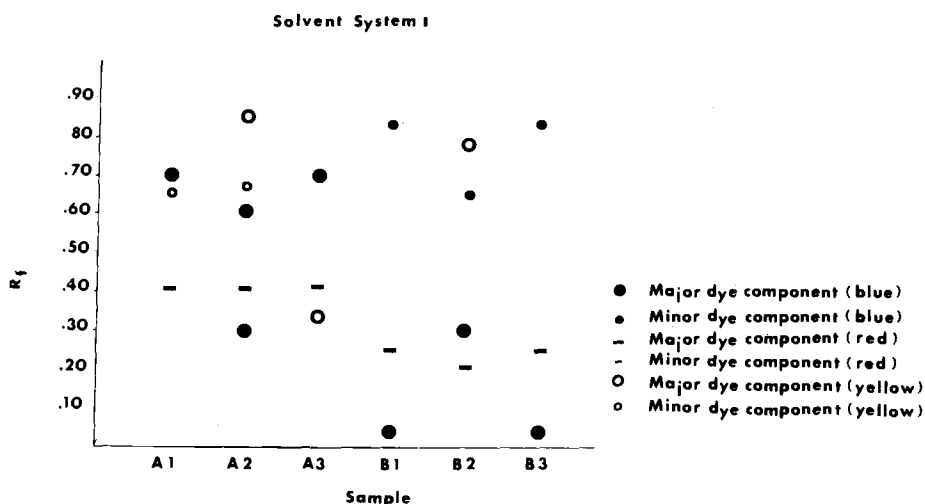
Solvent System I

A1—Basic dye mixture extracted from acrylic fiber Samples 57A, 58A, 59A, 60A, 62A, 63A, 64A, 65A, 66A, 68A, and 70A
A2—Basic dye mixture extracted from acrylic fiber Samples 61A and 67A
A3—Basic dye mixture extracted from acrylic fiber Sample 71A
B1—Acid dye mixture extracted from nylon fiber Samples 57B, 58B, 59B, 60B, 62B, 63B, 64B, 65B, 66B, 68B, and 70B
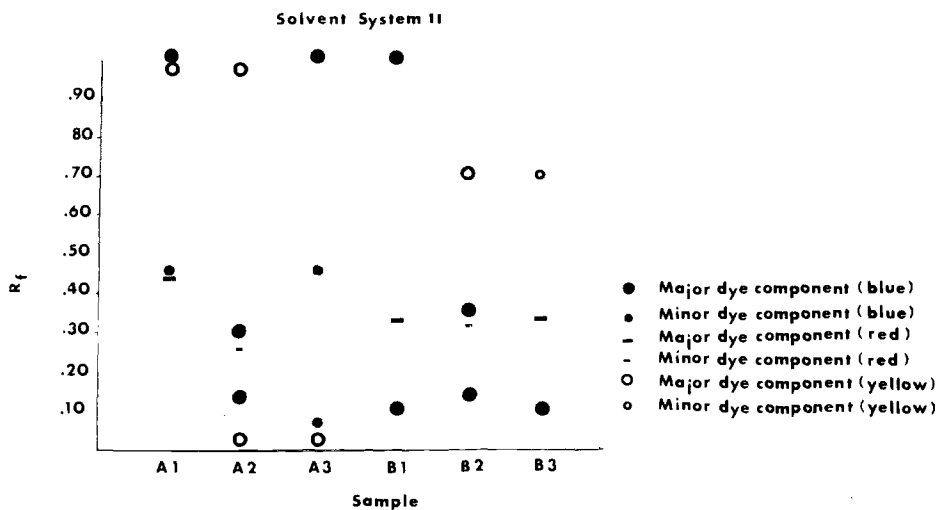B2—Acid dye mixture extracted from nylon fiber Samples 61B and 67B
B3—Acid dye mixture extracted from nylon fiber Sample 71B

FIG. 13—*Graphic representation of results obtained with solvent system I for dyes extracted from fiber Samples 57A and B through 71A and B.*

degree of association of data having a curvilinear relationship, scatter diagrams must be used with it to demonstrate a random distribution of plotted R_f values.

Examination of the correlation coefficients of the ten paired solvent systems employed in this study (Table 4) shows solvent systems I and IV to have the lowest correlation coefficient (0.13) and solvent sytems IV and V to have the highest correlation coefficient (0.92). Scatter diagrams of these paired solvent systems, shown in Figs. 3 and 10, clearly illustrate this relationship. Figure 3 shows a broad and random distribution of coordinates, whereas Fig. 10 shows an almost linear distribution of coordinates, indicating a very strong degree of association between solvent systems IV and V. In general, the shapes of the scatter diagrams show a direct relationship to the corresponding correlation coefficient for each set of paired solvent systems. Paired solvent systems I and IV, I and V, II and IV, and III and IV all have correlation coefficients of 0.39 or less and show a broad and random distribution of coordinates in their corresponding scatter diagrams. These paired solvent systems would appear to be suitable for use in TLC of acid/basic textile dyes.

The resolving power of the individual solvent system is evaluated through its ability to resolve major and minor colored components in solid dye Samples 1 through 34, as shown in Fig. 12. Of the 34 solid dye samples studied, four failed to exhibit any minor colored components after separation in solvent systems I through V. Solvent systems I, III, IV, and V separated an average of 70 colored components each, representing approximately 2.0 colored components per sample. Solvent system II separated 95 colored components, representing approximately 2.8 colored components per sample. The superior resolving power of solvent system II should be considered when paired solvent systems are chosen for use in TLC, as increased resolving power should result in an increase in discriminating power. However,

A1—Basic dye mixture extracted from acrylic fiber Samples 57A, 58A, 59A, 60A, 62A, 63A, 64A, 65A, 66A, 68A, and 70A
A2—Basic dye mixture extracted from acrylic fiber Samples 61A and 67A
A3—Basic dye mixture extracted from acrylic fiber Sample 71A
B1—Acid dye mixture extracted from nylon fiber Samples 57B, 58B, 59B, 60B, 62B, 63B, 64B, 65B, 66B, 68B, and 70B
B2—Acid dye mixture extracted from fiber Samples 61B and 67B
B3—Acid dye mixture extracted from nylon fiber Sample 71B

FIG. 14—*Graphic representation of results obtained with solvent system II for dyes extracted from fiber Samples 57A and B through 71A and B.*

of those paired solvent systems studied that included solvent system II, all but II and IV had a correlation coefficient greater than 0.39. Paired solvent systems with relatively high correlation coefficients may be acceptable for use in TLC when the resolving power of the individual solvent systems is high; the high resolving power results in increased discriminating power because of the number of colored components resolved in questioned and known dye samples.

The ability of the individual solvent systems to discriminate between different lots of generically identical dyes made by the same manufacturer and of generically identical dyes made by different manufacturers is shown in Table 5.

Solvent systems I, II, IV, and V failed to discriminate between six samples of Basic Blue 3. Solvent system III resolved these samples into three identical groups, containing two, three, and four dye components, respectively.

Eight out of nine samples of Acid Blue 25 were separated identically in solvent systems I, II, III, and IV. Six samples of Acid Blue 25 were separated identically in solvent system V, as was another group of three samples.

Solvent systems I, III, and V failed to discriminate between any of the seven samples of Acid Orange 128. Solvent system II discriminated between samples according to manufacturer. Solvent system IV separated the seven samples into two groups of identical dye mixtures, one containing four colored components and the other containing five colored components.

There is no clear-cut relationship between the resolving power of the individual solvent systems (Fig. 12) and their ability to discriminate between generically identical samples made by the same manufacturer and by different manufacturers. Each of the solvent
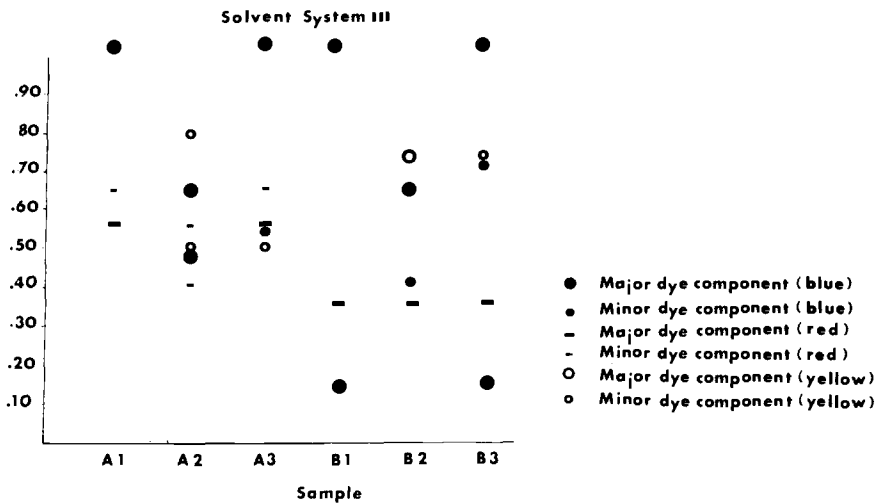
A1—Basic dye mixture extracted from acrylic fiber Samples 57A, 58A, 59A, 60A, 62A, 63A, 64A, 65A, 66A, 68A, and 70A
A2—Basic dye mixture extracted from acrylic fiber Samples 61A and 67A
A3—Basic dye mixture extracted from acrylic fiber Sample 71A
B1—Acid dye mixture extracted from nylon fiber Samples 57B, 58B, 59B, 60B, 62B, 63B, 64B, 65B, 66B, 68B, and 70B
B2—Acid dye mixture extracted from nylon fiber Samples 61B and 67B
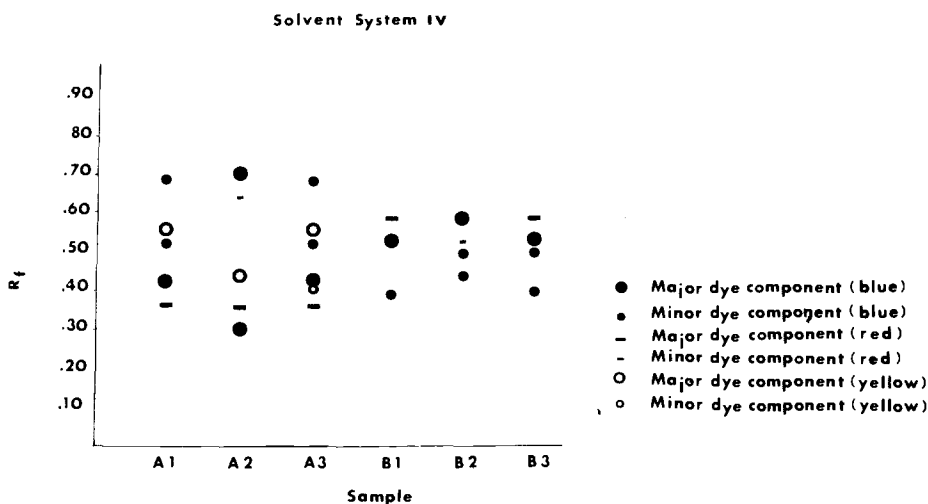B3—Acid dye mixture extracted from nylon fiber Sample 71B

FIG. 15—*Graphic representation of results obtained with solvent system III for dyes extracted from fiber Samples 57A and B through 71A and B.*

systems demonstrated some degree of discriminating power, but it would be difficult to choose one as being superior to the others in this regard.

Fiber Samples 57A and B through 71A and B represent black acrylic and nylon yarn from acrylic-nylon blends used in manufacturing socks. The acrylic and nylon fibers separated from each individual sample are identified by the letters A and B, respectively. The manufacturer states that the acrylic and nylon yarns used in these samples were dyed with different lots of otherwise identical dye mixtures: a mixture of a green, a yellow, and a red basic dye for the acrylic fibers and one black acid dye for the nylon fibers. The TLC examination of the dyes extracted from these samples reveals the nylon fibers to have been dyed not with a single black acid dye, but with a mixture of red, blue, and yellow dyes. It also becomes obvious that not one but three different dye mixtures were used in dyeing both the acrylic and nylon yarns.

The separated dye components from fiber Samples 57A and B through 71A and B are shown graphically in Figs. 13 to 17. As previously stated, three distinct sets of different dye mixtures are apparent: one for Samples 61A and B and 67A and B, one for Samples 71A and B, and one for the remaining paired acrylic and nylon fiber samples. Although minor colored components were resolved in all of the samples, it was not possible to discriminate between fiber samples containing the same dye mixtures. The resolution of major and minor colored components did, however, result in the formation of identical complex dye patterns, adding weight to determinations of similarity.

The advantages of graphically depicting the separated dye components are many. It would be difficult to relate information contained in a table listing R_f values and colors of individual separated dye components to the corresponding correlation coefficients and scatter

FIG. 16—*Graphic representation of results obtained with solvent system IV for dyes extracted from fiber Samples 57A and B through 71A and B.*

diagrams for the paired solvent systems employed in this study. In contrast, an evaluation of Figs. 13 to 17 clearly illustrates these data in graphic form. The use of solvent system V in combination with solvent systems I, II, III, and IV resulted in consistently high correlation coefficients and relatively tight groupings of plotted coordinates in the corresponding scatter diagrams. Figure 17 (solvent system V) illustrates a poor resolution of separated dye components, many of which have an R_f value at or near 0.10. Figures 13 and 16 (solvent systems I and IV) clearly illustrate good resolution of the separated dye components, with few of the dyes separating at R_f values under 0.10 or at the solvent front. Paired solvent systems I and V have the lowest correlation coefficient (0.13), and the corresponding scatter diagram reveals a broad and random distribution of coordinates.

Each of the solvent systems used in this study was initially screened to insure that TLC of solid dye Samples 1 through 34 resulted in a minimum of 32 of the dye samples migrating and being assigned R_f values. Those solvent systems in which more than two of the spotted dyes remained at the origin (less polar) were eliminated, as were those in which more than two of the dyes ran with the solvent front (more polar). This procedure, in effect, resulted in setting a definite range of polarities for the five solvent systems selected for use in this study. Acid (anionic) and basic (cationic) textile dyes are moderately polar compounds, disperse dyes are comparatively less polar, and vat, direct, and reactive dyes are comparatively more polar. Successful TLC of an extracted dye, or mixture of dyes, in two of the solvent systems would therefore be a strong indication of an acid or basic dye. Solvent system I has been reported as a screening solvent system for use in the comparison of textile dyes [17]. The use of solvent system I in paired solvent systems would result in eliminating a large percentage of the general population of textile dyes when extracts of questioned and known fiber samples

Solvent System V

A1—Basic dye mixture extracted from acrylic fiber Samples 57A, 58A, 59A, 60A, 62A, 63A, 64A, 65A, 66A, 68A, and 70A
A2—Basic dye mixture extracted from acrylic fiber Samples 61A and 67A
A3—Basic dye mixture extracted from acrylic fiber Sample 71A
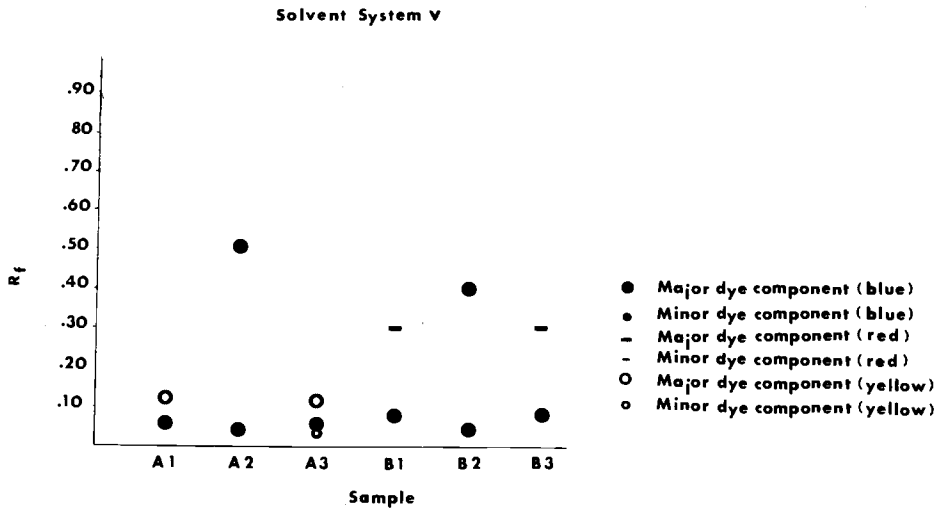B1—Acid dye mixture extracted from nylon fiber Samples 57B, 58B, 59B, 60B, 62B, 63B, 64B, 65B, 66B, 68B, and 70B
B2—Acid dye mixture extracted from nylon fiber Samples 61B and 67B
B3—Acid dye mixture extracted from nylon fiber Sample 71B

FIG.17—*Graphic representation of results obtained with solvent system V for dyes extracted from fiber Samples 57A and B through 71A and B.*

are being compared. The shape of the separated dyes in solvent system I (acid system) will also give the criminalist an indication of the usage class of dyes being examined: acid dyes generally separate as tight spots, whereas basic dyes separate as broader oval spots with some "bearding."

Conclusion

A number of factors must be considered in the evaluation of paired solvent systems for use in TLC of textile dyes. The paired solvent systems should result in an increase of discriminating power over a single solvent system. In most instances the discriminating power of paired solvent systems is evaluated through a combination of mathematical evaluation (correlation coefficients) and R_f frequency distributions (scatter diagrams). Clearly, another factor must be considered with colored compounds that can be seen without spraying. Under such a circumstance, the ability of the individual solvent systems to resolve major and minor colored components in textile dyes may result in the formation of very complex multicolored dye patterns. In actual case work the extracted dyes from questioned and known fiber samples are spotted on the same plate so that a side-by-side comparison of the separated dye components may then be made. The discriminating power of individual solvent systems will increase as their resolving power increases, resulting in an increased level of confidence on the part of the criminalist reporting similarities, or dissimilarities, in textile fiber comparisons.

In the selection of solvent systems for use in TLC, a compromise must be made between ideal R_f distributions and low correlation coefficients within paired solvent systems and max-

imum resolving power in individual solvent systems. Therefore solvent systems I and IV appear to be most suitable for use in combination. However, the superior resolving power of solvent system II must also be considered. Although the use of solvent system II in paired solvent systems resulted in consistently higher correlation coefficients, a combination of solvent systems II and IV appears to be equally acceptable. The results in this study clearly indicate that the proper selection of TLC solvent systems with high resolving power and low correlation produces a tool of very high discriminating power for the analysis of dyed textile fibers.

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