Relationship between direct dye characteristics and coverage of immature fibre neps in dyed cotton fabric

Lenore Cheek* and Anne Wilcock†

*School of Home Economics, Louisiana State University Agricultural Center, Baton Rouge, LA70803, USA

†Dept of Consumer Studies, University of Guelph, Guelph, Ontario NIG 2W1, Canada

Cotton fabric containing a large number of neps was dyed with each of 17 azo direct dyes. Visible coverage of neps composed of immature fibres varied widely among the dyes. An evaluation of those structural characteristics of the dyes that might account for their differential ability to achieve coverage of neps was undertaken. Direct dyes containing more than one amino or amido group in their structure were found most likely to achieve relatively good nep coverage. Scanning electron micrographs revealed considerable variation in the types of fibres making up the individual neps in a single piece of cotton fabric. Differences in direct dye behaviour towards nep coverage were most evident with those neps composed of immature fibres with some secondary wall development.

INTRODUCTION

Clumps of tangled fibres, known as neps, are often found scattered throughout the surface of cotton fabric. Neps are a problem to textile dyers because they often seem to resist dye and appear as white or pastel-coloured specks on the dyed fabric. The contrasting appearance of the neps is considered to be primarily optical and has been attributed to the shortness of the length of the path of light through the thin-walled fibres of which most neps are composed [1,2]. This seems an incomplete explanation in view of data showing variation among direct dyes in their ability to achieve visible coverage of neps [3].

A limited number of studies in the textile literature have examined structural characteristics as determining the relative ability of a given direct dye to cover neps. The early work by Lawrie [4] indicated no known connection between the molecular structure and diffusion characteristics of a dye and its ability to produce visible coverage of neps. Fargher and co-workers [2] observed that blue and green dyes are more sensitive to the differential dyeing of cotton neps than yellow or red dyes because of luminosity characteristics of the different hues and the sensitivity of the human eye to distinguish colour differences. Furvik [5] demonstrated that immature fibres have a faster rate of sorption and desorption than mature fibres and concluded that the rinsing of dyed fabrics containing neps should be minimised. Holme [6] stated that only highly substantive dyes colour immature cotton under normal conditions. Giles [7] presented data that demonstrate a positive relationship between the number of primary and secondary amino groups on a dye molecule and the affinity characteristics of that dye. Abrahart [8] also noted that the presence of amide linkages in a direct dye molecule increases substantivity.

These studies suggest several potential lines of related inquiry. The work of Furvik suggests the possibility that the retention of dye by immature fibres may be optimal for dyes with poor migration properties and high substantivity. These characteristics should be readily identifiable by use of wet fastness ratings and by Society of Dyers and Colourists (SDC) classifications, which rate direct dyes based on migration properties and sensitivity to salt [9]. Holme's statement regarding substantivity [6] is in need of further examination since the structural characteristics that determine substantivity have not yet been elucidated. The traditional explanation for the attraction between direct dyes and cellulose was based on the assumption of hydrogen bond formation between the hydroxyl groups on cellulose and polar groups on the dye molecule, although this has been questioned [7,10,11]. Van der Waals forces are now thought to play an important role in dye–fibre association. The aggregation of dye molecules within the fibre is believed to be another important factor. In addition, the potential existence of an attractive force between direct dyes and cellulose involving a weak electrostatic interaction between the hydroxyl groups of cellulose and the amino groups of the dye molecules has been suggested [7,8,10].

The ASTM procedure for determining the proportion of immature and mature fibres in a sample of cotton is based on the use of two dyes, C.I. Direct Red 81 and C.I. Direct Green 26, known to have different affinities for immature cotton [12,13]. These two dyes differ in molecular weight, molecular shape and rate of diffusion. This suggests that molecular weight or shape may also be a factor in the comparative ability of direct dyes to achieve coverage of immature fibre neps. An additional factor may be the diffusion characteristics of the dye.

The purpose of our research was to investigate the relationship between ability to cover neps composed of immature fibres and the structural and dyeing characteristics of selected direct dyes. The specific dye characteristics evaluated in this study were molecular size and structure, SDC classification and wash fastness ratings.

*To whom correspondence should be addressed at: School of Home Economics, Louisiana State University, Baton Rouge, LA70808, USA

MATERIALS AND METHODS

Fabric and dyes

The fabric substrate was bleached cotton printcloth, style 400 (Testfabrics Inc., Middlesex, NJ). The fabric weight was 106 g/m^2, it contained 31.5 × 31.5 yarns/cm^2, and had a large number of readily visible neps. The specimen size was 35.5 × 11.5 cm.

Seventeen azo direct dyes with closely related chemical structures were used in this study (Table 1). Thirteen of the 17 dyes have linear structures. Two of the experimental dyes (C.I. Direct Green 26 and C.I. Direct Green 28) have non-linear configurations, and the remaining two (C.I. Direct Blue 76 and C.I. Direct Blue 218) are copper complexes [14].

The fabric samples were dyed in a laboratory dyeing machine (Atlas Launder-Ometer, Atlas Electric Devices Co.) using 2% o.w.f. dye, 20% sodium chloride and a 40:1 liquor ratio. To facilitate comparison of results, all dyeing was done at 90°C for 45 min.

TABLE 1

Dyes used in present study

Dye (C.I. Direct)	Chemical class	Supplier[a]
Red 23	Disazo	ATL
Red 80	Tetrakisazo	CKC
Red 81	Disazo	CKC
Violet 7	Disazo	ATL
Violet 9	Disazo	ATL
Blue 1	Disazo	ICI(O)
Blue 76	Disazo–Cu complex	CKC
Blue 78	Trisazo	ATL
Blue 81	Trisazo	ATL
Blue 120A	Trisazo	CKC
Blue 126	Trisazo	CKC
Blue 218	Disazo–Cu complex	CKC
Green 26	Trisazo	CKC
Green 28	Monoazo-anthraquinone	ATL
Brown 1	Trisazo	JC
Black 22	Tetraksazo	CKC
Black 80	Trisazo	CKC

(a) ATL – Atlantic Industries, Nutley, NJ
CKC – Crompton & Knowles Corpn, Charlotte, NC
ICI(O) – ICI Americas Inc., Wilmington, DE
JC – John Campbell & Co., Perkosie, PA

Evaluation of nep coverage

Two different procedures were used to evaluate the relative degree of nep coverage by the various direct dyes. The purpose of the first procedure was to isolate individual immature neps prior to application of the experimental dyes. This was done by pre-dyeing all samples using the procedure specified in ASTM D-1464 [12], using only one dye, C.I. Direct Red 81, which has minimal substantivity for immature fibres. After the boiling water rinse, each sample was air dried. Twenty-five immature fibre neps, which appeared as white specks, were circled on each. The majority of the remaining red dye was then stripped from the samples by a 30 min extraction with boiling water. Each of the marked fabrics was then dyed using one of the 17 experimental dyes. Dyed fabrics were mounted at a 45° angle in a viewing box and the number of previously circled neps appearing as contrasting light specks against the dyed fabric background was counted.

Ten dyes were then selected from the original group of 17. These included the five dyes that had the best coverage and the five dyes that had the worst. These dyes were used to dye unmarked cotton printcloth samples. The relative ability of each of these ten dyes to produce uniform coverage of the neppy cotton fabric was re-examined using a different procedure for evaluation of relative nep coverage [15]. This second procedure was an adaptation of a method for counting neps in card webs developed by Linnert [16]. Briefly, the procedure involved mounting a dyed sample at a 45° angle behind a black template containing 24 evenly spaced windows, each of which measured 2.54 cm^2. The number of cells that contained one or more uncovered neps was counted and the mean nep count calculated. Twelve replications were performed and the average of the twelve individual mean nep counts for each dye was calculated.

Micrographs of visibly covered and uncovered neps were taken with a scanning electron microscope (Hitachi S-570). Linear regression analysis was used to test the relationships between structural characteristics of the dyes and visible coverage of immature fibre neps.

RESULTS AND DISCUSSION

Microscopic examination of neps

In the early stages of this research, it was noted that, while there were large numbers of neps composed of masses of tangled fibres readily visible on the undyed fabric, only some appeared as contrasting light spots on the dyed fabric. This suggested that there were differences in dyeability characteristics among these individual fibre neps. The observation that some of the neps present on the surface of the undyed fabric appeared to be dyed to the same depth of shade as the background fabric while other neps appeared as contrasting light specks suggested a need for closer observation of the neps themselves. Therefore a microscopic examination of visibly covered and uncovered neps on dyed fabric was undertaken. This microscopy was based upon the findings of a preliminary experiment in which C.I. Direct Red 23 was shown to produce almost uniform dyeings on neppy cotton print fabrics and C.I. Direct Black 80 to produce dyed fabrics with many contrasting light specks.

Although almost all the neps on samples dyed with C.I. Direct Red 23 appeared covered, there were still a few light specks scattered throughout the fabric. Scanning electron micrographs revealed that these undyed neps were composed of compact masses of very flat, ribbon-like fibres, which appear to be lying on the surface of the rounder mature fibres making up the bulk of the yarns (Figure 1). Such extremely flat fibres are 'dead' and have almost no secondary wall development. In addition to the

Figure 1 – Undyed nep composed of flat, dead fibres on fabric dyed with C.I. Direct Red 23; left 105×, right 350×

fact that such fibres have minimal dye substantivity, the compaction of the fibre mass forms a reflective surface that produces a mirror-like effect. Therefore this type of dead fibre nep is unlikely to appear covered by any direct dye.

Figure 2 shows an immature nep which was taken from the same sample of fabric dyed with C.I. Direct Red 23 and which appeared to be covered. The fibre mass itself is less compact and individual fibres are thin, but much more swollen than the flat fibres in Figure 1. These thin-walled fibres would be categorised as 'immature' fibres and have partial secondary wall development. Figure 3 shows another type of nep which also appeared to be covered by the red dye. It appears considerably less compact and flat than the nep in Figure 1. It contains both dead and immature fibres.

Figure 2 – Dyed nep composed of immature fibres on fabric dyed with C.I. Direct Red 23; left 105×, right 350×

Figure 3 – Dyed nep composed of both dead and immature fibres on fabric dyed with C.I. Direct Red 23; left 105×, right 350×

Figures 4 and 5 show neps that appeared to be dyed the same depth of shade as the background fabric in one of the samples dyed with C.I. Direct Black 80, a dye that produced very high nep counts. The fibres in the nep in Figure 4 appear to be fully mature, i.e. have considerable secondary wall thickness, but are of smaller diameter than the surrounding fibres. Figure 5 illustrates yet another type of nep, this one a mass of torn mature fibres. It is assumed that this is process nep, i.e. a nep composed of fibres torn and tangled during the ginning or spinning process.

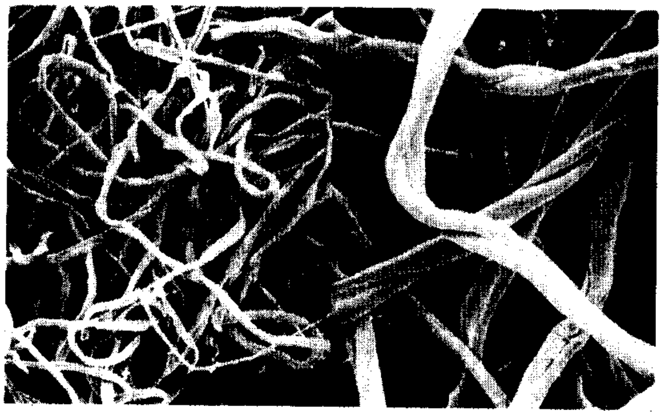

Figure 4 – Dyed nep composed of thin, mature fibres on fabric dyed with C.I. Direct Black 80; left 105×, right 350×

Figure 5 – Dyed nep composed of torn mature fibres on fabric dyed with C.I. Direct Black 80; left 105×, right 350×

The s.e.m. study demonstrated a difference in the dyeing properties of neps composed primarily of dead, immature, small diameter mature and torn mature fibres. It showed that these several types of neps are likely to be present in a single piece of cotton fabric. Therefore it would appear that the dyeing characteristics of neps depend not only on the dyeing characteristics of the dyestuffs but also on the relative amount of secondary wall development of the individual fibres and on the degree of packing of the fibres.

Coverage of immature cotton neps after dyeing

Twenty-five immature cotton fibre neps were identified on individual samples of cotton printcloth by pre-dyeing with C.I. Direct Red 81. Subsequent to stripping the dye from each sample and redyeing it with one of the 17 test dyes, the average number of the previously identified 25 neps appearing as contrasting light specks ranged from three to 19. Table 2 presents the dyes in order of decreasing coverage of immature neps. Molecular weight, number of

TABLE 2

Relationship between visible coverage of isolated immature neps on dyed fabrics and other properties

Dye (C.I. Direct)	No. of undyed immature neps on dyed fabric[a]	Mol. wt	No. of hydrogen bonding groups	Wash fastness rating[b]	SDC class
Black 22	3	1135	11	3	C
Red 23	6	865	7	4	C
Green 26	7	1325	10	4	B
Green 28	8	973	7	2	B
Brown 1	9	657	6	2–3	C
Black 80	10	986	8	3	B
Blue 218	11	1139	8	3	A
Blue 1	11	1044	8	3–4	B
Blue 120A	13	955	5	4	B
Red 80	13	1424	8	3	B
Blue 76	14	1139	8	3	B
Blue 126	15	983	5	4	C
Violet 9	16	717	5	2	A
Blue 78	16	1133	5	3	B
Violet 7	17	721	4	1	A
Blue 81	18	1225	6	4	B
Red 81	19	701	4	1	A

(a) Mean number of undyed neps on dyed samples out of a possible 25
(b) AATCC wash fastness (colour change) rating [15]

potential hydrogen bonding groups, SDC application class and AATCC wash fastness (colour change) ratings are listed for each dye.

It was obvious that some of the experimental dyes were more successful than others in producing visible coverage of immature neps. An examination of the 17 experimental dyes, based on structural and dyeability characteristics of each one, was undertaken in an attempt to identify characteristics which might identify a direct dye as being likely to produce relatively good or poor visible coverage of immature fibre neps.

Since direct dyes are thought to associate with cellulose via van der Waals forces, and possibly through hydrogen bonding, an obvious initial step was to examine the relationship between molecular weight and shape on the one hand, and immature cotton coverage on the other. No readily observable pattern was found to exist. For example, C.I. Direct Black 22, a high molecular weight dye with a long, linear structure, showed the best nep coverage of all the 19 dyes tested, while C.I. Direct Blue 81, another dye having high molecular weight and linear structure produced the second worst. In addition, while the two dyes producing the best apparent nep coverage, i.e. C.I. Direct Black 22 and C.I. Direct Red 23, both had linear structures, the two dyes differed markedly in molecular weight. The two dyes with non-linear configurations, C.I. Direct Green 26 and C.I. Direct Green 28, also produced relatively good coverage.

More fruitful than the evaluation of molecular size and shape was the pursuit of a correlation between the number of potential hydrogen bonding groups on each dye molecule and coverage of immature fibres. There was a definite tendency for dye molecules containing numerous hydrogen bonding substituents to offer nep coverage superior to those with fewer such groups . C.I. Direct Black 22, with eleven potential hydrogen bonding sites, covered all but 12% of the immature fibre neps, while C.I. Direct Red 81, with only four potential sites, covered only 24%. It seems reasonable that a larger number of hydrogen bonds would decrease the rate of desorption of dye from fibre during post-dye rinsing, thereby resulting in improved visible nep coverage.

However, while the AATCC wash fastness ratings of the four class A dyes used in the study were low, i.e. between 1 and 3, wash fastness characteristics were not consistently related to nep coverage. For example, C.I. Direct Green 28 with a wash fastness rating of 2 gave good coverage; C.I. Direct Blue 81 with a rating of 4 gave poor coverage. The five dyes giving best nep coverage had wash fastness ratings ranging from 2 to 4, while the five dyes giving the poorest nep cover had ratings of from 1 to 5.

The dyes that produced the best coverage were most commonly rated SDC class B or C rather than class A. These dye molecules had comparatively high molecular weights or numerous hydrogen bonding sites, or both. Only one class A dye, C.I. Direct Blue 218, showed reasonable nep coverage. However, this dye closely resembled members of classes B and C in its molecular weight and hydrogen bonding potential. This result is consistent with the theoretical basis of the ASTM differential dyeing test in which a class A dye is used to identify immature cotton fibres and a class B dye for mature fibre identification [12]. Class A dyes are characterised by their

TABLE 3

Relationship between number of amino and amido groups on dye structure and visible coverage of immature fibre neps

Dye (C.I.Direct)	No. of undyed immature neps on dyed fabric[a]	No. of amino or amido groups in molecule				
		NH_2	NH	CONH	NHCONH	Total
Black 22	3	4	1			5
Red 23	6			1	1	3
Green 26	7		3			3
Green 28	8	1	4			5
Brown 1	9	2				2
Black 80	10	2				2
Blue 218	11	2				2
Blue 1	11	2				2
Blue 120A	13	1				1
Red 80	13				1	2
Blue 76	14	2				2
Blue 126	15	1				1
Violet 9	16		1			1
Blue 78	16		1			1
Violet 7	17		1			1
Blue 81	18		1			1
Red 81	19			1		1

(a) Mean number of undyed neps on dyed samples out of a possible 25

high migration and low aggregation properties. Since immature fibres have more rapid rates of sorption and desorption than mature fibres, it is not surprising that dyes with high migration characteristics would produce relatively poor coverage of the thin-walled fibres. Aggregation of individual molecules into larger units within the fibre may account for some of the substantivity between direct dyes and cellulose. Since there is an established relationship between substantivity and dyeability of immature cotton [7], the observation that class A dyes with their low aggregation properties give inferior coverage of neps to class C dyes with their high aggregation properties is consistent with theory.

An interesting observation was that there appeared to be an inverse relationship between the number of amino or amido groups on the dye molecule and the number of undyed immature fibre neps (Table 3). C.I. Direct Blue 126 contains only one primary amino group per dye molecule and covered only 40% of the pre-identified immature cotton neps, whereas C.I. Direct Black 22 contains four primary and one secondary amino group and covered 88% of the immature fibre neps. Four of the dyes examined contained only one secondary amino group, and their nep coverage ranged from only 28 to 36%. The one dye molecule that contained three secondary amino groups, C.I. Direct Green 26, produced good coverage of 72%. These observations are consistent with the data presented by Giles [7], which relate substantivity to the presence of amino groups on the dye molecules.

Evaluation of mean nep count

Table 4 presents the average of the mean nep counts of twelve individual dyeings using each of the five dyes that

TABLE 4

Mean nep count of direct dyed cotton printcloth

Dye (C.I. Direct)	Mean nep count (per 100 cm^2)
Group 1[a]	
Black 22	4
Red 23	8
Green 28	13
Brown 1	14
Green 26	16
Group 2[b]	
Violet 9	20
Blue 78	26
Red 81	26
Blue 81	29
Violet 7	30

(a) Group 1 dyes covered a high proportion of isolated immature neps

(b) Group 2 dyes produced poor coverage of isolated immature neps

produced the best and the worst coverage of immature neps. In this portion of the experiment Linnert's grid procedure for calculating mean nep count per unit area of dyed fabric was used. The relative magnitude of the mean nep counts of the five dyes within each group were consistent with the data on coverage of isolated immature fibre neps from the earlier dyeing procedure.

CONCLUSIONS

Coverage of the various types of neps by direct dyes appears to be a function of fibre size and the degree of compaction of the fibres within the neps. Those neps composed of flat, compact masses of dead, extremely thin-walled fibres commonly appear as light specks regardless of the specific direct dye used. Neps composed of mature, small-diameter fibres or torn mature fibres are likely to be covered by most direct dyes. Differences among direct dyes in their ability to cover neps is most evident with those neps composed of immature fibres with some secondary wall development.

There appears to be a relationship between the number of amino or amido groups on a direct dye molecule and the dye's ability to produce visible coverage of neps composed of thin-walled fibres. There is no obvious relationship between the molecular size or shape of a dye and its relative ability to cover neps. There does appear to be some relationship between the aggregation and migration properties of direct dyes and their ability to cover neps.

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