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Dye Batch Variation in Textile Fibers

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ABSTRACT: Fiber samples from a number of different sources have been examined for dye batch variation. The manufacturers who supplied material included producers of knitting yarn, clothing, carpets, and car seat covers. Microscopy, microspectrophotometry, and thin-layer chromatography have been used for comparison of the dyes.

Degrees of variation were found. With some knitting yarns there was none at all, but some clothing fabrics showed large differences. Thin-layer chromatography is the best means of discriminating between dyes extracted from these materials.

The reasons for these results and their implications for the court-going officer are discussed.

KEYWORDS: forensic science, fibers, synthetic fibers, dyes, microscopy, spectroscopic analysis, chromatographic analysis, dye batch variation

It is common knowledge that all the yarn used to hand knit a jumper must be bought from one dye batch since the shade can vary so much between batches that differences in the final garment would be obvious.

Manufactured garments can also be used to illustrate this variation. An acrylic jumper examined in a case of sexual assault contained black fibers of two microscopically indistinguishable types. They differed only in that one had an additional color component which was detected on a thin-layer chromatogram of the extracted dye. The distribution of the two types indicated that the manufacturer had changed yarn halfway through the garment.

It was considered important to establish the incidence of dye batch variation and our ability to detect it. It is often put to a forensic scientist in court that the finding of fibers matching a suspect's jumper is not significant, as many thousands of the garments in question were produced. If, however, the dye combination is often changed during production, this conclusion would not be valid as relatively small numbers of garments are dyed in any one batch.

Sources of Samples

Retail clothing chains usually specify to manufacturers that the color of some product lines remain the same over long periods of time. This means, for example, that suit jackets and trousers can readily be matched even though they were made from different rolls of cloth.

Small cloth samples are often retained by the manufacturer on what are called "continuity cards." These form a record of the dyes used to produce a specific shade and are ideal material for a project on the variation of dye batches.

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A number of companies were approached for samples and were very generous in their response. Samples from five companies were examined in detail. All five wished to remain anonymous and will be described in this paper as Companies A through E.

Company A produced hand knitting yarns and provided batches from three samples:

A1 brown wool—16 batches,
A2 brown wool—16 batches, and
A3 blue wool—32 batches.

Company B was a car carpet manufacturer who again provided three groups of samples:

B1 brown nylon—20 batches,
B2 orange nylon—26 batches, and
B3 mustard nylon/viscose mixture—21 batches.

Company C was a large manufacturer of piece dyed knitted garments. They provided nine groups of samples:

C1 navy blue wool—14 batches,
C2 red wool—19 batches,
C3 brown wool—27 batches,
C4 navy blue acrylic—13 batches,
C5 green acrylic fibers—21 batches,
C6 camel acrylic fibers—10 batches,
C7 light-blue acrylic fibers—28 batches,
C8 light-pink acrylic fibers—22 batches, and
C9 navy blue 80% wool/20% nylon—11 batches.

Company D was another carpet manufacturer who provided six series of batches from their 80% wool/20% nylon range:

D1 red wool and nylon—10 batches,
D2 beige wool and nylon—10 batches,
D3 blue wool and nylon—10 batches,
D4 brown wool and nylon—10 batches,
D5 pink wool and nylon—10 batches, and
D6 purple wool and nylon—10 batches.

Company E produced fur fabric seat covers. They provided twelve batches from one of their products—a champagne colored fur fabric with an acrylic pile and polyester backing.

Where details of sampling were provided, batches were taken over periods from 2 to 25 months.

Experimental Procedure

The following techniques were used to compare one sample with another in each series.

Comparison Microscopy

Fibers from all the samples described above were mounted on standard glass slides in XAM neutral medium-improved white. They were covered by glass coverslips. The comparison microscope used (E Leitz [Instruments] Ltd) consisted of two Orthoplan microscopes connected by a comparison bridge with a binocular head. White light illumination was from quartz-iodine sources and ultraviolet (UV) light from mercury vapor sources.

Fibers were compared under transmitted white light and a broadband of UV and blue

light (BG 12 filter). The Leitz Ploemopak system was used for fluorescence examination. The powers of magnification for all comparisons were ×100 and 400.

Microspectrophotometry

No further preparation of the fibers was necessary for microspectrophotometry. Slides were placed on the stage of a Leitz Ortholux II microscope and observed under a magnification of ×220. Attached to the phototube of the microscope was a Nanospec 10S microspectrophotometer which was linked to a Nanometrics SDP 2000 spectral data processor.

Visible absorbance spectra between 390 to 730 nm were produced on a Tekman TE200 flatbed recorder. The absorbance scale varied from 0-0.1 to 0-2.3 A full scale according to the depth of dye in the fibers being compared.

Five spectra from different fibers in each sample were recorded and compared.

Thin-Layer Chromatography

Dyes were extracted from each of the fiber samples and further compared using thin-layer chromatography (TLC). Solvents used for dye extraction varied and are summarized in Table 1. A number of different solvents were also used for elution and these are detailed in Table 2. These were based partly on our own experience but mainly on the work of a number of authors [*1-5*].

Different methods of dye extraction were used for bulk or single fibers. In the case of bulk samples (small fiber tufts), extraction was carried out by placing the fibers in the bottom of clean Durham tubes, adding enough solvent to cover the fibers, and heating in a sand bath at 100°C until extraction had occurred. With single fibers, however, the method was that described by Cook [*6*]. The dye was extracted by placing the fiber and solvent into short lengths of capillary tube sealed at one end. The other end was subsequently sealed and the tube placed in a preheated oven again until extraction was complete. The tube was then broken after scoring with a carborundum stone.

The extracts were spotted 1 cm from the base of DC-Alufolien Kieselgel 60F 254 TLC plates and elution was completed in covered glass beakers. Plates were warmed under a hot air blower while spotting so that the spot size remained approximately 2 mm in diameter.

Initially all plates of bulk extracts were placed in methanol and run for a distance of 2 to 3 mm beyond the point of application to concentrate the dye into a sharp line. The plates were dried and finally developed to a distance of up to 3.5 cm from the original dye spot depending on the separation and clarity of the bands.

A standard dye solution was also included on each plate as an internal standard. The TLC results were compared visually and under long wavelength UV light.

TABLE 1—*Solvents used for dye extraction.*

Extraction Solvent	Conditions	Where Used
Pyridine : water (4 : 3)	90°C for 10 min	A1, A3, C2, C5, C9 (nylon) D1 (wool), D2 (wool), D3 (wool), D4 (wool), D5 (wool), D6 (wool)
2% Aqueous oxalic acid then pyridine : water (4 : 3)	90°C for 20 min 90°C for 10 min	A2, C1, C3, C9 (wool)
Pyridine : water (4 : 3)	100°C for 20 min	B1, B2, B3 (nylon), D2 (nylon), D3 (nylon), D4 (nylon), D5 (nylon), D6 (nylon)
Pyridine : water (4 : 3)	100°C for 10 min	B3 (viscose)
Formic acid : water (1 : 1)	100°C for 20 min	C4, C6, C7, C8, D1 (nylon)

TABLE 2—*Different solvents used for elution.*

Elution Solvent	Where Used
Chloroform : ethyl acetate : ethanol 14 : 4 : 3	A1
Chloroform : ethyl acetate : ethanol 7 : 2 : 1	A2, B1
n-butanol : ethanol : water : acetic acid: sodium sulphate 50 : 10 : 10 : 1 : 1	A3, B2
Chloroform : isopropanol : pyridine : acetic acid : water 6 : 8 : 3 : 1 : 1	B3 (nylon)
Pyridine : *n*-butanol : ammonia 3 : 2 : 2	B3 (viscose), E (acrylic), E (polyester)
Chloroform : methanol : water : ammonia 11 : 7 : 1 : 1	C1, C5, C6, C9 (wool), C9 (nylon), D1 (wool), D2 (nylon), D3 (nylon)
Pyridine : amyl alcohol : 10% ammonia 4 : 3 : 3	C2, D1 (nylon), D3 (wool)
Methanol : amyl alcohol : water : toluene 5 : 5 : 2 : 1	C3, D2 (wool)
Chloroform : methanol : toluene : water : ammonia 11 : 7 : 1 : 1 : 1	C4
n-butanol : acetone : ammonia : water : 5 : 5 : 2 : 1	C7, C8, D4 (wool), D4 (nylon), D5 (wool), D5 (nylon), D6 (wool), D6 (nylon), E (acrylic), E (polyester)

Infrared Spectroscopy

This technique was not used to monitor dye batch variation but only for any changes which may have occurred in the fiber substrates. Spectra of all synthetic fibers were recorded on a Perkin Elmer 157 infrared spectrophotometer fitted with a Beckman-RIIC beam condenser. The latter gave a 6 : 1 reduction in beam size. The techniques used were the lead foil method of Paterson and Cook [7] or the production of films by casting from solvent. The solvents used were *m*-cresol in the case of the nylons and dimethylformamide for the acrylic fibers.

Dye Class Identification

Dyes on all batches sampled were identified using the extraction and TLC methods described in Refs *1*, *4*, and *8*.

Results

The results obtained for each company in turn will be discussed. To simplify comparison microscopy of so many samples, one from each series of batches was used as a control and all other batches compared with it.

Company A

A1—All 16 batches were closely similar microscopically. Sample 6 was, however, slightly darker and could be distinguished from the others. The visible spectra showed a large degree of overlap and could not be used to distinguish one batch from another.

On extraction, the dye was identified as an acid type. Examination of the TLCs showed that Samples 1 to 8 and 13 to 16 were indistinguishable. Samples 9 to 12, however, were the same as one another, but differed from the remainder in one dye component. Five dye components were separated on each chromatogram, and the one nearest the origin was changed from purple to red in Samples 9 to 12. Both of these colors were represented in other spots on the chromatogram, therefore, it is not surprising that the differences did not show in the visible spectra.

A2—The 16 samples examined showed no differences in microscopy, visible spectroscopy, or TLC. The dye was identified as being premetallized.

A3—No variation between the 32 samples examined were observed using any technique. Acid dyes were used on these samples.

Company B

B1—These were samples of nylon 66 dyed with acid dyes. There were no detectable differences between the 20 batches, although there was some variation in the degree of delustering.

B2—Again, these were all samples of nylon 66 dyed with acid dyes. Of the 26 batches, Number 3 was microscopically slightly darker brown than the others. No other differences were noted.

B3—Samples from the 21 batches were examined after separation of the nylon and viscose components of the mixture. The nylon fibers were nylon 66 dyed with acid dyes. Fibers from all batches were indistinguishable.

The viscose fibers from all 21 samples were the same in microscopic appearance and visible spectrum. There was considerable variation in the TLCs however. Direct dyes of 3 colors were detected (blue, yellow, and orange/brown), but there were significant differences in R_f between batches, particularly in the blue component.

Company C

C1—This was easily the most variable of the series of batches we examined. Microscopy split them into two groups. Samples 1, 3, and 8 were indistinguishable from one another but different from the other eleven batches. The latter were all closely similar.

Chrome dyes had been used on the fibers, and enormous variation was obvious in both visible spectra and TLCs. The two techniques indicated that Samples 1, 3, and 8 were closely similar, as were Batches 9 and 10. Four, 7, 12, and 14 all appeared unique and the remainder (2, 5, 6, 11, and 13) were similar but quite different from all the others. On the TLCs, six major components were common to all fourteen samples and up to ten components were present in the most complex chromatograms (Fig. 1—unfortunately the black-and-white photograph does not reveal all components clearly).

C2—The red wools in this series of 19 samples were dyed with reactive dyes and 18 showed no variation in microscopy, visible spectroscopy, or TLC. The 19th sample, however (the last chronologically), was different in all respects (Fig. 2).

C3—All 27 of the brown wool samples were microscopically indistinguishable. None could be separated using visible spectroscopy, but considerable discrimination was achieved using TLC. A combination of at least 5 dyes had been used to achieve the final end shade. The dyes were premetallized.

C4—Direct dyes had been used on these 13 samples and no differences could be detected between them. The acrylic fibers had a methyl acrylate copolymer.

C5—No variation between these 21 samples was noted. Basic dyes had been used on the acrylic fibers that had a methyl acrylate copolymer.

C6—These were the same acrylic type as C4 and C5 and basic dyes had been used. Batch 8 was found to be slightly darker than the others when observed on the comparison microscope. This difference could not be detected using any other technique. No differences were noted between the other nine samples.

C7—Again these were acrylic fibers with a methyl acrylate copolymer and dyed with basic dyes. They were very pale green and appeared almost colorless under the microscope. No microscopic differences were observed, but Sample 3 had an additional blue component on TLC. This difference was not detected on the visible spectrum.

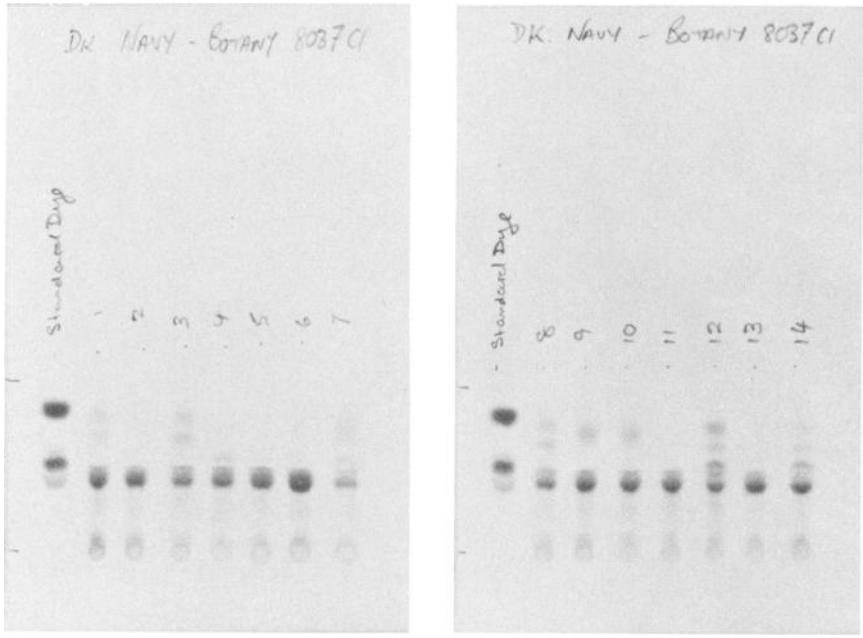

FIG. 1—*TLC plates showing dye batch variation between samples from Series C1.*

C8—These were acrylic fibers of the same type as C4 to 7 and dyed with basic dyes. No dye variation was observed in the visible spectra or TLC, but Sample 9 was darker than all other samples under the comparison microscope.

C9—The samples all consisted of wool and nylon fibers. The former were dyed with premetallized dyes and the latter with acid dyes. No variation was observed in any of the samples.

Company D

Acid dyes had been used on all the samples from this company.

D1—No differences in wool fibers were noted when comparison microscopy and visible spectroscopy were used. Thin-layer chromatography, however, showed distinct differences between Samples 1 and 2 and the other eight (Fig. 3).

The nylons were also microscopically indistinguishable. Again, Samples 1 and 2 were different from the others using TLC, but in this instance the differences were also obvious on the visible spectra.

D2—No variation could be detected in this series.

D3—In this series of blue carpet fibers there was a distinct difference in all methods of comparison between the first seven samples and the last three.

D4—No variation could be detected between any of these samples except using TLC. All ten batches contained three dye components—yellow, red, and blue. The blue component in Sample 9 had a different R_f from those of the other nine batches.

D5—Of the ten samples in this series, all appeared the same microscopically, but the first two were different on both visible spectroscopy and TLC.

D6—No variation could be detected in this series.

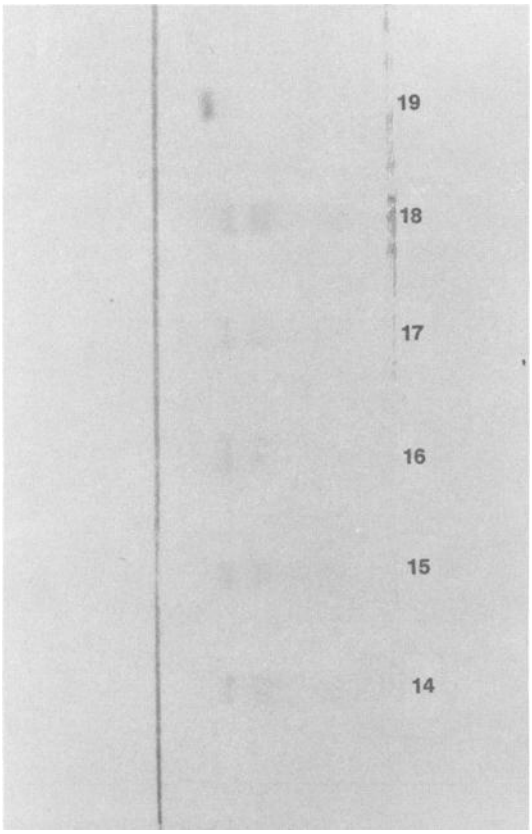

FIG. 2—*TLC plate showing dye batch variation between samples (14 to 19) from Series C2.*

Company E

The twelve samples from this company consisted of polyester and acrylic fibers. Both were dyed with basic dyes and no variation was detected between any of the batches.

Thin-Layer Chromatography of Single Fibers

Comparison microscopy and microspectrophotometry are performed on single fibers in casework and the same was true in this project. With TLC, however, larger quantities of material than normal were used. It was considered important, therefore, to attempt to distinguish single fibers from different batches using TLC.

The material chosen for this work was the C1 series which comprised 14 batches of navy blue wool dyed with chrome dyes. The extracts from these all contained a series of components which were seen as strong bands on the chromatogram. The other dyes present, which resulted in more variation than any other series of batches, were often there in much smaller quantities. It was felt that this series would be a suitable test for TLC on single fibers.

Fibers of varying lengths (2.0, 1.5, 1.0, and 0.5 cm) were extracted, and TLC carried out in the manner described for single fibers. Specific extraction and elution conditions can be seen in Tables 1 and 2 (C1).

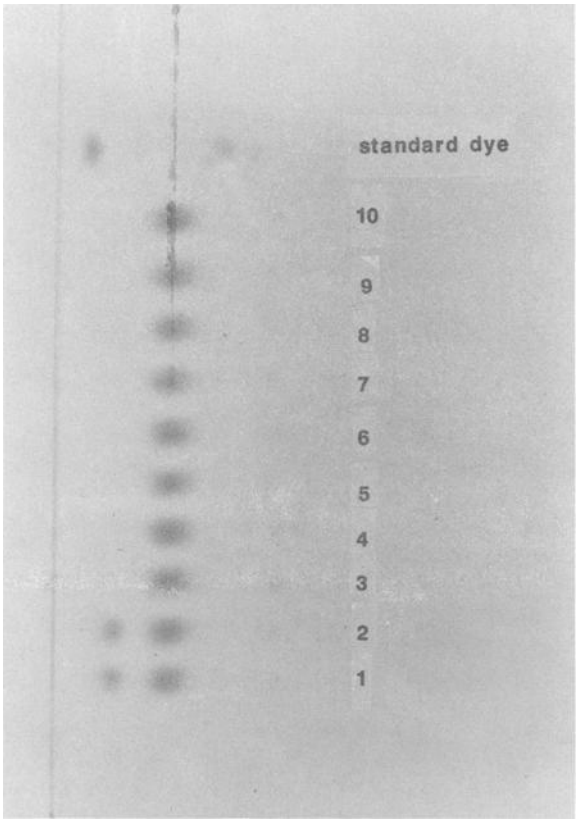

FIG. 3—*TLC plate showing dye batch variation between samples from Series D1.*

The results indicated that all batch differences could be detected on the 2.0-, 1.5-, and 1.0-cm lengths of fiber. However, at 0.5 cm, some of the weaker spots were not visible.

Discussion

No variation was detected in 9 of the series of batches examined in this project (13 fiber types—bearing in mind that some materials consisted of 2 fibers). However, variation was found in 18 fiber types. There are a number of reasons why detectable differences in dye batches can occur including the following:

1. The dyers may alter one or all of the components used in the dye mixture to reduce costs or produce a more effective dyeing.
2. A single component may change as a result of supply difficulties. The dye manufacturer will occasionally change some of the dyes within his range.
3. Many dyers use the process of "topping up." This involves the addition of components to the dye bath to adjust the final cloth shade to a predetermined standard.
4. A number of dyers will admit to overdyeing pale shades that "went wrong" to save wastage of the material. Redyeing occurs to a much darker shade.
5. It is acceptable for dyes listed in the color index to contain up to 5% impurities (deliberate additions using shading colors).

TABLE 3—*Relative value of the different comparison techniques.*

No Variation Detected	Variation Detected		
	Microscopy	Visible Spectroscopy	Thin-Layer Chromatography
A2, A3, B3 nylon, C4, C5, C9 wool, C9 nylon, D2 wool, D2 nylon, D6 wool, D6 nylon, E polyester, E acrylic.	A1, B1, B2, C1. C2, C6, C8, D3 wool, D3 nylon.	C1, C2, D1 nylon, D3 wool, D3 nylon, D5 wool, D5 nylon.	A1, B3 viscose. C1, C2, C3, C7, D1 wool, D1 nylon, D3 wool, D3 nylon, D4 wool, D4 nylon, D5 wool, D5 nylon.

The relative value of the different comparison techniques is illustrated in Table 3. Comparison microscopy will occasionally discriminate between batches when all other methods fail to do so. This can be seen in Batches B1, B2, C6, and C8 where a sample may have a slightly different depth of dyeing or the fiber substrate has more or less delusterant. The latter, of course, is not strictly a change in the dye, but it does illustrate the value of microscopy.

Visible spectroscopy will sometimes discriminate where microscopy fails, for example, C1 and D1 nylon. This would be particularly important where fibers were too small for dye extraction and TLC.

In many instances TLC highlighted differences between batches that were not detected with microscopy or visible spectroscopy. Examples of this can be seen in Samples A1, B3 (viscose), C3, C7, and D1 (wool). In no cases did visible spectroscopy discriminate where TLC did not. This is another example of the power of this simple technique and an illustration of how essential it is as a method of comparison.

It has been shown that dye batch variation has occurred in some samples from each of Companies A to D. However, it should not be presumed that it will never be seen in car seat covers (Company E). In fact, quite the reverse was shown by Wiggins and Allard [9].

Problems can arise when small fiber fragments are examined (under 1 cm in length). In those circumstances, differences between batches may be missed on TLC especially where the banks are weak.

The significance of this work to the court-going officer is well illustrated by the case outlined in the introduction. Both types of black acrylic fiber were found on the victim. The fact that the manufacturer had changed batches halfway through the garment transformed good into exceptional evidence as that garment was probably unique. Admittedly this was a very unusual case, but if it can be proved that batch variation is a feature of a manufacturing process (for example, Series C1), then the fibers findings will be considerably enhanced.

There can be no doubt that background information of this kind can only be obtained from the manufacturers themselves. Wherever possible, therefore, in cases where fiber evidence is likely to be significant, we attempt to contact manufacturers to find out information about their dyeing processes and the numbers and distribution of garments made. This can be very difficult, particularly if the item is unlabelled or made abroad.

Acknowledgments

We would like to thank numerous contacts in the textiles and dyeing industry for their help and samples without which this project would not have been possible. Thanks are also due to Zillah Barnes for her technical assistance and the photography department at the Metropolitan Police Forensic Science Laboratory for Figs. 1 to 3.

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