A preliminary investigation into the low washfastness of indigo carmine during wet cleaning

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Abstract

This research sought a basic level of understanding of the variability exhibited by indigo carmine during conservation wet cleaning, by studying its inherent properties. Thus far, causes and mechanisms behind indigo carmine bleeding have been minimally explained in published literature.

A methodological approach was adopted to answer if the dye's low washfastness showed variations according to dyeing conditions and formulations. Historical dye recipes were critically reviewed to find trends in use and manufacture. After identifying relevant variables in preparation and dyeing methods, different formulations of indigo carmine were recreated. Dye transfer and solubilisation for replica wool samples were experimentally assessed by eye-examination and colourimetry. For the first time, a study that discusses relations between lightfastness and washfastness was developed, showing that numerous interconnected factors impact on indigo carmine's wet behaviour. Further experimentation with historical samplers allowed for comparison between theoretical arguments and expectations from practical conservation experience.

This research contributed to the understanding of the historical and technological context of indigo carmine production. It concluded that assumptions about the dye's properties led to an overly simplistic view of its behaviour during wet cleaning. Informed decision-making is needed, balancing the benefits of wet cleaning against the likelihood of dye loss and colour change.

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Contents

List of Figures

List of Tables

List of Abbreviations and Acronyms

AATCC	American Association of Textile Chemists and Colorists
AIC	American Institute for Conservation of Historic and Artistic Works
cmc	critical micelle concentration
CTCTAH	Centre for Textile Conservation and Technical Art History
DHA	Dyes in History and Archaeology
g	grams
h	hour / hours
IIC	International Institute for Conservation of Historic and Artistic Works
ICOM	International Council of Museums
ICOM-CC	International Council of Museums – Committee for Conservation
IR	infrared
IUPAC	International Union of Pure and Applied Chemistry
lbs	pounds
min	minutes
mL	mililitres
o.w.f.	of weight fibre
oz	ounces
pH	power of hydrogen
RH	relative humidity
TSG	Textile Specialty Group
UofG	University of Glasgow
UV	ultraviolet
w/w	weight by weight

1. Introduction

During aqueous conservation treatments, the low washfastness of indigo carmine is often evidenced by blue colour that bleeds from the object into the wash-bath. In some cases, the solubilised dye may also transfer and stain adjacent fabric, creating visually displeasing haloes.[1] Although dye transfer can be controlled to minimise staining, textile conservators try to avoid any eventualities by addressing the risks from the start. The basis of this research was formed after observing the variable behaviour of indigo carmine during wet cleaning practice and realising that little is known about the factors behind its low washfastness, leaving conservators to manage unexpected situations.

1.1 Indigo Carmine in Context

Before the mid-eighteenth century, the options for dyeing blue textiles were limited. Iris, hollyhock flowers, berries, and logwood were used,[2] but dyers mostly relied on natural indigotin-containing plants to obtain long-lasting blues. For centuries, these plants were cultivated for local dyeing,[3] although this was laborious and expensive. In 1883, the development of synthetic indigo overtook natural indigo production because it allowed for consistent supply and quantity.[4] However, dyeing remained more complicated than procedures for other natural dyes because the preparation of indigo, natural or synthetic, requires reduction to deposit on the fibres followed by oxidation in air to fix the colour.[5]

Since 1740, a straightforward option for direct-dyeing became available to dyers when, in Saxony, Johann Christian Barth invented indigo carmine, the first semi-synthetic dye.[6] By treating natural indigo powder with concentrated sulfuric acid, he created a blue,

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[1] Katherine Sahmel et al., "Removing Dye Bleed from a Sampler: New Methods for an Old Problem," in *AIC 40th Annual Meeting, May, Postprints vol. 22*, ed. Amanda Holden et al., 78-90 (Albuquerque: TSG, 2012).

[2] Dominique Cardon, *Natural Dyes: Sources, Tradition, Technology and Science*, (London: Archetype Publications, 2007), 242-272.

[3] Jenny Balfour-Paul, *Indigo*, (London: Archetype Publications, 2006), 2, 90, 97, 100-116, 234. Notably from indigo (Indigofera), woad (Isatis) and dyer's knotweed (Polygonum).

[4] Cardon 2007, 336.

[5] Cardon 2007, 335-353.

[6] A discrepancy in dates was found: earlier publications mention 1740, while newer sources mention 1743, after Lowengard's.
Cardon 2007, 362.
Sarah Lowengard, *The Creation of Colour in 18th-Century Europe*, (Columbia: Columbia University Press, 2006).

water-soluble dyeing matter. Based on the number of indigo carmine recipes published throughout the nineteenth-century,[7] it can be suggested that dyers quickly welcomed the product. Some advantages of indigo carmine over indigo vats include time-efficiency, consistency, and ease of the procedure.[8] Indigo carmine was also a cheaper substitute since more fabric could be dyed using the same amount of indigo powder, and a broader range of tonalities was obtained.[9] Nevertheless, low colourfastness was a recurring for dyers and consumers.[10,11,12]

Throughout the eighteenth and nineteenth centuries, there was no consensus in terminology between dyers, causing naming conventions to change across time and place. The dyestuff was first named Saxon blue, although it is now more commonly known as indigo carmine. The terms found in historical recipes are vast, including words such as chemique, composition, indigo extract, and, misleadingly, Prussian blue, an organometallic pigment of similar blue shade (Table 1.1). The name 5'5-indigodisulfonic acid sodium salt is used by conservation scientists, making reference to the chemical structure (Figure 1.3).

Dominique Cardon, *The Dyer's Handbook: Memoirs of an 18th-Century Master Colourist*, (Havertown: Oxbow Books, 2016) 107.

[7] Appendix 2.

[8] Lowengard 2006, 98.

[9] David Smith, *The English Dyer,* (Manchester: Palmer and Howe, 1882) 253.

[10] Appendix 2.

As cited in Sarah Lowengard, "Colour Quality and Production: Testing Colour in Eighteenth-Century France," *Journal of Design History*, vol. 14, no. 2 (2001): 91-103.

[11] Claude-Louis Berthollet, *Elements of the Art of Dyeing*, trans. William Hamilton, (London: Stephen Couchman, 1791) 98-102.

[12] Ferguson, et al., *The Dier's Assistant in the Art of Dying Wool and Woolen Goods,* trans. and ed. James Haigh, (Philadelphia: James Humphreys, 1810) 242.

Table 1.1. Terminology Referring to Indigo Carmine	
Term	**Description**
3,3'-dioxo-2,2'-bisindolyden-5,5'-disulfonic acid disodium salt	IUPAC name
blue and green vitriol	Indigo dye mixed with oil of vitriol (sulfuric acid)
CI Acid Blue 74	C.I. denomination when synthetic indigo is used.
CI Natural Blue 2	C.I. denomination when natural indigo is used.
chemique, chemic, chemick, chymick, chemical blue, chemic blue	Common names given by eighteenth-century dyers
composition or compound	Common names given by eighteenth-century dyers
indigo carmine	The use of this name seems to start in the nineteenth-century. It is now considered the common name for the dyestuff and used in the industrial context.
indigo disulfonic acid or disulfonic acid	Most papers written by conservation scientists use this term.
Indigo paste, indigo extract, liquid extract or extract	Name given by eighteenth and nineteenth-century dyers referring to the fact that no mordant was required.
Prussian blue	One of the names given by French dyers to Saxon blue in the mid-eighteenth century. It does not correspond with the blue pigment known today by this name.[13]
Saxon blue or green	Eponymous name used by eighteenth and early nineteenth-century dyers.
sour extract	J.J. Hummel (1888) uses it specifically to refer to an extract with free sulfuric acid.[14]
Sulfate/sulphate of indigo	Name suggested by the dyer Edward Bancroft (1814).[15]

It is complicated to define indigo carmine's spread across world-wide textile collections since few studies have aimed to rigorously identify it. Textile conservators have often encountered the dyestuff in green and blue threads from British and European nineteenth-century samplers.[16,17] However, its presence has also been reported in Viennese folding-screens,[18] Oriental rugs,[19] Kashmir and Paisley shawls,[20,21] William Morris' early

[13] Michael Douma, "Prussian Blue" in *Pigments Through the Ages*, WebExhibits, 2001. http://www.webexhibits.org/pigments/indiv/recipe/prussblue.html (accessed June 24, 2018).
[14] J.J. Hummel, *The Dyeing of Textile Fabrics,* (London: Cassell & Company, 1888) 317.
[15] Edward Bancroft, *Experimental Researches Concerning the Philosophy of Permanent Colour,* (Philadelphia: Thomas Dobson, 1814) 172-173.
[16] Judith Hofenk de Graaff, *The Colourful Past: Origins, Chemistry and Identification of Natural Dyestuffs*, (London: Abegg-Stiftung and Archetype Publications, 2004) 258-261.
[17] Sahmel et al.
[18] Matthijs de Keijzer et al. "Indigo Carmine: Understanding a Problematic Blue Dye," *Studies in Conservation* 57 (2012): S87-S95. doi: 10.1179/2047058412Y.0000000058
[19] Jennifer Barnett, "Synthetic Organic Dyes, 1856–1901: An Introductory Literature Review of Their Use and Related Issues in Textile Conservation," *Studies in Conservation* 52 (2007): 67-77. doi: 10.1179/sic.2007.52.Supplement-1.67
[20] Balfour-Paul, 116.
[21] David Duff, Roy Sinclair, and David Stirling, "The Fastness to Washing of Some Natural Dyestuffs," *Studies in Conservation* 22:4 (1977): 170-176. http://www.jstor.org/stable/1505833

work,[22] needlework accessories,[23] Subarctic Athapaskan quillwork,[24] and as ink for underdrawings.[25] In summary, the variety of objects dyed with indigo carmine suggests that conservators could encounter the dye more often than realised.

Figure 1.1. CTC.425 sampler, 1816, 34 x 46 cm.
Green and blue threads dyed with indigo carmine, detail enlarged on front (bottom) and back (top)
Private Collection. © CTCTAH, University of Glasgow, 2018. Photo by Chuance Chen.

Contested views exist about how quickly indigo carmine fell out of favour. Cardon suggests it was discredited in the early nineteenth-century;[26] Hofenk de Graaff limits its use to the eighteenth and nineteenth centuries;[27] Wood establishes that it was most favoured from 1740-1850, when there was no competition from synthetic dyes;[28] and artists and

[22] G.W Taylor, "Identification of Dyes on Early William Morris Embroideries from Castle Howard," Textile History 16:1 (1985): 97-102. doi: 10.1179/004049685793701197
[23] Anita Quye and Jan Wouters, "An Application of HPLC to the Identification of Natural Dyes," in *10th Meeting of DHA, held at the National Gallery, London 1991*, ed. Walton Rogers, 48-54 (York: Textile Research Associates, 1991).
[24] LG Troalen et al., "A Multi-analytical Approach Towards the Investigation of Subarctic Athapaskan Colouring of Quillwork and its Sensitivity to Photo-degradation," *Microchemical Journal* 126 (2016): 83-91. doi: 10.1016/j.microc.2015.11.053
[25] Balfour-Paul, 210.
[26] Cardon 2016, 108.
[27] Hofenk de Graaff, 258-261.
[28] Susan Wood, "A Preliminary Investigation into Green Dyed Embroidery Threads on Samplers During the Period 1780 to 1849 and their Susceptibility to Dye Bleeding" (MA dissertation, Textile Conservation Centre, University of Southampton, 2006) 37.

craftsmen still recommend its use for dyeing, expanding its timeframe to the twentieth-century.[29] These conflicting time-spans indicate that indigo carmine's presence on textiles is difficult to establish solely by date. As explained, the issue gains complexity because of differences in terminology.

The broad time-span indicates that synthetic indigo could have been used as the starting compound for indigo carmine.[30] Early discussions address plausible differences between indigo types,[31] however, it is unknown whether indigo carmine dye is the same irrespective of the parent compound. There are currently no analytical means to properly distinguish between indigo types. These aspects show that more research is needed to provide foundations for indigo carmine object-based studies.

1.2 Technical Aspects

Indigo carmine is a levelling acid dye with strong affinity for proteinaceous fibres, bearing negative charges that form ionic bonds with the substrate.[32] Levelling acid dyes rely strongly on acidic conditions during dyeing for exhaustion, uptake and even distribution to occur.[33] Despite sharing the chromophoric structure of indigotin (the main colouring component of indigo),[34] the presence of sulfonate groups significantly modifies the behaviour of the dye as it confers water solubility and allows for brighter hues than the parent compound. The sulfonation also impacts on the poor lightfastness and washfastness properties[35] – which are indicators of low strength in the dye-fibre bond.[36]

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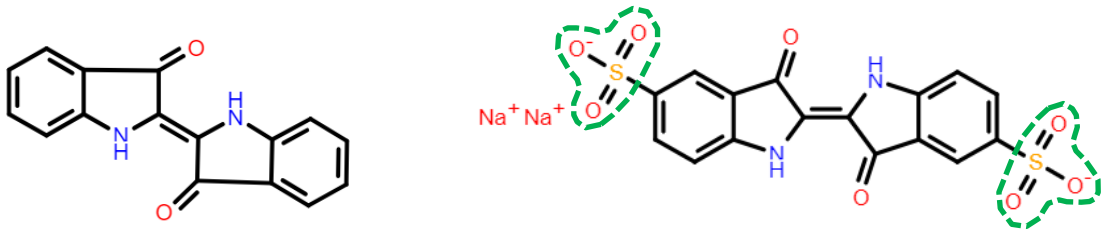
[29] Trudy Van Stralen, *Indigo, Madder & Marigold: A Portfolio of Colors from Natural Dyes*, (Colorado: Interweave Press, 1993) 112-120.
[30] de Keijzer et al.
[31] Alfred Schmidt, "Substitutes for Natural Indigo in Wool Dyeing and the Artificial Indigo," *Journal of the Society of Dyers and Colourists* 14:3 (1898): 63-74. doi: 10.1111/j.1478-4408.1898.tb00143.x
[32] Appendix 1.
[33] David Duff and Roy Sinclair, *Giles's Laboratory Course in Dyeing*, (Bradford: Society of Dyers and Colourists, 1989), 17-18, 67.
[34] Cardon 2007, 338.
[35] Duff and Sinclair, 67-68.
[36] K.R. Millington, "Colorfastness," in *Engineering of High-Performance Textiles*, ed. Menghe Miao and John Xin, (Kidlington: Woodhead Publishing, 2017) 159-160.



Figures 1.2 and 1.3. Chemical formula of indigotin (left) and indigo carmine (right), which has sulfonate groups, as marked with a dotted line.
Na+ are counter ions, added after treatment with a sodium salt, such as sodium sulfate.
ChemSpider, © Royal Society of Chemistry, 2015.

Colourfastness is mostly defined by the structure of the dye-fibre bond and the dyeing conditions.[37] Other factors of indigo carmine production that may affect colourfastness include the size of the granules, the mixture with other dyes for shading, and the presence of additives or impurities. Furthermore, environmental factors – such as light – can alter the stability of the dye-fibre system. This has led to the development of colourfastness tests by twentieth-century manufacturers, including artificial ageing. It is possible that some of the above factors affect indigo carmine's colourfastness, thus causing variations on its wet behaviour during treatment.

Despite indigo carmine's numerous advantages, the major fault of its poor fastness has always been an issue. Industrial production has favoured other dye alternatives for obtaining similar colours. However, historical objects constituted by sensitive dyes endure in museum and private collections. As explained in the next section, conservation can prove challenging when aqueous treatments are involved.

1.3 Wet Cleaning of Textiles with Indigo Carmine Elements

In the past, some textile conservators followed a domestic approach where 'hygienic purity' was sought and cleaning was routinely completed, but current practice recognises the risks of over-cleaning.[38] Since wet cleaning is an irreversible treatment, decisions are made regarding the goals of treatment, method, and extent of the process. In the past, localised cleaning,[39] solvent cleaning, and isolation[40] have been tested and used for

[37] Ibid, 155-156.
[38] Dinah Eastop and Mary Brooks, "To Clean or Not to Clean: The Value of Soils and Creases (1996)," in *Changing Views of Textile Conservation*, ed. Mary Brooks, and Dinah Eastop, 228-235 (Los Angeles: Getty Conservation Institute, 2011).
[39] Sahmel et al., 82.

avoiding indigo carmine bleed or reducing staining; yet some of these options are not accessible for smaller textile conservation studios. Overall, wet cleaning remains the desired course as it is believed to allow sufficient control of dye migration with minimal action.

Paradoxically, by solely looking at the risk of dye-bleed, wet cleaning might be rendered unfeasible. Occasionally, risks are outweighed by the physical, chemical, and aesthetic benefits of wet cleaning,[41] making conservators recognise the compromises to be made and take additional preventive measures to ensure the object's integrity. However, results might not be successful, impacting on aesthetics and condition. Not only does staining undermine aesthetic values, but it also presents tangible proof of 'an accident' taking place. Preventing dye solubilisation and migration is problematic for conservators in practical and theoretical terms and, so far, a consensus on how to approach indigo carmine elements has not been discussed.

Figures 1.4 and 1.5. Turkish towel and cloth with metallic threads, 19th century.
Staining likely caused by indigo carmine, showing blue haloes nearby green or blue threads
Karen Finch Reference Collection. © CTCTAH, University of Glasgow, 2018. Photo by author.

1.4 Research Question, Aims, and Objectives

Based on the observation that objects dyed with indigo carmine pose difficulties for standard wet cleaning treatments, a better understanding of the dyestuff's wet behaviour is needed. Research into which properties of indigo carmine result in low washfastness would offer a foundation to improve current understanding in the context of textile conservation. Hence, the research question was formulated:

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[40] de Keijzer et al., S94.
[41] Ágnes Timár-Balázsy and Dinah Eastop, *Chemical Principles of Textile Conservation*, (Oxford: Butterworth-Heinemann, 1998) 185-194.

DOES THE WASHFASTNESS OF INDIGO CARMINE SHOW VARIATIONS ACCORDING TO INHERENT PROPERTIES DETERMINED BY DYEING CONDITIONS AND FORMULATIONS?

In order to answer this, three aims were established:

i. To distinguish variations in traditional dyeing practices of indigo carmine.
ii. To identify patterns in wet behaviour between formulations of indigo carmine.
iii. To correlate the degree of solubilised dye with variations in dyeing conditions.

The dissertation's objectives included:

- To complete a literature review that reflects current knowledge on the topic.
- To conduct a review of indigo carmine's dyeing recipes amongst historical sources in order to find significant variations and trends in dyeing conditions.
- To find a method that allows for reproducing and preparing replica dyed samples.
- To measure dye solubilisation of replica samples through the simulation of a conservation wet cleaning procedure.
- To measure colour change after exposure to water on replica samples.
- To provide useful and accessible recommendations for textile conservators dealing with aqueous treatments on objects with indigo carmine presence.

This methodology was chosen to provide an answer to the research question; however, the experimental phase resulted in unexpected findings that led to additional experiments to clarify the results. The preliminary nature of this research was used to design and complete two more experiments as the project evolved. The corresponding aims and objectives of the new experiments are introduced in those chapters.

Overall, this research contributes to the field by raising discussion on a topic that has been under-researched in the past, as shown through the literature review. This project is founded on the basis that conservators strike a balance between the known current needs and the future possible needs of an object to prevent loss in value.[42] It is expected that this preliminary investigation will open paths for future research on the topic to promote best practice for this kind of objects.

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42 Barbara Appelbaum, *Conservation Treatment Methodology,* (Boston: Butterworth-Heinemann, 2007) 368.

1.5 Outline

This dissertation is divided into three sections: the BACKGROUND describes the key terms and information that shape this research. The EXPERIMENTAL PHASE explains the samples preparation, data collection, and results of each experiment. Finally, the third section discusses the CONCLUSIONS of the project.

Section 1 is composed of three chapters. In the introduction, the context and technical aspects of indigo carmine are presented. The research question, aims and objectives are posed to narrow the scope of the investigation. The next chapter presents the literature review, providing a critical evaluation of the existing body of knowledge. Finally, historical dyeing recipes are analysed to explain indigo carmine's history and use.

Section 2 comprises four chapters. It defines the test groups and variables used in the dyed replica samples for experimentation. Each experiment and research aim is discussed in an individual chapter, including methodology, results, discussion, and conclusion.

To conclude, Section 3 evaluates the project, summarizes findings, and suggests future areas of research. The appendices are gathered at the end of this dissertation to provide an insight into the theoretical framework used, as well as raw data that could be of academic and scientific interest. Information related to materials and health and safety procedures is also included.

2. Literature Review

2.1 Dealing with the Problem: Low Washfastness in Textile Conservation Practice

Textile conservators deal with the issues of indigo carmine's washfastness in two scenarios: when the object has embedded soiling and requires wet cleaning, or when it has already been stained by dye re-deposition and requires haloes to be reduced.

Since the main aim of wet cleaning treatments is to solubilise certain types of soiling from the fibres, the choices of detergent, water type, and pH range are based on the fibre needs and soiling nature.[43] Although it could be argued that the presence of fugitive dyes is a secondary consideration, conservators consider the degree of dye solubilisation an important factor to document and visually assess. This is usually evaluated in practice by collecting samples of the wash-bath solutions.

Figure 2.1. Solubilised blue dye, likely indigo carmine, during wet cleaning treatment.

Written documentation generated at the CTC shows that encountering fugitive blue dyes in practice is more common than what is shown in published sources. Treatment reports tend to include testing for washfastness and show the selection of the wash-bath solution for minimal dye bleed. Despite the risk of dye solubilisation, wet cleaning treatments carried on when the condition assessment signalled that a positive change was possible and desirable. However, when reports are seen as a whole, it becomes evident that controlling indigo carmine bleed is variable.

Dilute acetic acid has been tested by students to provide acidic conditions in the wash-bath solution to prevent bleeding of acid dyes – although chemistry of this process is

[43] Tarja Reponen "The Effects of Conservation Wet Cleaning on Standard Soiled Wool Fabric: Some Experimental Work," in *ICOM-CC 10th Triennial Conference 2008 Preprints,* ed. Janet Bridgland, 321-326 (London: James & James, 1993).

unclear.[44] The observations about its effectiveness are contradictory: Knight reported that it reduced bleeding, while Gabbutt said it increased.[45,46] During wetting, the bleeding stage also proved inconsistent: most loss happened during initial soaking for Schmitt's object;[47] Gabbutt reported that the immersion with detergent might have triggered the fugitive behaviour of the dye;[48] and Kinti observed that dye solubilisation occurred after only 10 minutes.[49] It should be noted that dye solubilisation at an early stage is conflicting as it is not advised to remove objects from the wash-bath during the induction time, before the rapid soil release stage is reached.[50]

Conservators mostly agree about controlled drying being crucial to prevent dye absorption in adjacent fabric.[51] The suggestion is to favour drying of elements with fugitive dyes over surrounding areas to avoid staining by dye migration.[52] It is well-known that staining depends on the rate of diffusion, where particles move from regions of higher to lower concentration.[53,54] However, a disadvantage of accelerating the drying process is that little time is left for weave alignment, regardless of using suction, blotting with absorbent materials,[55] or air circulation.[56] Wood suggests this topic be explored further to confirm if drying is the most problematic stage for wet cleaning this type of object.

The lack of clarity and the high variability of why and when dye bleed occurs shows that more research is needed to understand the situation. So far, washfastness tests have been unclear indicators of bleeding during practice, and current practice has not provided

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44 Timár-Balázsy and Eastop, 216.
45 Beth Knight (unpublished), "Treatment Report CTC.246," (MPhil in Textile Conservation, UofG, 2016).
46 Freya Gabbutt (unpublished), "Treatment Report CTC.210," (MPhil in Textile Conservation, UofG, 2015).
47 Emma Schmitt (unpublished), "Treatment Report CTC.75," (MPhil in Textile Conservation, UofG, 2013).
48 Gabbutt (unpublished).
49 Maria Kinti (unpublished), "Treatment Proposal CTC.RC11," (MPhil in Textile Conservation, UofG, 2014).
50 Ágnes Timár-Balázsy, "Wet Cleaning of Historical Textiles: Surfactants and Other Wash Bath Additives," *Reviews in Conservation, IIC* 1 (2000): 55.
51 Kathy Francis, "Predicting the Drying Behavior of Textiles" in *AIC 20th Annual Meeting, Postprints vol. 2,* ed. Suzanne Thomassen-Krauss et al., 1-6 (Buffalo: TSG, 1992).
52 Timár-Balázsy and Eastop, 97.
53 Millington, 165.
54 Sarah Foskett and CTCTAH (unpublished), *Wet Cleaning Handbook,* MPhil in Textile Conservation, UofG, 2017, 20.
55 Karen Finch and Greta Putnam, *Caring for Textiles,* (London: Barrie & Jenkins, 1977) 48.
56 Wood, 35.

useful parameters, formulae, or guidelines to evaluate this problem. It is unknown if the solubilised blue matter is excess dye, loose dye molecules, or constitutive dyeing matter. In this sense, it becomes apparent that conservators have significant practical experience in assessing dye bleed, and can contribute to the assessment of patterns for indigo carmine's wet behaviour. This understanding is crucial to formulate the best course of action needed to control risks.[57]

2.2 Scope and Key References

Only two articles scientifically address indigo carmine within conservation, although many papers have been published with regards to its broader uses as a colourant in the food and cosmetic industry, dyestuff for arts and crafts, pH indicator, biological stain, detection reagent for nitrates and chlorates, toxic component for sea-life, and wastewater pollutant. Besides presenting the relevant sources on indigo carmine, this literature review seeks to select valuable information that is scattered in publications from other areas of knowledge.

The article "Indigo Carmine: Understanding a Problematic Blue Dye" is currently the only accessible publication dedicated solely to the topic from a conservation perspective, and was written by a cross-disciplinary group of European heritage scientists and conservators.[58] It provides a solid starting point with the washfastness issues of indigo carmine, names some of the analytical techniques for identification, and provides an overview of the dye's history. The content is easily understandable and the suggested ways of responding to poor washfastness are representative of the few standard techniques available. However, degradation effects are described vaguely and the mechanisms omitted entirely, leaving conservators without the basic information required to apply science to practice. The participation of the authors in international conferences and student projects suggests that some findings might not be published, and it is unclear if the research is on-going.[59,60,61]

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[57] Cordelia Rogerson and Paul Garside, "Increasing the Profile and Influence of Conservation - An Unexpected Benefit of Risk Assessments," *Journal of the Institute of Conservation*, 40:1 (2017): 34-48. doi: 10.1080/19455224.2016.1214848

[58] de Keijzer et al.

[59] Matthijs de Keijzer et al. (unpublished), "The Early Synthetic Organic Dyestuffs: Indigo Carmine: Favored but Fading," in *29th Meeting of DHA, held at Gulbenkian Foundation, Lisbon, 12 November 2010*.

In 2012, a multidisciplinary team of conservators and scientists at the Philadelphia Museum of Art published one of the few known treatments where indigo carmine is clearly identified with analytical techniques, and its low washfastness is addressed and controlled.[62] Gels were tested to minimise staining on a nineteenth-century Scottish sampler, selecting agarose to deliver a chelating solution to the stained areas while the threads prone to bleeding were confined with cyclododecane. Although this case study shows a successful example of the application of conservation science into practice, it could be argued that this time-consuming treatment can only be implemented on certain objects and by institutions with specific infrastructure. Therefore, it represents an unfeasible option for most textile conservation studios on tighter budgets.

Wood's dissertation is another key reference on the topic.[63] Historical samplers were used to explore control methods for bleeding of green threads by modifying wash-bath solutions during wet cleaning. Identification of indigo carmine is only completed with solubility tests. The degree of dye bleed is described in relation to variations on water type and surfactant. Her conclusion is that the use of acidic conditions and non-ionic detergents provide less risk of dye bleeding. The major drawback of this work is that data was taken on a per-object basis, making it impossible to draw broad conclusions.

The literature review shows that research on indigo carmine's washfastness is scattered across various references, inhibiting the consolidation of theoretical and practical knowledge needed to address the dye's tendency to bleed during wet cleaning. Furthermore, none of these sources explain why indigo carmine has such unstable properties or why it solubilises in water. This leaves important questions regarding the dyestuff's wet behaviour and the effects of conservation treatments.

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[60] Maarten van Bommel and Enrica Fantini (unpublished), "Unravelling the Colour Palette of 19th Century Furniture: Reconstruction and Analysis of Synthetic Dyes Used as Stains," in *31st Meeting of DHA, held at Antwerp, Belgium, 2012*.

[61] Marguerite Caycedo, "Identification of Fifteen First Priority Textile Dyes from the Schweppe Collection with Raman and Surface Enhanced Raman Spectroscopy" (MSc dissertation, University of Amsterdam, 2012). https://esc.fnwi.uva.nl/thesis/centraal/files/f446931068.pdf (accessed May 17, 2018).

[62] Sahmel et al.

[63] Wood.

2.3 Gaps in Knowledge

In 1999, Scharff claimed that conservators should understand the history of early synthetic dyestuffs and the chemistry behind dye bleed to inform practice.[64] She also emphasised that poor dye washfastness impacts on conservation treatments and that little was found on the literature on how to minimise bleeding. Unfortunately, these arguments remain valid twenty years later.

The core texts of textile conservation offer little insight into dye bleed and disregard the particularities of indigo carmine. In *Chemical Principles of Textile Conservation,* a brief section is dedicated to washfastness, mostly linking problematic issues to pH.[65] In *The Textile Conservator's Manual,* a technical explanation to test washfastness is provided, as well as warnings about the use of fixing agents.[66] Although Tímár-Balázsy's article on stain removal mentions accidental stains, it entirely ignores dye bleed,[67] despite blue staining being a common feature within sampler collections.[68]

In *Caring for Textiles,* the authors rely on personal experience to provide cautionary statements about "one green colour, very much used for embroidery skills, which is a great culprit"[69] for bleeding into surrounding areas. Even if indigo carmine is not explicitly targeted, the description matches its behaviour. Although there are several explanations why in-depth study of the dyestuff has not been completed yet, the fact that indigo carmine is barely mentioned by name in publications calls into question if proper identification is the major factor hindering research.

Over the past 30 years, heritage scientists have developed new means of identifying indigo carmine (Table 2.1), but these sophisticated methods for characterisation have not been adopted by conservators. The lack of proper identification is often justified because

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64 Annemette Bruselius Scharff, "Synthetic Dyestuffs for Textiles and Their Fastness to Washing (1999)," in *Changing Views of Textile Conservation*, ed. Mary Brooks, and Dinah Eastop, 199-209 (Los Angeles: Getty Conservation Institute, 2011).
65 Timár-Balázsy and Eastop, 96-97.
66 Sheila Landi, *The Textile Conservator's Manual*, (Oxford: Butterworth-Heinemann, 1992) 50-51.
67 Ágnes Timár-Balázsy et al., "Effect of Stains and Stain Removal Methods on Historical Textiles" in *ICOM-CC 10th Triennial Conference 2008 Preprints*, ed. Janet Bridgland, 330-335 (London: James & James, 1993).
68 Naomi Tarrant, *Remember Now Thy Creator: Scottish Girls' Samplers, 1700-1872*, (Edinburgh: Society of Antiquaries of Scotland, 2014) 101, 136, 160.
69 Finch and Putnam, 19.

many conservation studios cannot afford analytical tests and there are only a limited number of facilities offering dye analysis for third parties.

Table 2.1. Identification Techniques for Indigo Carmine	
Method	**Notes**
Visual examination	By tonality or presence of greenish-blue haloes.[70] Not entirely reliable because it was common to mix indigo carmine with other dyes for green, purple, and grey tonalities. Haloes will only be observed once the object has already been stained.
Solubility tests	Wetting and boiling a small sample of thread. If present, the blue dye should be stripped from the sample, colouring the water.[71]
Microchemical tests	Use of reagents to find dye class.[72] No longer reported in conservation literature.
Near-infrared reflectography	Tested on inks. These are observed as transparent because they do not absorb IR radiation.[73]
False-colour infrared photography	Tested on inks. These appear red.[74]
Method	**Notes**
Fibre optic reflectance spectroscopy (FORS)	Selection of signals that discern indigo carmine from other blue dyestuffs, regardless of the substrate.[75]
UV-visible spectroscopy (UV-Vis)	The main absorption band is between 500-700 nm, with a maximum peak at 610-620 nm.[76,77]
Fourier transform infrared spectroscopy (FTIR)	Complementary technique to define dry dye constituents with more precision.[78]
Gas chromatography-mass spectrometry (GC-MS)	Allows for the identification of degradation products as marker compounds for fugitive dyes.[79]
High or ultra-high performance liquid chromatography (HPLC or UHPLC)	Data can provide the degree of sulfonation of indigotin through a chromatogram.[80]
Raman Spectroscopy	Used as a complementary technique.[81,82]

[70] de Keijzer et al., S93.
[71] Wood, 70-71.
[72] Helmut Schweppe, *Practical Information for the Identification of Dyes on Historic Textile Materials*, (Washington DC: Smithsonian Institution, 1988).
[73] Agata Klos, "Non-Invasive Methods in the Identification of Selected Writing Fluids from Late 19th and Early 20th Century," *CeROArt* (2014): 7.
[74] Ibid, 9.
[75] M. Gulmini et al., "Identification of Dyestuffs in Historical Textiles: Strong and Weakpoints of a Non-invasive Approach," *Dyes and Pigments* 98 (2013): 136-145. doi: 10.1016/j.dyepig.2013.02.010
[76] Caycedo, 17-18.
[77] Quye and Wouters, 52-53.
[78] Sahmel et al., 81.
[79] Jennifer Poulin, "A New Methodology for the Characterisation of Natural Dyes on Museum Objects Using Gas Chromatography-Mass Spectrometry," *Studies in Conservation* (2017): 1-26. doi: 10.1080/00393630.2016.1271097
[80] de Keijzer et al., S90.
[81] Troalen et al., 86.
[82] Caycedo, 18-19.

Another debate is whether proper identification is necessary in practice or if treatments can carry on as long as the sensitivity of indigo carmine to aqueous treatments is acknowledged.[83] Standard treatment methodologies include testing dyes for washfastness prior to completing an aqueous treatment. The test is supposed to show how fugitive a colour is and inform on the best way to mitigate bleeding.[84] However, it has been recognised that washfastness tests are only an indication of what may happen during treatment, leaving the conservator to manage unexpected situations.[85]

Although conservators are aware of the sensitivity of blue/green fugitive dyes, so far, little interest to understand the dye's degradation has been shown by conservators and conservation scientists. The lack of research has resulted in unsubstantiated claims, such as that the colour changes from blue to green to yellowish during fading.[86,87] Linking relevant information to conservation is complicated and a complete understanding of the uptake mechanism by the fibres and the thermodynamics of transfer (staining mechanism) has proven challenging; even specialists from specific fields such as quantum chemistry,[88] thermodynamics,[89] spectrophotometry,[90] and catalysis[91] have reported strange dye behaviours.

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83 Barnett, 67.
84 Helen Cartwright and Alain Colombini, "Detergent Monitoring during the Washing Process at the Textile Conservation Studios, Hampton Court Palace," in *ICOM-CC 10th Triennial Conference 2008 Preprints*, ed. Janet Bridgland, 293-298 (London: James & James, 1993).
85 Foskett and CTCTAH (unpublished).
86 de Keijzer et al., S87.
87 Cardon 2016, 108.
88 M. El-Mansy, "Quantum Chemical Studies on Structural, Vibrational, Nonlinear Optical Properties and Chemical Reactivity of Indigo Carmine Dye," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 183 (2017): 284-290. doi: 10.1016/j.saa.2017.04.047
89 Uma Lakshmi et al., "Rice Husk Ash as an Effective Adsorbent: Evaluation of Adsorptive Characteristics for Indigo Carmine Dye," *Journal of Environmental Management* 90 (2009): 710-720. doi: 10.1016/j.jenvman.2008.01.002
90 Baoen Shen et al., "An Optical and Spectroelectrochemical Investigation of Indigo Carmine," *International Journal of Research in Physical Chemistry and Chemical Physics* 173:2 (1991): 251-255.
91 Agileo Hernández-Gordillo et al., "Photodegradation of Indigo Carmine Dye by CdS Nanostructures Under Blue-light Irradiation Emitted by LEDs," *Catalysis Today* 266 (2016): 27-35. doi: 10.1016/j.cattod.2015.09.001

2.4 The Need for Research

Appelbaum states that "the job of a professional is not risk avoidance but risk management."[92] In this sense, this dissertation does not suggest stopping the wet cleaning of objects with presence of indigo carmine, but rather emphasises that conservators would be more likely to find effective ways to deal with the issues raised by its instability if they understood its use, history, properties, and behaviour, which so far have been minimally explained in the published literature.

At present, ethical issues and chemical understanding that inform conservation decision-making processes seem to have some grey areas. Concerns about dye solubilisation are mostly based on aesthetics or visual appreciation. Conservators may be unaware of changes that could be occurring in the chemical structure during wet or solvent cleaning. Publications and reports make limited mention of colour change after treatment, despite the idea that loss of blue components would tend to produce greener or lighter shades. However, the wide variety of effects and unexpected responses suggest that an unknown variable – perhaps related to dye formulation or degradation – is not being considered.

This review showed that not enough research has been generated from inside conservation. Before exploring methods to efficiently control dye bleed, it is necessary to find what makes this dye problematic by investigating the conditions that affect its washfastness. A basic level of understanding is needed before aiming to look at changes from a purely chemical perspective or trying to build-on the knowledge generated in the industrial context. The next chapter reviews traditional dyeing recipes in order to find trends and variations in indigo carmine's dyeing conditions and formulations, to later explore if these impact on its low washfastness.

[92] Appelbaum, 366.

3. History and Use of Indigo Carmine

3.1 Introduction

In order to understand the inherent properties of indigo carmine and distinguish variations in traditional dyeing practice, it was necessary to learn more about the dye's chemistry, manufacture, and use. A study of indigo carmine recipes found in dyers' manuals was undertaken from a material perspective, to gain insight into the act of making. These recipes were correlated with secondary sources, the aim of which was to ultimately support decision-making for conservation treatments through a better understanding of historical indigo carmine dyeing and what factors influence the stability of the dye.

In total, nineteen indigo carmine recipes ranging from 1750 to 1908 were studied to find differences in historical dyeing practice.[93] The selected recipes focus on dyeing wool, which is commonly embroidered in historical samplers across collections. This dye was also used for silk, cotton,[94] and leather[95], but these substrates were not included in order to narrow the scope of the research.

The study of dyers' manuals offers an opportunity to evaluate how traditional dyeing practices developed. Subtle differences in dyers' testimonies evidence their choices, frustrations, understanding, and judgments, revealing the degree in which the recipe is reliable or representative of a wider tradition.[96] A close inspection of the recipes allows for assumptions about the technology that prevailed amongst dyers, which can be chronologically linked to certain periods.

Indigo carmine recipes spread widely after 1748, when the dyeing method was revealed in Leipzig in exchange for money. Then, it was patented in Norwich, England.[97] From then on, the proliferation of recipes suggests that technical inventions and information circulated between dyers in the United Kingdom, United States, and Europe. It is difficult to ascertain the intended audience for these manuals, but it is likely that small

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[93] Appendix 2.
The digital availability of dyers' manuals offered an opportunity for research.
[94] Smith 1882.
[95] de Keijzer et al., S88.
[96] Anita Quye, "The Dyer's Handbook: Memoirs of an 18th-Century Master Colourist," *Textile History* 49:1 (2018): 135-136. doi: 10.1080/00404969.2018.1440799
[97] de Keijzer et al., S87.

workshops[98] and households[99] that undertook dyeing on a regular basis would have benefitted from reading these publications.

The historical recipes for indigo carmine dyeing of wool were studied to identify trends amongst dyers, discussed in the following sections. The following table summarises some of these variations, focusing on three specific factors: the use of dye-assistants such as mordants or additives, the ratio of sulfuric acid to indigo, and the temperature of the dye-bath (Table 3.1). These factors were selected because they signalled areas of disagreement between recipes, and also because of the potential impact they could have on dye chemistry and the final dyed product. It is likely that dyers controlled the duration of dyeing stages to obtain a specific shade or quality; however, this factor was not considered because of its variability.

Variations in recipes were motivated by the dyers' quest for improvements in the dye process. For example, Bancroft highlights the importance of finely powdering indigo[100] and Cooper dwells on the problematics of impure indigo powder.[101] It is inferred that the search for standardisation in dyeing procedures was triggered by isolated technological factors,[102] like the introduction of concentrated sulfuric acid,[103] new methods for water purification, availability of less costly materials, and the revision of practices from renowned dyers to achieve better quality.

98 Ibid, S93.
99 Lowengard 2001, 92.
100 Bancroft, 171.
101 Thomas Cooper, *A Practical Treatise on Dyeing and Callicoe Printing,* (Philadelphia: Thomas Dobson, 1815) 192.
102 Lowengard 2001, 95.
103 William Partridge, *A Practical Treatise on Dying of Woolen, Cotton, and Skein Silk with the Manufacture of Broadcloth and Cassimere,* (1823), ed. K.G. Ponting, (Edington: Pasold Research Fund, 1973) 105.

Table 3.1. Variations Across Dyers' Recipes			
Dyer	**Dye-assistant**	**Ratio (w/w)(sulfuric acid to indigo)**	**Temperature**
Hellot (1750)	Alum and cream of tartar	4:1	Boiling
Paul Gout (1768)	Alum and cream of tartar	6:1 and 8:1	Boiling and below boiling
Luis Fernández (1778)	Alum and "rasuras"	8:1	Boiling
Berthollet (1791)	Alum and cream of tartar / No mordant	4:1 and 3:1	Boiling and cold
Ferguson et al (1810)	Alum, cream of tartar and else	5:1 and 8:1	Below boiling
Bancroft (1814)	Not specified	4:1, 6:1 and 8:1	Not specified
Elijah Bemis (1815)	Salt	4:1 and 6:1	Boiling
Thomas Cooper (1815)	Alum and cream of tartar	6:1 and 8:1	Boiling or below boiling
William Partridge (1823)	Alum and cream of tartar / No mordant	4:1	Boiling
J.B. Vitalis (1829)	Alum and cream of tartar / No mordant	8:1	Below boiling and cold
Berthollet & Berthollet (1841)	Alum and cream of tartar / No mordant	4:1 and 8:1	Boiling, below boiling and cold
Thomas Love (1855)	No mordant	8:1	Not specified
David Smith (1860)	Alum	Not specified	Boiling
Crace-Calvert (1876)	Alum and cream of tartar	4:1, 6:1, 10:1 and 12:1	Not specified
David Smith (1882)	Sodium sulfate (Glauber salts)	3:1	Boiling and below boiling
Frederick J. Bird (1882)	Alum and cream of tartar	Not specified	Boiling
J.J. Hummel (1888)	Sodium sulfate / No mordant / Alum	Not specified	Boiling and below boiling
Hellot et al (1901)	Alum and cream of tartar / No mordant	4:1	Boiling
Théophile Grison (1908)	Sodium sulfate / Sodium chloride / Alum and cream of tartar	3:2	Below boiling

3.2 Manufacture and Composition

3.2.1 Historical Methods of Manufacture

The basic preparation of indigo carmine consists of grinding fine indigo powder and mixing it with concentrated sulfuric acid (Figure 3.1). Recipes suggest that the dye was prepared by the dyers themselves and not purchased. Dyers differed in opinion on the ratio to be used (Table 3.1). It can be argued that the most popular ratios were 4:1 and 8:1

(sulfuric acid to indigo powder, w/w), with eight mentions each. Some dyers advise against adding too much sulfuric acid, as it can be damaging for the fibres,[104] while others believed that the success in the reaction was dependant on specific conditions such as tempering the heat during preparation.[105]

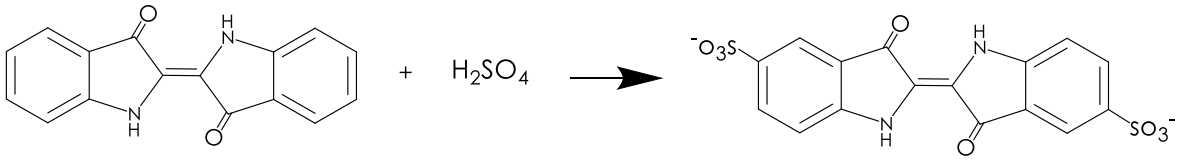

Figure 3.1. Sulfonation reaction by which indigo is converted into indigo carmine

The reported time-span required for the sulfonation reaction to take place was also variable. Most dyers argued that 24 hours made the extract suitable for use,[106,107,108] with some suggesting longer periods of three days.[109] According to research undertaken in 2004, the reaction can take 30 minutes to be completed under controlled laboratory conditions.[110] Historical processes would not have had modern laboratory conditions for environmental control available, and were carried out on a much larger scale. As a result, this might have impacted on the time required for the reaction to proceed.

3.2.2. Chemical Composition

The consequences of the manufacture on indigo carmine's chemical composition have been barely studied.[111] In 1876, Crace-Calvert wrote about two types of indigosulfonic acids that could be obtained depending on the quantity of acid used for preparation.[112] Cardon oversimplifies the impact of the sulfonation reaction by mentioning that sulfuric acid was sold in various concentrations, leading to variations in ratio.[113]

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104 Partridge, 106.
105 Claude-Louis Berthollet, and Ammédée Berthollet, *Elements of the Art of Dyeing and Bleaching*, trans. Andrew Ure, (London: Thomas Tegg, 1841) 306.
106 Berthollet, 99.
107 Ferguson et al., 242.
108 Partridge, 106.
109 Luis Fernández, *Tratado Instructivo y Practico sobre el Arte de la Tintura,* (Madrid: Blas Román, 1778) 169.
110 Iqbal Shadi et al., "Analysis of the Conversion of Indigo into Indigo Carmine Dye Using SERRS," *Chemical Communications* 12 (2004): 1436-1437. doi: 10.1039/B403601H
111 M.X. Sullivan et al., "Electrode Potentials of Indigo Sulphonates, Each in Equilibrium with Its Reduction Product," *Studies on Oxidation-Reduction IV* 38:30 (1923): 1669-1718. doi: 10.2307/4576820
112 Frederick Crace-Calvert, *Dyeing and Calico Printing*, ed. John Stenhouse and Charles Edward Groves, (Manchester: Palmer & Howe, 1876) 175-177.
113 Cardon 2016, 107.

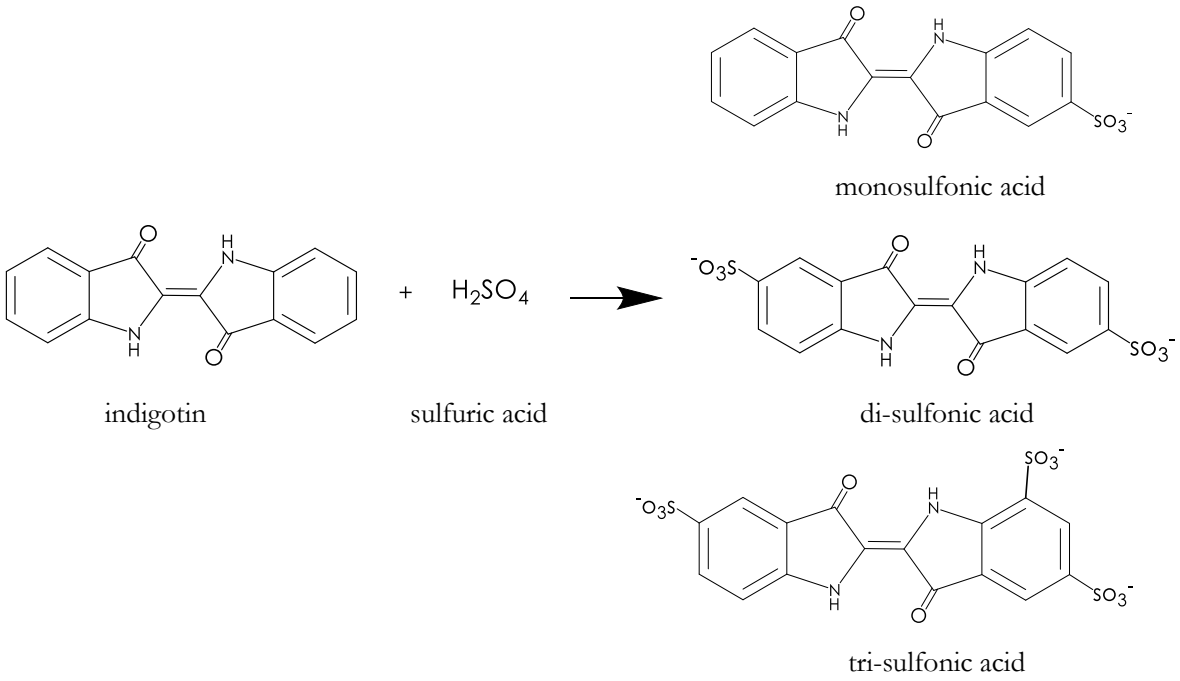

Figure 3.2. Different degrees of sulfonation. Indigo carmine is mostly constituted by di-sulfonic acid, which imparts higher solubility in water than monosulfonic acid. Poly-sulfonic compounds with three or more sulfonate groups can also form under extreme conditions, but these do not comprise part of indigo carmine dye.[114]

Incomplete sulfonation occurs when the amount of sulfuric acid, temperature, or time of action are insufficient, creating monosulfonic acid (Figure 3.2). The difference between ratios of indigo to sulfuric acid is a defining factor in the degree of sulfonation, which increases the solubility of sulfonic acids.[115] This means that water solubility of indigo carmine is variable because of inconsistencies in the historical dye preparation, although this might be different with present manufacture, which is done under strict laboratory conditions. This information is essential for conservators to understand the variable behaviour of indigo carmine.

To test indigo's conversion, dyers historically diluted small amounts of the viscous extract to ensure the dyeing matter was entirely soluble in water.[116] The recipes do not reveal a consensus about the shelf-life of the product: variations from 15 days[117] to 6 months[118] were reported. Furthermore, dyers do not mention a finishing step for the

[114] Sullivan et al., 1673-1674.
[115] Ibid.
[116] Crace-Calvert, 176.
[117] Cardon 2016, 63.
[118] Fernández, 169.

extract before using it for dyeing, suggesting that the solution was highly acidic when applied to the fibres. This is important for conservation as it suggests that fibres could have suffered structural damage during the dye process, leaving them inherently more susceptible to further damage over time.

Occasionally, dyers recommend the addition of alkaline salts, such as potassium, calcium, or sodium carbonate.[119] Although the topic requires further investigation, these non-essential ingredients would likely neutralize the sulfuric acid and create lighter shades due to a less acidic dye-bath. It is worth noting that some dyers reported bursting of pots,[120] extracts boiling in a 'terrible manner',[121] or the generation of 'great heat'[122] while treating indigo powder with concentrated sulfuric acid. This effect seems to be unrelated to the sulfonation of indigotin and, upon a closer inspection of the recipes, two possible explanations were found. It can be attributed to the unusual inclusion of orpiment (As_2S_3), cobalt,[123] or antimony,[124] which are strong reducing agents, or to the eventual presence of water, which can be used to remove the impurities from indigo. This might explain why Hummel specifies in his manual that indigo powder should be ground in the dry state for indigo carmine,[125] to avoid the exothermic hydration reaction that occurs when mixing sulfuric acid with water. This topic is important for revealing that a large number of variables could have been modified during the dyeing process; however, only essential factors determine the characteristics of the final product.

3.2.3. Relevant Changes in Terminology

Tracking the terminology used by dyers is useful to elucidate changes in dyeing practice. In 1814, Bancroft introduces the concept of 'sulphate of indigo', which slowly replaced the common name of Saxon blue, with a preference to allude to chemical composition.[126] This testimony exemplifies the increasing interest in understanding dye

119 Berthollet, 101.
120 Cardon 2016, 63.
121 Elijah Bemiss, *The Dyer's Companion* (1815), ed. Rita Adrosko, (New York: Dover Publications, 1973) 14.
122 Bancroft, 168.
123 Hellot et al., *The Art of Dyeing Wool, Silk, and Cotton*, ed. R. Baldwin, (London: Scott, Greenwood & Co, 1901) 572.
124 Ferguson et al., 242.
125 Hummel, 296.
126 Bancroft, 172-173.

chemistry. In 1882, Bird makes one of the first mentions of 'indigo carmine'[127] and the name persists from then on. Although a clear explanation for the change to indigo carmine has not been found yet, the origin might be linked to Crace-Calvert's contribution, in 1876, describing the process to create "an ordinary quality of carmine."[128]

De Keijzer et al. mention that the term 'indigo carmine' was used in the twentieth century to define a colour shade.[129] Cardon suggests that variations in nomenclature respond to recipe specifications:[130] e.g. that indigo carmine is a high-quality version of indigo extract, which is obtained by precipitating the solution with carbonate of soda or a saturated solution of salt.[131] However, this statement vaguely explains in which sense the dye formulation improved, considering it kept lacking fastness. Further study on the matter is required but it is possible that improvements were linked to the synthesis of indigo and the consecutive use of N-phenylglycine and its derivatives as the starting material for indigo carmine, from 1890 onwards.[132]

Cardon's discussion about the dye's high-quality acquires importance because, coincidently, sodium sulfate began to be used as an additive around this time. In 1882, David Smith reports the use of Glauber salts (sodium sulfate) for dyeing Saxon blue. Then, Hummel specifies that indigo carmine is the sodium salt of indigotin-disulfonic acid.[133] This broadly suggests that the great difference between the less stable compound (Saxon blue) and the so-called 'perfected version' (indigo carmine) could be the incorporation of a sodium salt to precipitate and fix the colour. Since the addition of sodium sulfate is not mentioned in earlier recipes, but quickly becomes a trend for the late nineteenth-century, it is worth questioning in which way it modified indigo carmine dyeing.

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127 Frederick Bird, *The American Practical Dyer's Companion,* (Philadelphia: Henry Carey Baird & Co, 1882) 214, 233.
128 Crace-Calvert, 178.
129 de Keijzer et al., S92.
130 Cardon 2016, 107.
131 Cardon 2007, 362.
132 de Keijzer et al., S89-S91.
133 Hummel, 317-318.

3.3. Dyeing

3.3.1 About Dye-Assistants

The use of alum as mordant and cream of tartar as dye-assistant remained consistent throughout the first 130 years of indigo carmine's production. Out of 25 mentions across recipes, 13 recommend the use of alum and cream of tartar, indicating that this formulation was common. Overall, it is noticeable that dyers rarely write about the impact of dye-assistants on the final product.

Berthollet is one of the few dyers to mention a variation; he says that alum and cream of tartar create a less vivid but more durable colour than a dye-bath without additions.[134] Cooper acknowledges that alum and cream of tartar have no affinity with indigo powder,[135] but does not discourage their use. Apart from these issues, there is hardly any discussion on the topic until the 1880's, when sodium sulfate is introduced as a new additive.

3.3.2 About Dyeing Temperature

Most dyers suggest the use of boiling baths for levelling colours. Gout adds that if the boiling point is not reached, the colour will be poor and lack fastness.[136] Conversely, Hummel advises against higher temperatures because he considers them detrimental for the attainment of bright colours.[137] Some recipes report that temperature affects colours and makes shades greener.[138] To avoid greener shades, some dyers argued that cooler temperatures could be used since the cold bath acted equally to the boiling one.[139] This was seen as an advantage, as disregarding the need for temperature allowed for dip-dyeing and reuse of dye-baths until reaching the desired shade.[140] This information is important for conservators as it reflects that the lack of heat could result on insufficiently fixed dye, increasing the likelihood of bleeding.

134 Berthollet, 313.
135 Cooper, 84.
136 Cardon 2016, 65.
137 Hummel, 317.
138 Ferguson et al., 243
139 Berthollet, 98-102.
140 Cardon 2016, 63.

3.4 About Fastness

The testimonies of dyers also reveal expectations about colourfastness (Table 3.2). Some dyers state the acidic and destructive ingredients of indigo carmine as the main fault,[141] but most of them complain about the poor washfastness and lightfastness properties. Despite these poor properties, the dyestuff continued to be used, possibly due to the advantages in cost and ease of dyeing.

Table 3.2. Dyers' Expectations about Colourfastness

	Dyer	Description of Testimony
Washfastness	Cooper	The dye 'will stand the air' but will not be resistant to washing.[142]
	Kortum	Extreme effects such as rain and cold water "causing spots"[143]
	Hellot	Hired to examine green dyes for quality, managing to remove the blue component of Saxon green by using only fresh water.[144]
	Bancroft	Concludes that indigo will not be fast when treated with sulfuric acid, especially if boiling water and soap are used.[145]
Lightfastness	Bergman	After exposure to the sun for two months, deep blues are scarcely weakened in comparison to the lighter shades, which become dull and greenish.[146]
	Ferguson et al.	Twelve days of exposure are enough for the dye to lose great part of its colour.[147]
	Hummel	The only drawback of the dyestuff is its extremely fugitive character.[148]
	Thomas Love	Suggests avoiding damp air,[149] which may be related to sensitivity to oxidation, starting from when the dye is fixed to the fibre.

[141] de Keijzer et al., S87.
[142] Cooper, 85.
[143] As cited in de Keijzer et al., S87.
[144] Lowengard 2001, 98.
[145] Bancroft, 170.
[146] As cited in Berthollet, 100.
[147] Ferguson et al., 242.
[148] Hummel, 296, 489.
[149] Thomas Love, *The Art of Cleaning, Dyeing, Scouring, and Finishing, on the Most Approved English and French Methods*, (London: Longman, Brown, Green, and Longmans, 1855) 79.

New research confirms what dyers observed: indigo carmine is very sensitive to oxidation.[150,151] The testimonies evidence that, while degradation mechanisms were not necessarily understood by historic dyers, the practical effects were noted. Since dyers testimonies report degradation from an early stage, it can be inferred that the dye's colourfastness is particularly low.

3.5 Conclusion

The findings show that there is no evidence of consensus for one method of dyeing with indigo carmine from the period comprising its invention until the early twentieth-century, although trends can be identified. Conservation literature has not improved the understanding of how variations in historical dye recipes impact on the properties and stability of indigo carmine. Therefore, these sources remain fundamental for researchers to investigate, critically review, and gather information on the dyestuff, especially when traditional dyeing processes have been lost.

Dyers' manuals also give insight into the dye's behaviour. In this case, the study of historical recipes emphasises the need to question whether the washfastness of indigo carmine shows variations according to chemical structure, dyeing conditions and formulations, or degradation effects. The information gathered allowed educated guesses about the consequences of each variable on the final product. With this information, it becomes possible to recreate indigo carmine dye recipes, and to investigate inherent properties, test colourfastness, and explore degradation pathways at a macro level.

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150 Micaela Sousa et al., "A Photochemical Study on the Blue Dye Indigo: From Solution to Ancient Andean Textiles," *Photochemical & Photobiological Sciences* 7 (2008): 1353-1359. doi: 10.1039/b809578g

151 Catherine Galindo et al., "Photochemical and Photocatalytic Degradation of an Indigoid Dye: a Case Study of Acid Blue 74 (AB74)," *Photochemistry and Photobiology A: Chemistry* 141 (2001): 47-56. doi: 10.1016/S1010-6030(01)00435-X

4. Preparation of Indigo Carmine and Dyed Samples

Although commercially-manufactured indigo carmine is readily available from chemical suppliers, indigo carmine of historical interest and relevance to textile conservation is absent. Commercial products do not aim to reconstruct historical manufacture, and this has implications when research is directed towards understanding the behaviour of historical dyes. For this research, it was necessary that samples were prepared and dyed following historical dye recipes which represent more closely the chemical composition of the dye that conservators encounter on historical textiles. The recreation of dyed samples allowed for a better evaluation of the consequences that dyeing conditions have on colourfastness.

4.1 Labelling Test Groups and Variables

After studying historical dye recipes, the method and the quantities required for replication were adapted for consistency in laboratory conditions,[152] following health and safety regulations.[153] Calculations were based on weight of fibre (o.w.f) and molarity.[154] Materials and supplies used are listed at the end of this dissertation.[155] To provide control and validation of results throughout the experiment, three sample replicates (denoted 1*, 2* or 3*) were created for each set of variables.

The test groups and variables for dyeing textile fibres with indigo carmine were defined after finding trends in the recipes.[156] Samples were coded and labelled as described in an appendix,[157] summarised as follows (Figures 4.1 and 4.2) (Table 4.1):

[152] Jo Kirby et al., *Natural Colourants for Dyeing and Lake Pigments: Practical Recipes and their Historical Sources*, (London: Archetype Publications, 2014) 49.
[153] Appendix 9.
[154] Appendix 3.
[155] Appendix 8.
[156] Kirby et al., 35.
[157] Appendix 3.

Dye-Assistant / Dyeing Matter	A Alum and Cream of Tartar	B Sodium Sulphate	C No Mordant or Additive	Total
0 Fisher Indigo Carmine	W 45-50° / Y 85-90°	W 45-50° / Y 85-90°	W 45-50° / Y 85-90°	6
8 8:1 Indigo Carmine	W 45-50° / Y 85-90°	W 45-50° / Y 85-90°	W 45-50° / Y 85-90°	6
Total	4	4	4	12

Figure 4.1. Summary of test groups and variables for labelling dyed threads

Dye-Assistant / Dyeing Matter	D Alum and Cream of Tartar	E Sodium Sulphate	F No Mordant or Additive	Total
0 Fisher Indigo Carmine	W 45-50° / Y 85-90°	W 45-50° / Y 85-90°	W 45-50° / Y 85-90°	6
8 8:1 Indigo Carmine	W 45-50° / Y 85-90°	W 45-50° / Y 85-90°	W 45-50° / Y 85-90°	6
Total	4	4	4	12

Figure 4.2. Summary of test groups and variables during for labelling dyed fabric

Table 4.1. Variable Codes for Dyed Samples	
Dye-Assistants	
A	Threads; alum and cream of tartar
D	Fabric; alum and cream of tartar
B	Threads; sodium sulfate
E	Fabric; sodium sulfate
C	Threads; no mordant or additive
F	Fabric; no mordant or additive
Dyeing Matter	
0	Fisher indigo carmine
8	8:1 indigo carmine
Dyeing Temperature	
Y	Dyed at 85-90 °C
W	Dyed at 45-90 °C
Drying Method (for Experiment A: Dyeing Conditions and Washfastness)	
B	Blotting paper (absorption)
H	Direct fan (air circulation)
Lighting Scenario (for Experiment B: Photodegradation and Washfastness)	
α	Storeroom
β	Barkcloth lab
γ	First-year workroom
δ	Artificial ageing

4.2 Methodology

4.2.1 Scouring

For experiment A, wool threads were prepared for dyeing by loosely tying 12 skeins (2 g each). For experiment B, 12 pieces of wool fabric were cut (3.5 g each). Both were pre-washed to remove lanolin and oils in 1000 mL tap water with 3 mL Dehypon® LS54 for one hour at 40 °C.

Figure 4.3. Scouring of samples

4.2.2 Dye-Assistants

Prior to dyeing, dye-assistants were applied to threads and fabric. Groups **A** and **D** were mordanted with alum (aluminium potassium sulfate dodecahydrate, $AlK(SO_4)_2 \cdot 12H_2O$) (20% o.w.f.) and cream of tartar (potassium hydrogen tartrate,[158] $KC_4H_5O_6$) (6.6% o.w.f.) in 300 mL tap water. The solution was heated to 40 °C to dissolve the salts.

Anhydrous sodium sulfate (Na_2SO_4) (15% o.w.f), also called Glauber's salt, was added in 300 mL tap water to Groups **B** and **E**.

Groups **C** and **F** remained without additives. All baths were heated at 90 °C for one hour. After cooling for 3 hours in the bath, the skeins and fabric were stored wet inside a plastic bag in the fridge.

[158] Potassium hydrogen tartrate (mono) was used instead, since it was readily available at the CTCTAH. The quantities of the compound were duplicated.

4.2.3 Preparation of Dyeing Matter

Indigo carmine (80% dye-content) supplied by ACROS Organics™, part of Thermo Fisher Scientific, was used as a comparative reference for the replica dye. This dyeing matter (Group **0**) was prepared by dissolving Fisher indigo carmine in 150 mL deionised water.[159]

For the replica dye, an 8:1 w/w ratio (Group **8**) was used.[160] Dry indigo grains were ground to turn them into a fine powder;[161] then, slowly added to the sulfuric acid in a glass beaker. A bain-marie on a hot plate was used to heat the mixtures to 50-60 °C for 45 minutes. The solution was stirred regularly, removed from heat, and left to react overnight. The next day, the mixture was filtered and diluted in 150 mL deionised water.


Figures 4.4 and 4.5. Grinding indigo (left) and filtering indigo carmine (right)

4.2.4 Dyeing Process

One skein or piece of fabric was placed per beaker. The temperature of the dye-bath was set at 45-50 °C for Group **W** and at 85-90 °C for Group **Y**. The samples in Group **Y** were added directly to the dye-bath at 70 °C and the temperature was raised to 90 °C within 5 minutes. This was required for standardisation purposes,[162] however, this practice was not followed by dyers in practice as the quick change in temperature is harmful for wool.

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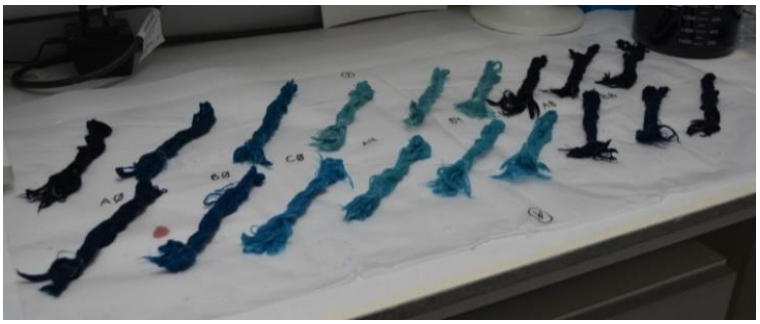
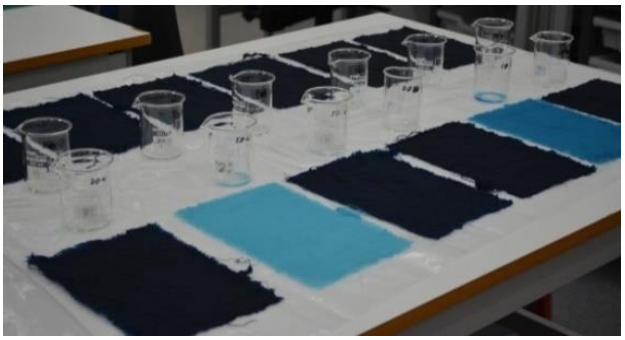
159 Quantities were not modified to reach 100% dye strength.
160 Three different formulations of indigo carmine were prepared. The other ratios (4:1 and 6:1) were not used because the resulting light tonalities were unlikely to provide visual evidence of bleeding. The density of sulfuric acid is 1.84 g/cm^3.
161 Particle size is key on this matter as finer particles will increase the surface area for reaction.
162 Kirby et al., 49.

The dyeing process was completed in 2 hours. The average pH of the solutions was 2, as measured with pH strips (Macherey-Nagel, 0-14 range). The fibres were thoroughly rinsed with running tap water to remove excess dye and acid, until water was clear and had a pH of 7. The samples were left to dry for 24 hours at room temperature (22-24 °C for skeins, 18-20 °C for fabric).

Figure 4.6. Use of two dye-baths with different temperatures
© CTCTAH, University of Glasgow, 2018. Photo by Staphany Cheng.





Figures 4.7 and 4.8. Skeins (top) and fabric (bottom) after dyeing process
© CTCTAH, University of Glasgow, 2018. Photos by author.

4.2.5 Particularities of Experiments

For experiment A, dyed threads were embroidered onto undyed wool fabric samples. Six replicates of each set were created for wet cleaning, acknowledging that the drying process would be completed in two different ways.

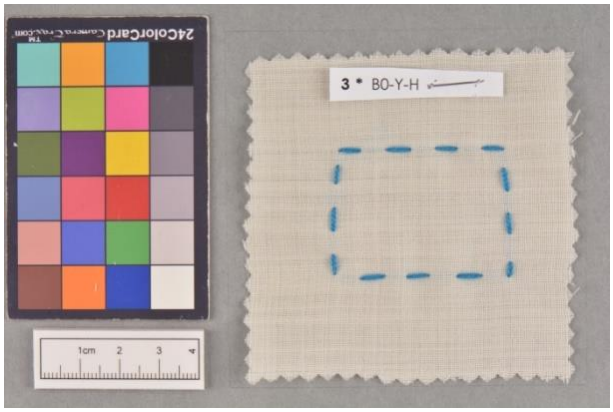


Figure 4.9. Example of embroidered sample
© CTCTAH, University of Glasgow, 2018. Photo by author.

For experiment B, three sloping racks for exposing samples to lighting scenarios and two flat trays for artificial ageing were made out of corrugated plastic sheets. The pieces of dyed fabric were cut into strips, separated by sets, and randomised. On each 45° angle rack, the strips were adhered by the top with double-sided tape. The strips meant for artificial ageing were affixed to the tray by one edge; the other end was temporarily held with a metallic pin to allow for cutting. The area of fabric that had contact with the adhesive was avoided throughout collection of data. An additional tray with dyed threads was created to support the interpretation of results from artificial ageing, after noticing variations in colour on the dyed fabric.

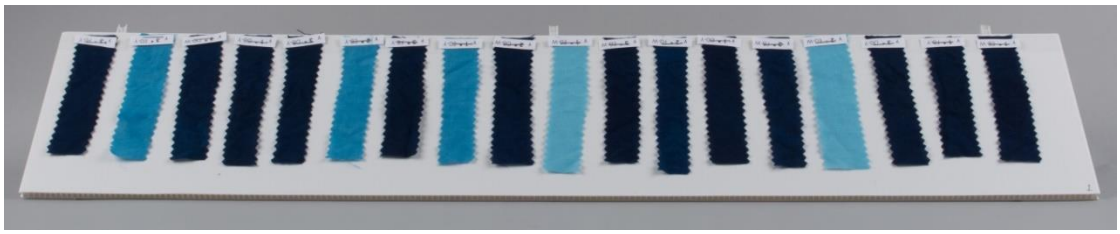
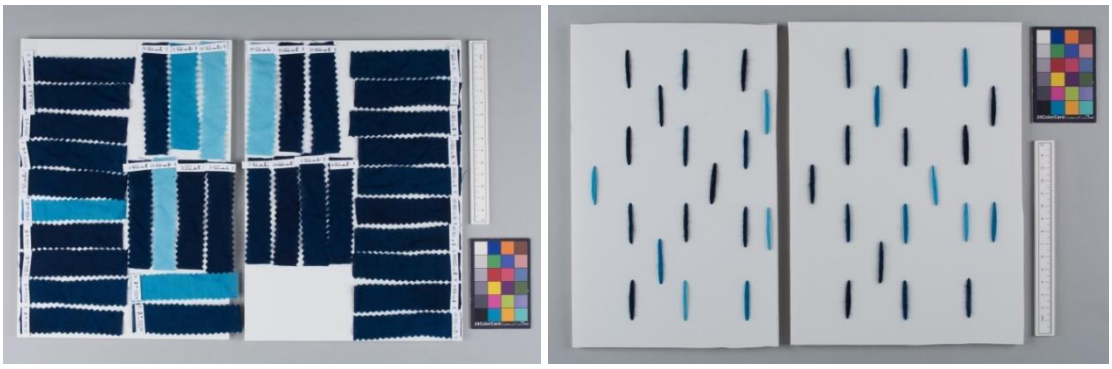


Figure 4.10. Example of rack used for lighting scenario
© CTCTAH, University of Glasgow, 2018. Photo by author.



Figures 4.11 and 4.12. Fabric tray (left) and thread tray (right) for artificial ageing
© CTCTAH, University of Glasgow, 2018. Photos by author.

4.3 Evaluation of Samples

A master dyer would have ensured his products were profitable by altering dyeing procedures until getting the desired result; i.e. by extending the duration of the dyeing process to hide skitteriness or unlevelled colour, or by overdyeing. In this case, the method was controlled for standardisation, causing dyeing rates to be variable (Table 4.2). As a result, some skeins show areas with less dye uptake and some fabric samples are speckled. These characteristics hinder comparisons across certain samples, although the results still allow for the objective evaluation by recognising variations in dyeing rates (Figure 4.13). Following these observations, important considerations were acknowledged before proceeding to the experimental phase.

4.3.1 About Dye Concentration

While filtering the 8:1 indigo carmine (**8**), it was noticed that the indigo powder partially reacted with the sulfuric acid. Hence, the exact quantity of dyeing matter and the depth of shade of the 8:1 indigo carmine cannot be established.

In agreement with the characteristics of levelling acid dyes, Groups **B** and **E** showed that sodium sulfate reduced the uptake of dye because it competed with indigo carmine for absorption by the fibre.[163,164] This produced bright blue tonalities instead of navy blue, which is important to consider since washfastness is dependent on depth of colour.[165] Throughout the experimental phase, these samples showed distinct patterns.

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163 Duff and Sinclair, 17.
164 Hummel, 245-247.
165 J. Valldeperas-Morell and F. Carrillo-Navarrete, "Colour Fastness" in *Understanding and Improving the Durability of Textiles,* ed. Patricia Annis, (Cambridge: Woodhead Publishing, 2012) 82-103.

Group **F** (fabric) did not match the tonalities of Group **C** (threads), despite both being non-mordanted samples. This may be the result of cross-contamination or presence of trace amounts of certain metals or impurities used for industrial purposes which were not rinsed during the scouring of the wool fabric.[166] This observation led to the creation of a thread tray for artificial ageing. However, colourimetric data is not comparable between thread and fabric samples.

4.3.2 About Acidic Conditions

Overall, it was difficult to replicate pH values used in historical dyeing practice because dyers did not report data under these terms.[167] Fibre loss during handling suggests that the low pH of the 8:1 indigo carmine damaged the wool fibres more than the formulation of Fisher indigo carmine. This could also mean the lower pH promoted dye uptake[168] because "the concentration of indigo carmine on wool tends to increase with lower pH due to an increase in the number of protonated sites at the surface of wool fibre."[169] Dyeing matters showed significantly different behaviours from the start, as observed on dye uptake, response to dye-assistants, and rinsing.

4.4 Conclusion

The preparation of samples was considered successful because it tailored historical dyeing recipes for the purposes of the experimental research. Gathering evidence from nineteen historical recipes allowed for complementing and creating a unique dye recipe. General knowledge on the process of dyeing and chemistry was also useful to fill in the gaps. As explained in the next chapters, the replica samples proved applicable to recreate indigo carmine elements present in historical objects, allowing for different experimental avenues to be explored.

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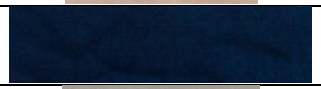
166 Kirby et al., 49.

167 The pH scale was only introduced in 1909.
William Jensen, "The Symbol for pH," in *Ask the Historian.* Chemical Education Today, 2004. https://pubs-acs-org.ezproxy.lib.gla.ac.uk/doi/pdf/10.1021/ed081p21 (accessed July 24, 2018).

168 S.R. Trotman and H. Horner, "The Action of Sulphuric Acid in Dyeing Wool with Acid Dyes," *Journal of the Society of Dyers and Colourists* 50 (1934): 65-72. doi: 10.1111/j.1478-4408.1934.tb01814.x

169 Sunsanee Komboonchoo and Thomas Bechtold, "Sorption Characteristics of Indigo Carmine as a Blue Colorant for Use in One-bath Natural Dyeing," *Textile Research Journal* 80 (2010): 734-743. 10.1177/0040517509342319

It can be concluded that the recreation of historically dyed samples was essential for a better understanding of indigo carmine's properties, and also to assess the reliability of dyers' testimonies. For example, temperature was not identified as a significant factor on colour change, although boiling temperatures promoted levelling (Table 4.2)(Figure 4.13). Furthermore, the preparation of samples showed that dye-assistants seem to be a key factor in determining depth of colour for Fisher indigo carmine, but not for 8:1 indigo carmine. The absence of this information in dyers' recipes and published literature shows that little is known about the historical use of dye-assistants and their influence in colour. Overall, these findings highlight the importance of generating knowledge through a technical approach.

Table 4.2. Range of Colours of Dyed Thread and Fabric Samples					
		Fisher Indigo Carmine (0)		8:1 Indigo Carmine (8)	
		Temperature: 85-90 °C (**Y**)	Temperature: 45-50 °C (**W**)	Temperature: 85-90 °C (**Y**)	Temperature: 45-50 °C (**W**)
Alum and cream of tartar	**A**				
	D				
Sodium sulfate	**B**				
	E				
No mordant	**C**				
	F				

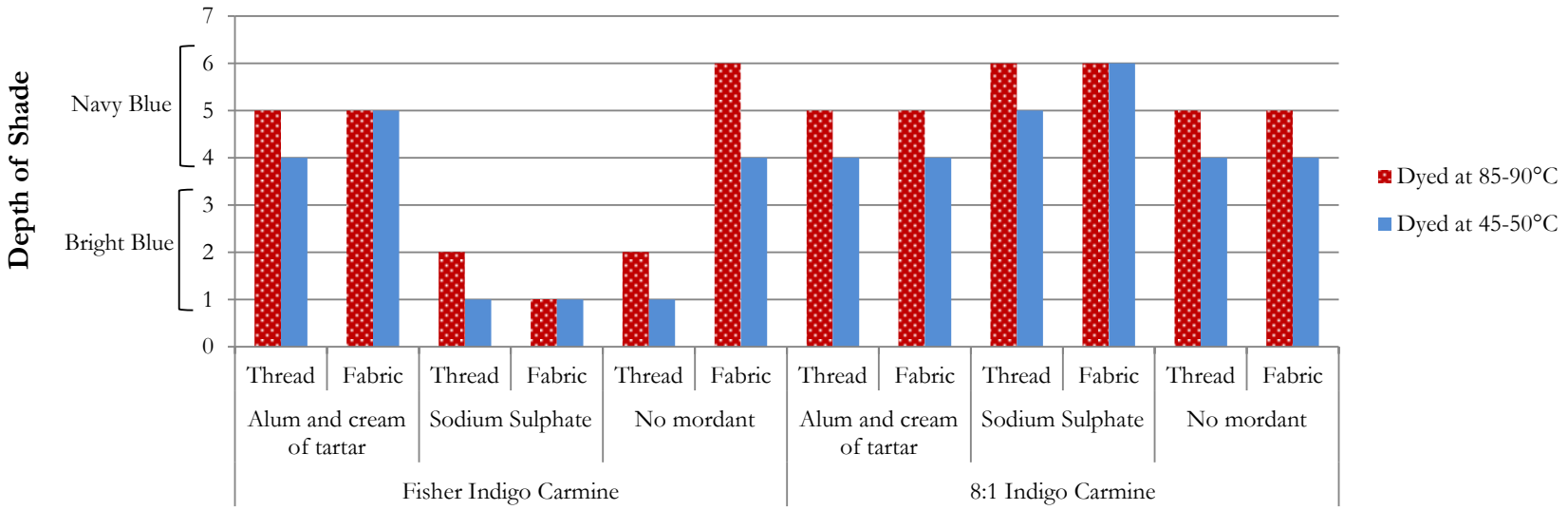


Figure 4.13. Graph displaying differences in colour between thread and fabric samples, especially in non-mordanted samples (Groups **C** and **F**) dyed with Fisher Indigo Carmine (Group **0**). These differences hinder comparisons between data referring to colour. Overall, samples that contain sodium sulfate as dye-assistant (Groups **B** and **E**) show the lightest colours and bright blue tonalities. The rest of the samples are navy blue.

5. Experiment A: Dyeing Conditions and Washfastness

5.1 Methodology

This experiment was designed to explore whether dyeing conditions and formulations impact on indigo carmine's low washfastness. A wet cleaning conservation treatment over the embroidered fabric samples was completed. Information was drawn from conservation literature[170,171] to identify trends in choice for wet cleaning treatments. This allowed the selection of a representative method in which variables – such as water type, detergent, temperature, duration, pH, and amount of mechanical action – were controlled throughout (Table 5.1).[172] Individual trays with Melinex® sheets were used at each stage, wet cleaning a 6-sample set at a time.

Figure 5.1. Sponging during wet cleaning process
© CTCTAH, University of Glasgow, 2018. Photo by Staphany Cheng.

Table 5.1. Variables During Wet Cleaning Stages

1. Soaking	2. Washing	3. Rinsing	4. Drying
For 7 minutes 100 mL deionised water	For 10 minutes 100 mL deionised water Dehypon LS54 at 1x cmc as detergent pH: 7.5	Around 10 minutes Running tap water Final rinse with 100 mL deionised water	With blotting paper by absorption (**B**) Around 20 minutes
			With a fan by air circulation (**H**) Around 30 minutes
Room temperature between 23-27 °C Room RH between 38-50%			

170 Reponen.
171 Moe Sato, "An Experimental Evaluation of Non-Ionic Surfactant Dehypon® LS54" (MPhil in Textile Conservation dissertation, UofG, 2014) 83.
172 Appendix 4.

Separate sets of three embroidered fabric samples were used as replicates and dried in two different ways to evaluate the significance of the drying process over bleeding. This was done by pressing the samples with blotting paper to absorb excess water (**B**) or by pointing a fan directly at them for air circulation (**H**).

Figures 5.2 and 5.3. Drying process of embroidered fabric samples by absorption with blotting paper (Group B)(left) and by air circulation with a fan (Group H)(right).

After wet cleaning, dye transfer from the threads into the undyed wool was ranked by type (none, dot, or dot & line) and degree of staining (from 0–4, where 0 is none and 4 is very evident)(Figure 5.4). This was done through visual examination and optical microscopy, with a set ranking scale. It was necessary to unstitch the embroidered thread to observe the effects since most threads stained the fibres that were directly underneath.

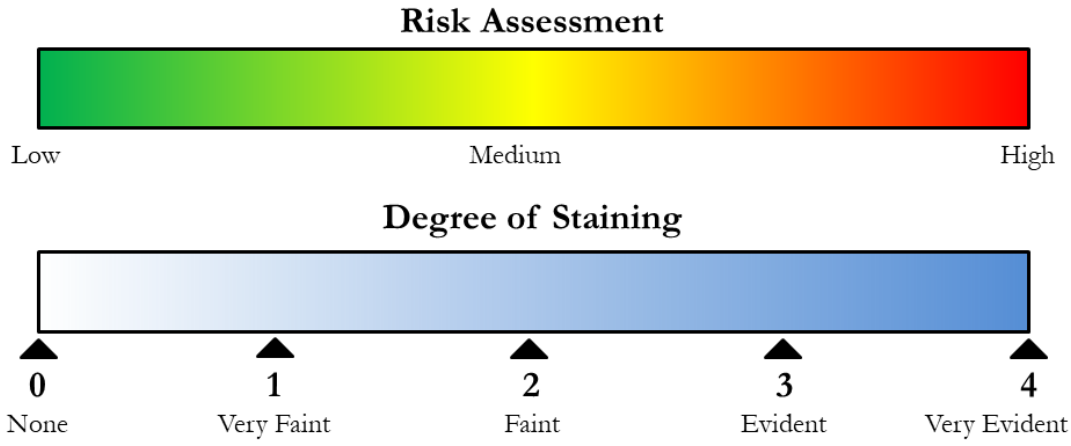


Figure 5.4. Scale for evaluating degree of staining in relation to assessment of risks

The initial methodology for this research considered complementing visual examination with UV-visible spectroscopy by collecting and analysing the dye residues from the washing solutions. This would have provided a quantitative approach to dye solubilisation; however, it was not possible due to null results. Experiment A is summarised as follows:

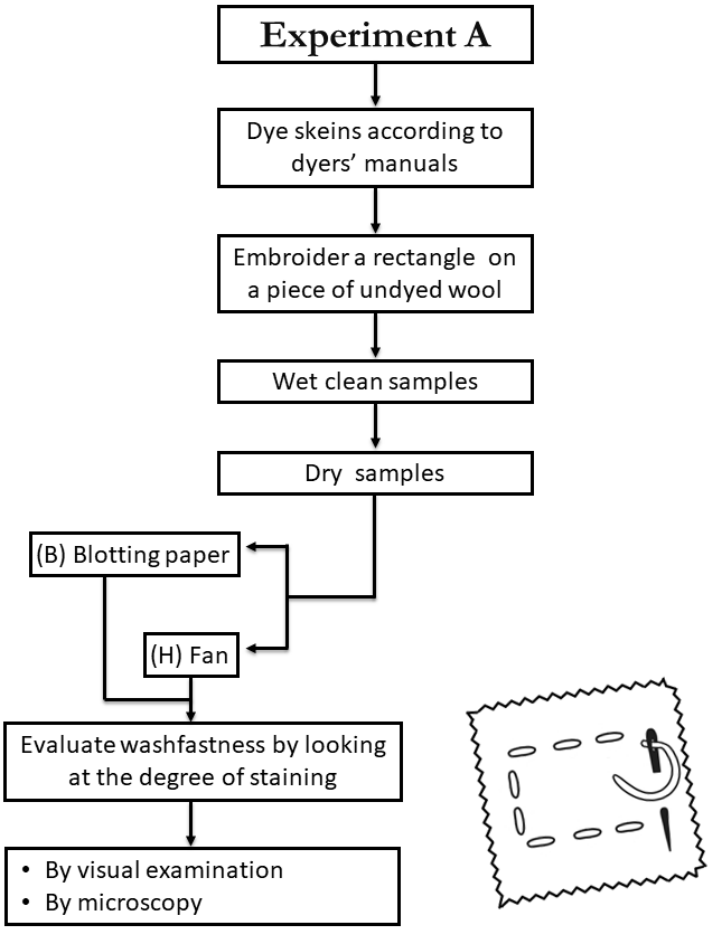


Figure 5.5. Summary of the methodology followed in experiment A

5.2 Results

Solubilised dyeing matter was not observed at any stage. Dye transfer only occurred during drying with blotting paper for two replicates of one sample group (B8-W-B), corresponding to threads dyed with 8:1 indigo carmine, sodium sulfate at a moderate temperature.[173] This indicates that only 2.8% of the samples showed evidence of low

[173] Appendix 4.

washfastness. These results were unforeseen because dyeing and conservation literature report that low washfastness is a key property of indigo carmine.

Interpretation of results was therefore directed towards the description of bleed and staining. The data set collected allowed for drawing conclusions through examination and classification of samples. Replicates showed consistent results throughout, enabling results to be grouped. Statistical analysis was precluded by the variation within dyed samples, as well as by the lack of precise measurements for staining.

In summary, out of the 24 groups of embroidered fabric samples, 16 were stained and 8 were not (Table 5.2). The unstained samples correspond to the ones dyed with Fisher indigo carmine (**0**) that used sodium sulfate as dye-assistant (**B**) or those which were left without mordant (**C**). These samples were excluded throughout graphics because of null results for staining. Conversely, samples dyed with 8:1 indigo carmine (**8**) were always stained, mostly showing 'dot & line' type of staining, which indicates more dye transfer.

Table 5.2. Types of Staining of Embroidered Fabric Samples

Dyeing matter:	Fisher Indigo Carmine (**0**)				8:1 Indigo Carmine (**8**)			
Temperature:	85-90 °C (**Y**)		45-50 °C (**W**)		85-90 °C (**Y**)		45-50 °C (**W**)	
Drying method:	Blotting (B)	Fan (H)	Blotting (B)	Fan (H)	Blotting (B)	Fan (H)	Blotting (B)	Fan (H)
Dye-assistants:								
Alum and cream of tartar (**A**)	dot	dot	dot	dot & line	dot & line	dot & line	dot & line	dot & line
Sodium sulfate (**B**)	–	–	–	–	Dot	dot & line	dot	dot & line
No mordant (**C**)	–	–	–	–	dot & line	dot & line	dot & line	dot & line

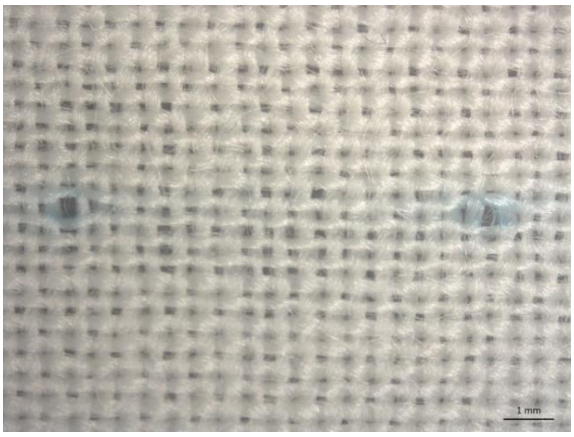


Figure 5.6. Micrograph - Dot and line staining on sample 2* B8-W-H

Overall, it was noticed that samples dyed at a higher temperature showed better washfastness, with the exception of **C8-Y-H** and **B8-Y-B**. In all cases, samples dried by absorption with blotting paper were less stained than samples dried by air circulation with a fan, despite following the same dyeing process (Figure 5.7). The only exception to this pattern was for non-mordanted samples dyed with 8:1 indigo carmine at a moderate temperature (**C8-W**) which showed equal staining results. These results agree with textile conservators' observations in practice.

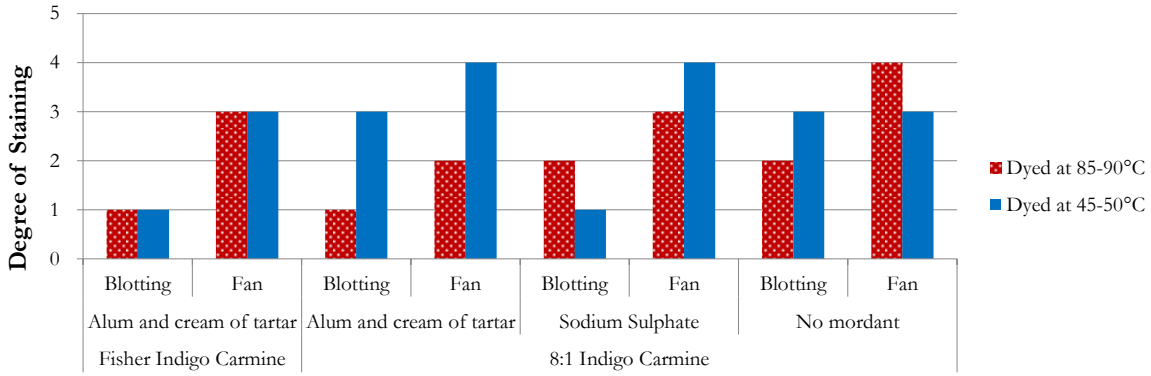
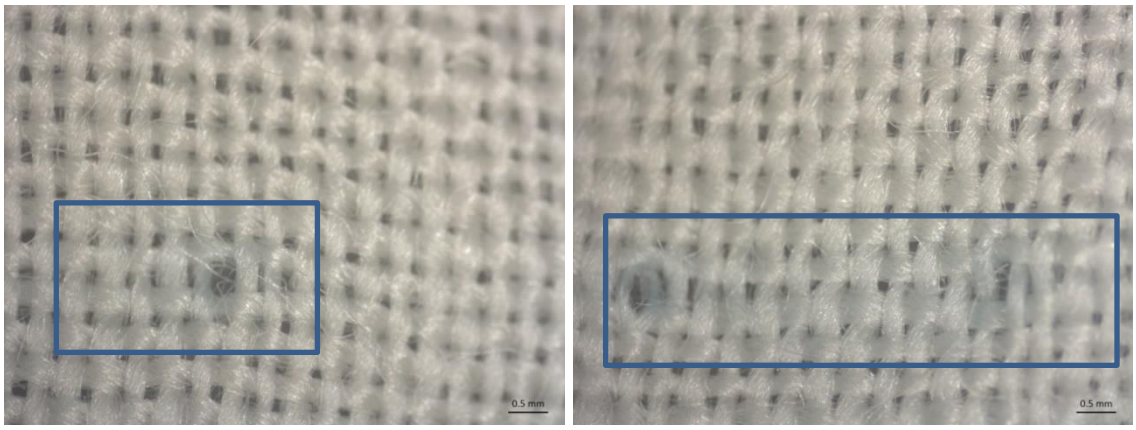


Figure 5.7. Graph showing staining per set of embroidered fabric samples. Samples dyed at a higher temperature (**Y**) mostly showed better washfastness. Samples dried by absorption with blotting paper (**B**) were less stained than those dried by air circulation with a fan (**H**).

Sample **C8-Y** is a good example to illustrate that less efficient drying is more likely to cause staining. While C8-Y-**B** staining was classified as level 2 (Figure 5.8), C8-Y-**H** was ranked at level 4 (Figure 5.9), showing that more dye transfer occurs if drying is not controlled.



Figures 5.8 and 5.9. Micrographs - Comparison in staining between sample 1* C8-Y-B (left) and 3* C8-Y-H (right), showing the impact of the drying stage.

5.3 Discussion

Regarding null solubilised dye throughout the wet cleaning stages, three possible explanations are proposed: first, that the amount of solubilised dye was so minimal it could not be accounted for visually; second, that the neutral pH of the wash-bath could have prevented indigo carmine from solubilising;[174] or third, that bleeding might increase as the dye degrades and these dyed samples had not been exposed to degradation agents. This last hypothesis has not been reported in the literature, nor is it known to have been researched; therefore, it was considered worth exploring through experiment B.

Significant differences in behaviour between dyeing matter were observed. It was therefore concluded that Fisher indigo carmine (**0**) has differing properties from 8:1 indigo carmine (**8**), prepared following historical recipes. Further testing has to be completed to define which dyeing matter is more representative of indigo carmine present in historical objects. This discrepancy interfered with exploring the influence of dye-assistants with respect to bleeding. Questions about the impact of the degree of sulfonation on the level of washfastness remain unresolved.

The dye's concentration was observed to impact on the degree of staining, mostly because visibility could be reduced.[175] Unstained samples correspond to the threads with the lightest tonalities, which might have been imperceptible if solubilisation occurred. Hence, null staining could be misleadingly interpreted as evidence of low washfastness, even though other possibilities exist. The human eye may not perceive staining, but this does not imply that dye solubilisation did not occur.

Results showed that most samples dyed at 45-50 °C were equally or more stained than samples dyed at 85-90 °C. This suggests that the dyeing temperature impacts on bleeding properties: wool fibres dyed with indigo carmine at low temperatures might be more prone to solubility in the aqueous treatments, leading to staining. This is supported by studies on the effect of temperature on dyeing systems which mention that increases in temperature accelerate the rate of chemical reactions, causing equilibrium to be reached

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[174] The quantity of levelling-acid dye absorbed by the fibres increases with acidity. During wet cleaning, the wash-bath acidity tends to increase when soiling is removed.
Trotman and Horner, 65.
Cartwright and Colombini, 294.

[175] Valldeperas-Morell and Carrillo-Navarrete, 87.

faster.[176] However, it is unlikely for this equilibrium to be reached under moderate temperatures.

At present, analytical methods cannot determine the temperature at which fibres were dyed in the past. This challenges the relevance of these findings for conservation practice. Nonetheless, this outcome could serve as word of caution for conservators, as it helps to better understand that inherent properties impact on the dye's sensitivity to water. Based on the quantity of dyers' testimonies mentioning cold or moderate dye-baths, it can be inferred that it was common practice.

5.4 Conclusion

Although distinct patterns were not identified for some dyeing conditions or formulations, this preliminary research provides good evidence and arguments for future focus on key factors. For example, this experiment consistently showed that the degree of staining is largely affected by differences in drying, which factors in the rate of diffusion of the solubilised dye into the wool fibres.[177] These findings are useful for conservators as they point the direction towards control methods during treatment to prevent staining.

Results also showed that dyeing temperature impacts on indigo carmine's sensitivity to aqueous treatments. This proves disadvantageous as the risk of bleeding is dependent on inherent properties of the object, over which conservators have no control. Nonetheless, both findings contribute to a better understanding of the dye's behaviour.

Regarding colour, lighter shades of indigo carmine seem less problematic than darker shades. Aesthetic appreciation would not be as compromised if lighter colours were to be solubilised and transferred in historical textiles, as if it happened with darker colours. Nonetheless, more experimentation is needed to find if staining is not occurring or if it is only less visible. The possibility of dye solubilisation or transfer should not be excluded, even if solutions are not tinted or adjacent fabrics are not stained. These observations raise new questions about whether current visual assessment of blue tonalities on collected wash-bath solutions objectively measures dye solubilisation, especially staining on samples was hidden beneath the embroidery threads.

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176 Duff and Sinclair, 126-127.
177 Millington, 165.

Another issue to consider in conservation practice is that visual appreciation of solubilised dye in the wash-bath is entirely dependent on the dye concentration. Higher volumes of water in the wash-bath will show less intense blue tonalities, even though the same amount of dye is solubilised. Similarly, textiles with several elements dyed with indigo carmine are more likely to evidence dye loss than those with reduced number of elements.

6. Experiment B: Photodegradation and Washfastness

6.1 Introduction

This experiment was designed to explore whether indigo carmine's low washfastness was affected by photodegradation. It was implemented after observing low amounts of dye solubilisation throughout experiment A. Since these observations did not match the characteristic low washfastness of indigo carmine described by dyers and conservation literature, it was hypothesised that the difference in behaviour could be caused by an external factor.

Washfastness of dyes can be altered by exposure to environmental conditions by triggering chemical changes that modify the dye's molecular structure.[178] Since radiant energy is known to affect some dyestuffs, exposure to light was considered a potential pathway for damaging effects to take place in the short-term.[179] The hypothesis gained relevance after revisiting mentions on indigo carmine's poor lightfastness, both on historical and contemporary sources.[180,181]

A simple trial was run by exposing indigo carmine dyed threads to diffused sunlight through a window-cell in Level 3 of the CTCTAH. After only two weeks, the samples showed significant fading towards lighter shades of blue. Additionally, when the threads were subject to washfastness tests, more evidence of dye solubilisation was perceived than before exposing them to light. Hence, a fourth aim for this research was established:

iv. To explore the relation between washfastness and the effects of light on samples dyed with indigo carmine.

The objectives included:

- To monitor environmental conditions for each light-ageing scenario.
- To correlate the effects of colour change with the resistance to water.

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178 Millington, 156.
179 Janet Gilliland Bowman and Barbara Reagan, "Filtered and Unfiltered Lights and Their Effects on Selected Dyed Textiles," *Studies in Conservation* 28 (1983): 36-44. doi: 10.2307/1506105
180 Ferguson et al., 242.
181 Troalen et al., 88.

6.2 Methodology

Sets of indigo carmine dyed fabric samples were exposed to different lighting scenarios.[182] Sloping racks were placed in the storeroom (absence of natural light, limited UV filtered artificial light), barkcloth lab (diffused natural light), and first-year workroom (UV filtered artificial light) to represent real-time scenarios. Flat trays were used for artificial ageing to show the results of extreme photodegradation in a shorter time-span. The colour change and resistance to water of each sample was correlated with the environmental conditions per scenario.

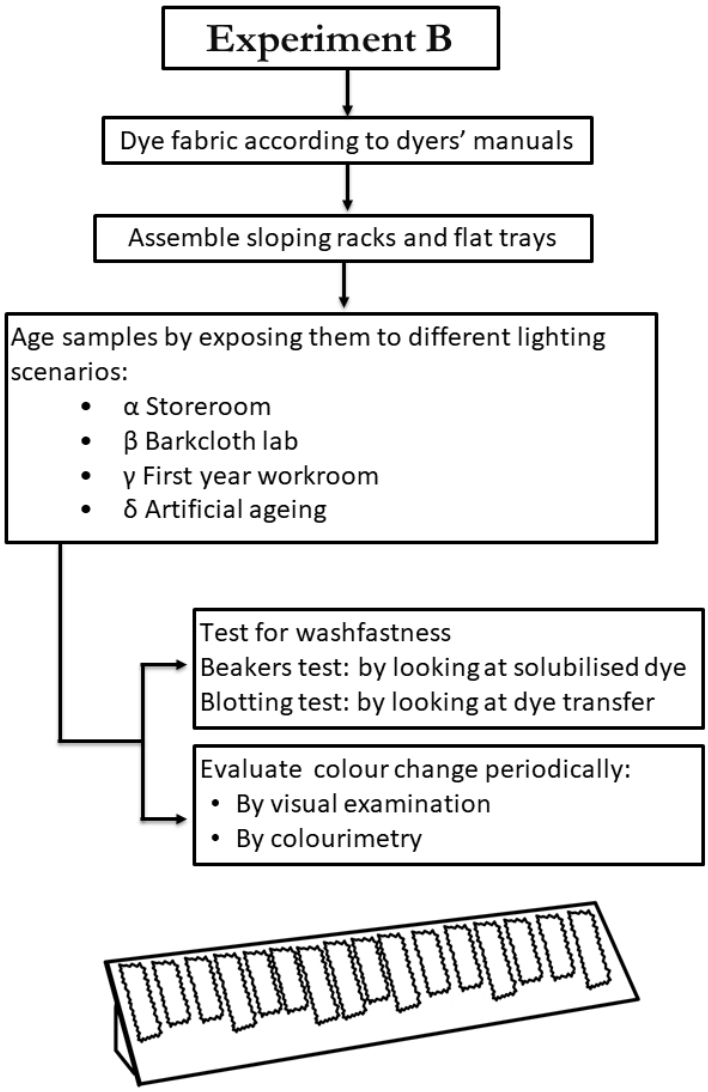

Figure 6.1. Summary of the methodology followed in experiment B

[182] Appendix 5.

6.2.1 Particularities of Artificial Ageing

Artificial ageing was used to imitate photodegradation over a short timescale. The flat trays with samples were placed inside the light-ageing machine Q-SUN Xe1 Xenon Test Chamber, with a 'Window–Q' specialty glass installed as a filter to simulate sunlight through a window. Samples were exposed to four continuous cycles of 24-hours, under standard testing conditions (ISO 105-B02:2014) (Table 6.1). The total energy elapsed was periodically registered, exposing samples to approximately 95 kJ/m^2 per cycle.[183] The temperature was maintained at 63 °C, as measured by the black panel sensor.[184] The type of equipment used did not allow for relative humidity control.

Table 6.1. Conditions for Artificial Ageing	
Irradiance[185]	1.1 W/m^2 at 420 nm
Light Cycle	Continuous for 24 hours
Average total energy	95 kJ/m^2 per cycle
Black Panel Temperature	63 °C
Relative Humidity	Uncontrolled (Extreme low humidity)

The position of the trays was shifted between cycles to promote even exposure.[186] Samples were not turned, as most historical samplers would only have the front face exposed to light on their usual type of display. The disadvantages of artificial ageing for experimental research were studied, acknowledging the unlikeliness of reproducing real-ageing scenarios.[187,188,189]

183 DM Grossman, "Errors Caused by Using Joules to Time Laboratory and Outdoor Exposure Tests," in *Technical Bulletin LU-8030*, Q-Lab Corporation, 2011. https://www.q-lab.com/products/q-sun-xenon-arc-test-chambers/q-sun-xe-1 (accessed June 27, 2018).
184 Q-Lab Corporation, "Q-SUN Xenon Test Chambers" 2018. https://www.q-lab.com/products/q-sun-xenon-arc-test-chambers/q-sun-xe-1 (accessed June 26, 2018).
185 AATCC. *AATCC Technical Manual vol. 68,* (North Carolina: AATCC, 1993) 36.
186 Khaled Elnagar et al., "Studying Irradiation Homogeneity in Light Aging for Historical Textile Conservation," *Fibers and Polymers* 14:9 (2013): 1581-1585. doi: 10.1007/s12221-013-1581-6
187 Quye et al., 9.
188 Robert Feller, *Accelerated Ageing: Photochemical and Thermal Aspects,* (Los Angeles: Getty Conservation Institute, 1994).
189 Appendix 5.

6.2.2 Particularities of Lighting Scenarios

The sloping racks were exposed to light from June 25th to July 16th, 2018 (672 hours total), following recommendations from previous work.[190] It was expected that the selection of lighting scenarios would provide a valid reference for real-time photodegradation, allowing for comparison with artificial ageing results. Conditions were monitored with data loggers to account for variability of natural daylight due to seasons or weather conditions. Spot readings for UV were recorded weekly.[191,192]

6.2.3 Colour Measurement

Colourimetry was used to periodically record the effects of light over the samples. This was done weekly for lighting scenarios and after each 24-hour cycle for artificial ageing. A Konica Minolta portable spectrophotometer (model CM-2300d) was used to analyse three different points on each wool replicate, selecting average specular component included values (SCI) for data interpretation. Data was analysed and graphed with JMP® and SpectraMagic™NX softwares.

The spectrophotometer works with a detector that measures the intensity of reflected light on each wavelength, allowing for precise and objective descriptions of colour.[193] Numerical values are triangulated under three spectral co-ordinates (Figure 6.2), describing the location of the colour in a three-dimensional sphere (Figure 6.3).[194] The difference between calculated values quantifies colour changes based on the CIE-L*a*b* system, which uses three variables (hue, saturation, and lightness) to communicate a colorimetric reference.[195]

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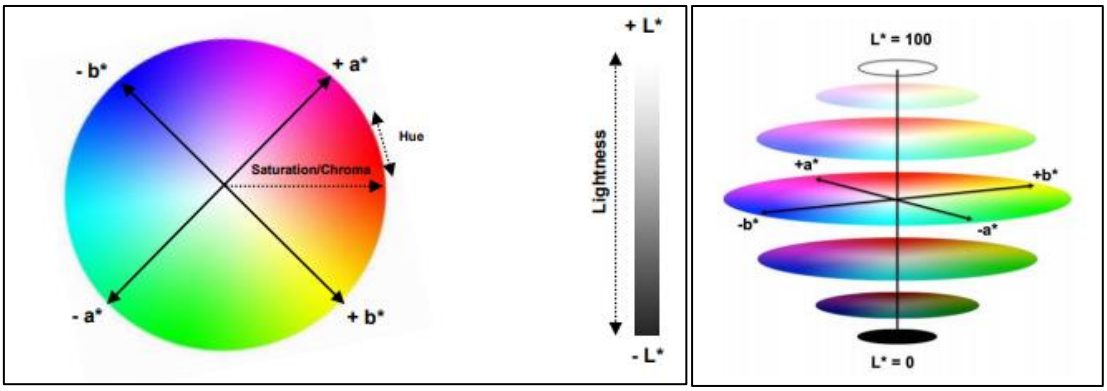
190 Michelle Hunter, "Let There Be Light? An Investigation into the Fading Characteristics of the Early Synthetic Dye Magenta" (MPhil dissertation, CTCTAH, UofG, 2016).
191 Valldeperas-Morell and Carrillo-Navarrete, 96.
192 Appendix 5.
193 Timár-Balázsy and Eastop, 82-87.
194 Anita Quye et al., *'Wroughte in gold and silk' Preserving the Art of Historic Tapestries,* (Edinburgh: NMS Enterprises Limited, 2009), 9.
195 Duff and Sinclair, 11, 148-158.



Figures 6.2. and 6.3. Spectral co-ordinates (left) that allow the location of a specific colour in the three-dimensional colour sphere (right) of the CIE-L*a*b* system.
Image © Sappi Fine Paper North America, 2013.[196]

The L* channel stands for lightness, where 0 is pure black and 100 is diffuse white. The other channels correspond to opposite chromatic axes: a* for red (+a) to green (-a), and b* for yellow (+b) to blue (-b). Differences in value of less than 2.0 points are not perceptible by the human eye, thus considered insignificant.[197]

Figure 6.4. Colour measurement of fabric samples with the spectrophotometer
© CTCTAH, University of Glasgow, 2018. Photo by Megan Creamer.

[196] Sappi Fine Paper North America, "Defining and Communicating Color: The CIELAB System," 2013. https://cdn-s3.sappi.com/s3fs-public/sappietc/Defining%20and%20Communicating%20Color.pdf (accessed July 30, 2018).
[197] Clare Richardson and David Saunders, "Acceptable Light Damage: A Preliminary Investigation," *Studies in Conservation* 52:3 (2007): 177-187.

6.2.4 Washfastness: Beakers Test

For each scenario, a small fragment was cut from the fabric strips (approximately 25 x 15 mm) and from the threads (approximately 15 mm). Samples were tested under two different methods which are representative of visual signposts for washfastness commonly used in conservation treatments: the beakers test and the blotting test.[198]

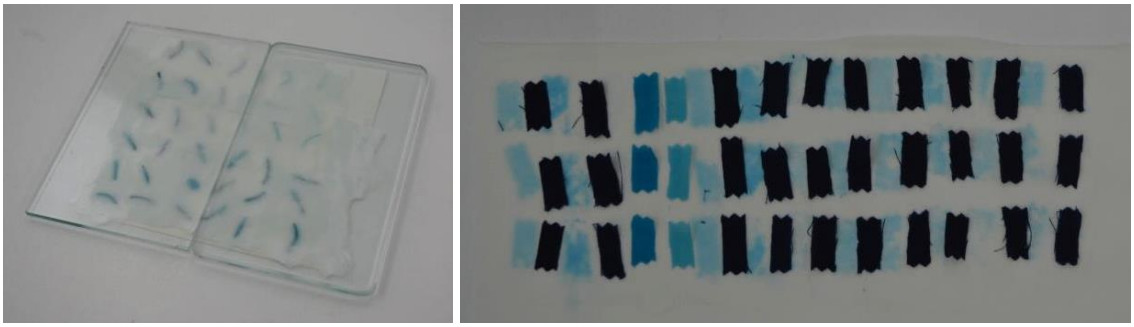
For the beakers test, each individual fragment was immersed in 10 mL tap water for 90 minutes at room temperature. Colouring of the solution was considered a positive indicator of solubilised dye. Visual colour matching was completed with an assigned scale, which went from 0–7, from 'low' to 'high' (Figure 6.8).

Figure 6.5. Beakers test to evaluate dye solubilisation

6.2.5 Washfastness: Blotting Test

Subsequently, the blotting test was completed to assess dye transfer by placing the wet samples between blotting paper and cotton wool. 50 mL tap water was uniformly poured over the cotton wool. Then, a glass plate was placed on top for pressure, preventing evaporation. After 30 minutes elapsed, the degree and amount of staining were ranked by visual colour matching on a scale from 0–3, where 0 means 'none' and 3 means 'very evident and much staining' (Figure 6.8).

[198] Foskett and CTCTAH (unpublished), 19.



Figures 6.6 and 6.7. Blotting test to evaluate dye transfer on threads (left) and fabric (right)
© CTCTAH, University of Glasgow. Photos by author.

Throughout these tests, it was acknowledged that the quality of colour matching depends on the viewing conditions of the observer[199] and that some tonalities could be situated on the colour discrimination threshold of the human eye.[200] Therefore, the same source of artificial illumination was used throughout, and pictures of the solutions were taken for consistency and objectivity in evaluation.

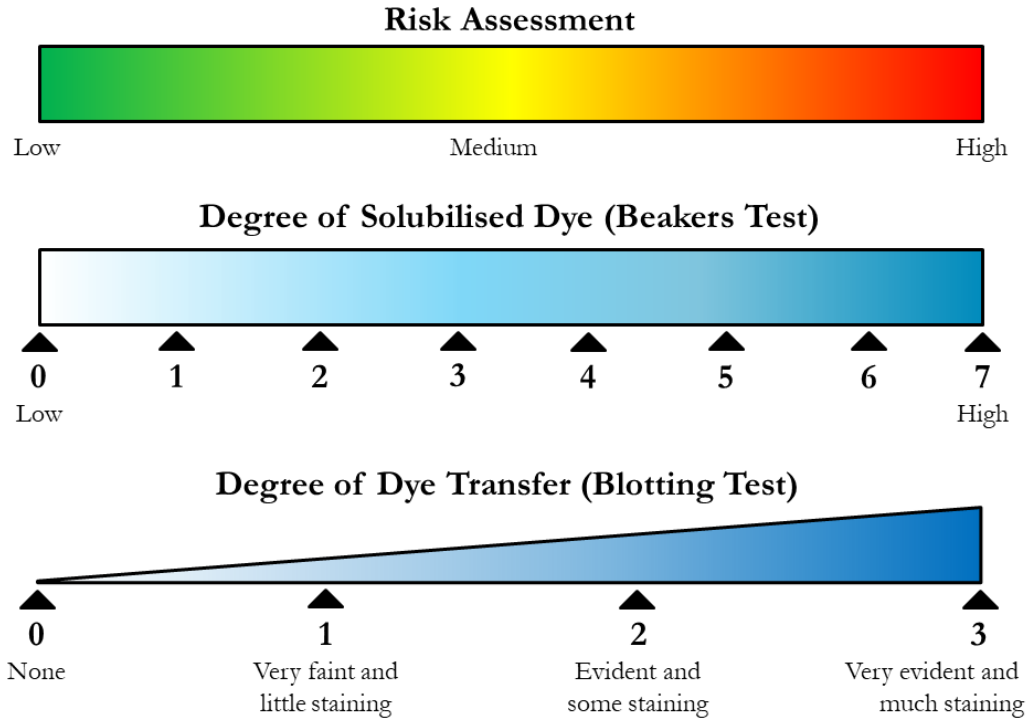


Figure 6.8. Scale for evaluating solubilised dye (beakers test) and dye transfer (blotting test) in relation to assessment of risks

[199] Duff and Sinclair, 10.
[200] Konica Minolta Inc., "Color Discrimination Threshold of the Human Eye" in *Konica Minolta Measuring Instruments*, 2018. https://www.konicaminolta.com/instruments/knowledge/color/part5/02.html (accessed August 2, 2018).

6.2.6 Additional Testing

Since the early stages of the experiment were not as informative as expected, it was decided to repetitively test the same set of fabric samples for washfastness to show the individual effects of wetting and drying cycles. Colour change was evaluated between cycles in order to quantify dye loss. Increments and reductions of dye solubilisation and transfer were evaluated to clarify issues about whether it is appropriate to refer to solubilised blue matter as excess dye. This exploratory phase was repeated three-times on samples from two representative scenarios: artificial ageing (48-hours) and storeroom (Week 3).

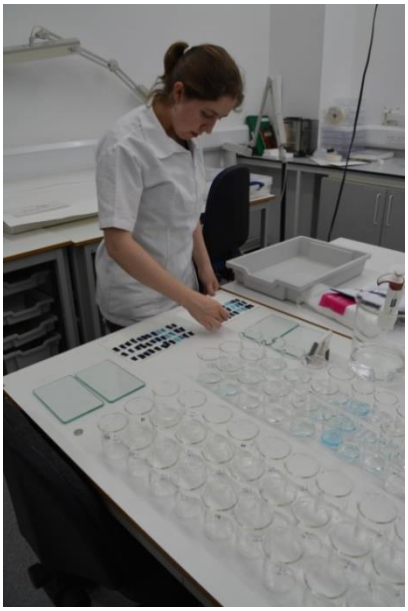


Figure 6.9. Repeated drying and wetting cycles of fabric samples to test washfastness
© CTCTAH, University of Glasgow, Photo by Megan Creamer.

6.3 Results

6.3.1 Colour Measurement for Artificial-Ageing

Regarding artificial ageing, differences in colour between non-mordanted fabric and thread samples (**C** and **F**) were evidenced. As an effect of the low dye concentration, fading was more evident on light bright blue samples (**B0** and **E0**). Based on colour change, it is inferred that photodegradation effectively took place and caused samples to become lighter, greener and less blue. Samples described in Table 6.2 were an exception, where colour change was not significant.[201]

[201] Appendix 5.

Table 6.2. Samples without Significant Colour Change during Artificial Ageing		
Sample	**Type**	**Description**
B8-Y after 24 hour cycle	Thread	With sodium sulfate, dyed with 8:1 indigo carmine at 45-50 C.
C8-W after 24 hour cycle	Thread	Non-mordanted, dyed with 8:1 indigo carmine at 45-50 °C.
D8-Y after 24 hour cycle	Fabric	With alum and cream of tartar, dyed with 8:1 indigo carmine at 85-90 °C.
E8-W after 24 hour cycle	Fabric	With sodium sulfate, dyed with 8:1 indigo carmine at 45-50 °C.

6.3.2 Colour Measurement for Lighting Scenarios

Overall, samples exposed to lighting scenarios showed insignificant colour change. These null results were clearly graphed with straight horizontal lines for all channels.[202] This obtruded correlating information with monitoring data for environmental conditions. Samples described in Table 6.3, which correspond to light depths of shade dyed with Fisher indigo carmine (**E0**), are an exception, as they were more susceptible to fading. This formulation has consistently shown a distinct behaviour which does not allow for comparison under the same parameters.

Table 6.3. Samples with Significant Colour Change from Lighting Scenarios		
Sample	**Scenario**	**Description**
E0-W in weeks 1, 2 and 3	Storeroom	With sodium sulfate, dyed with Fisher indigo carmine at 45-50 °C.
E0-W in weeks 1, 2 and 3	Barkcloth Lab	With sodium sulfate, dyed with Fisher indigo carmine at 45-50 °C.
E0-Y in weeks 2 and 3	Barkcloth Lab	With sodium sulfate, dyed with Fisher indigo carmine at 85-90 °C.
E0-W in weeks 1 and 2	Workroom	With sodium sulfate, dyed with Fisher indigo carmine at 45-50 °C.

[202] Appendix 5.

6.3.3 Washfastness: Beakers Test

The location of samples was evaluated by degree of solubilised dye. However, no broad trend was identified as to which variable factored. It was noticed that three types of sample **D0-W**, **E0-Y** and **F0-W** (Table 6.4) consistently showed dye solubilisation, although no pattern was established regarding changes in washfastness. As cycles and weeks elapsed, the visibility of solubilised dye decreased for all samples (Figure 6.10). Artificially-aged threads showed null results throughout.[203]

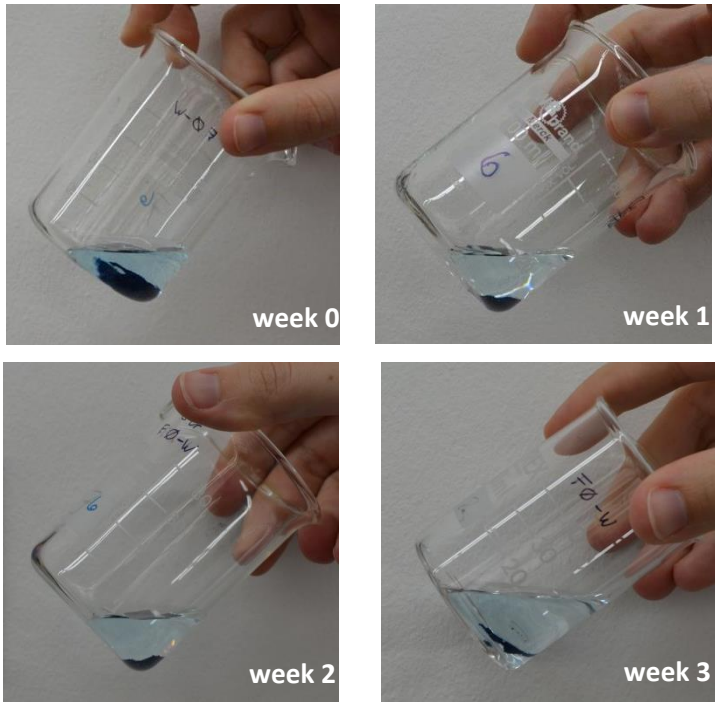


Figure 6.10. Washfastness results (beakers test) for non-mordanted sample, dyed with Fisher indigo carmine at 45-50 °C (**F0-W**) in the storeroom scenario. The visibility of solubilised dye decreased after week 1.
© CTCTAH, University of Glasgow, Photos by Staphany Chang and Kim Tourret.

Table 6.4. Samples Which Consistently Showed Solubilised Dye		
Sample	**Type**	**Description**
D0-W	Fabric	With alum and cream of tartar, dyed with Fisher indigo carmine at 45-50 °C.
E0-Y	Fabric	With sodium sulfate, dyed with Fisher indigo carmine at 85-90 °C.
F0-W	Fabric	Non-mordanted, dyed with Fisher indigo carmine at 45-50 °C.

[203] Appendix 5.

6.3.4 Washfastness: Blotting Test

The variations in results between replicates made it difficult to interpret results and withdraw conclusions. Patterns were not discernible for any scenario, although much staining and dye transfer was consistently evidenced on non-mordanted samples dyed with either dyeing matter at 45-50 °C (**F0-W** and **F8-W**). This test was considered unreliable.[204]

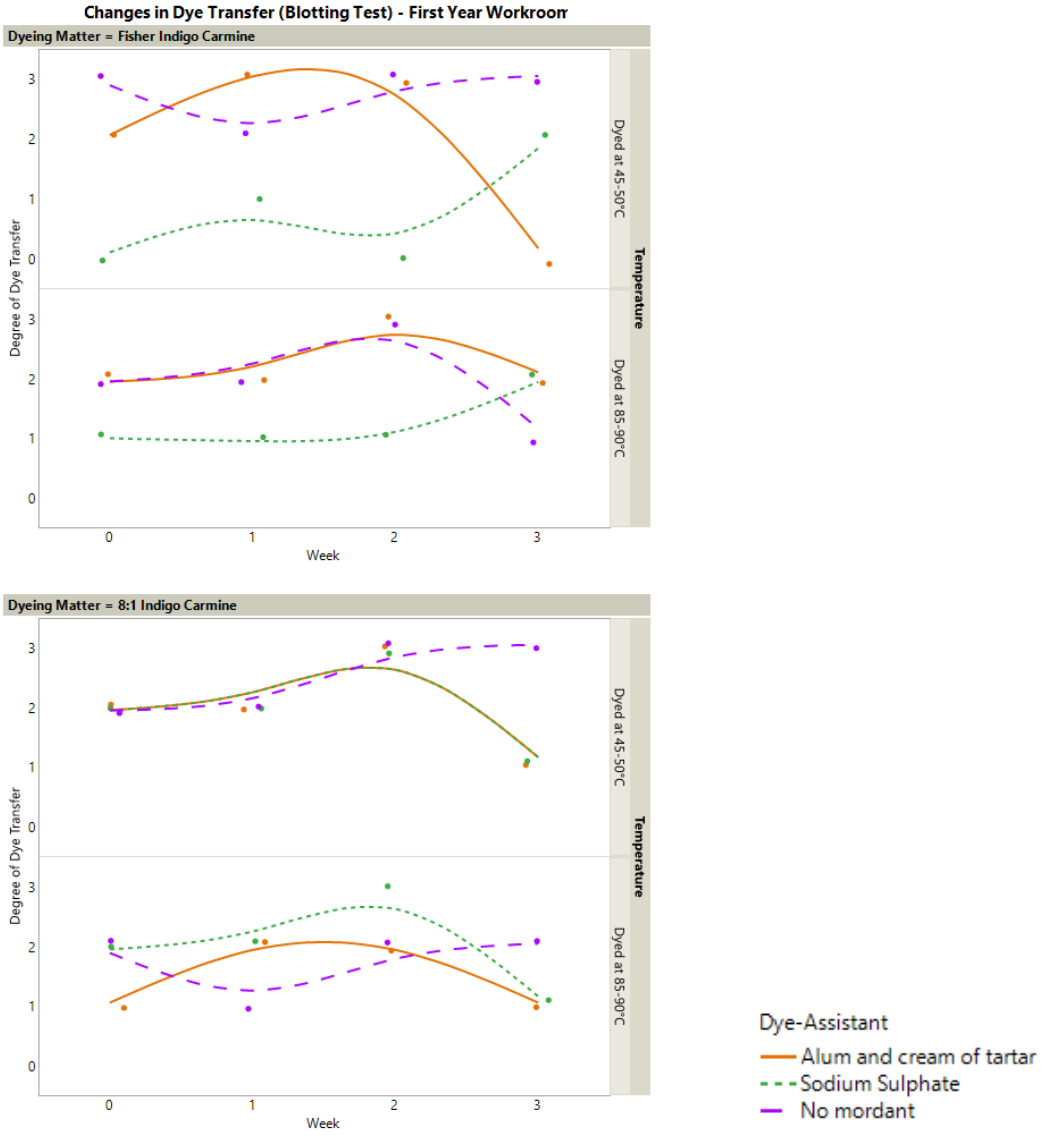


Figure 6.11. Washfastness results (blotting test) from a representative scenario (first-year workroom), showing lack of discernible patterns.

[204] Appendix 5.

6.3.5 Additional Testing

This exploratory phase revealed an unexpected behaviour of indigo carmine since the degree of solubilised dye increased noticeably after each wetting and drying cycle. The trend was consistent for both types of samples.[205] Colourimetry results agreed with significant loss of dye on artificially-aged samples, as those became lighter, greener, and less blue (Figure 6.14). Colour change was not as evident on storeroom samples (Table 6.5).

Table 6.5. Samples from the Storeroom Scenario (after week 3) with Significant Colour Change after Repeating Cycles	
Sample	**Description**
E0-Y in 2x and 3x	With sodium sulfate, dyed with Fisher indigo carmine at 85-90 °C.
E0-W in 2x and 3x	With sodium sulfate, dyed with Fisher indigo carmine at 45-50 °C.
D8-Y in 3x	With alum and cream of tartar, dyed with 8:1 indigo carmine at 85-90 °C.

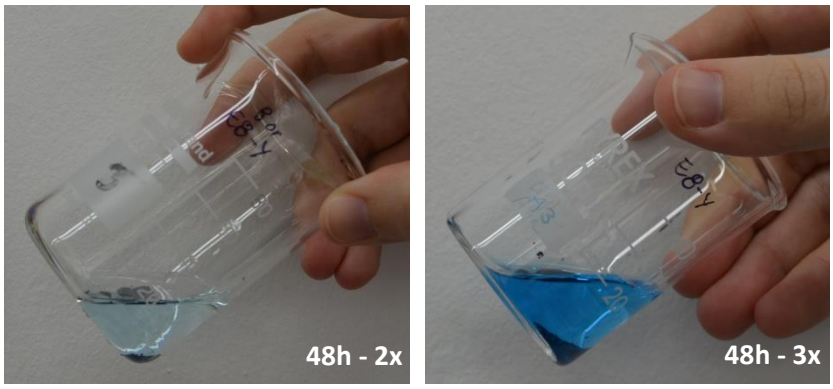


Figure 6.12. Washfastness results (beakers test) after repeated wetting and drying cycles for artificially-aged fabric sample with sodium sulfate, dyed with 8:1 indigo carmine at 85-90 °C (**E8-Y**) after week 48-hour cycle. The visibility of solubilised dye increased after each cycle.[206]
© CTCTAH, University of Glasgow, Photos by Staphany Chang.

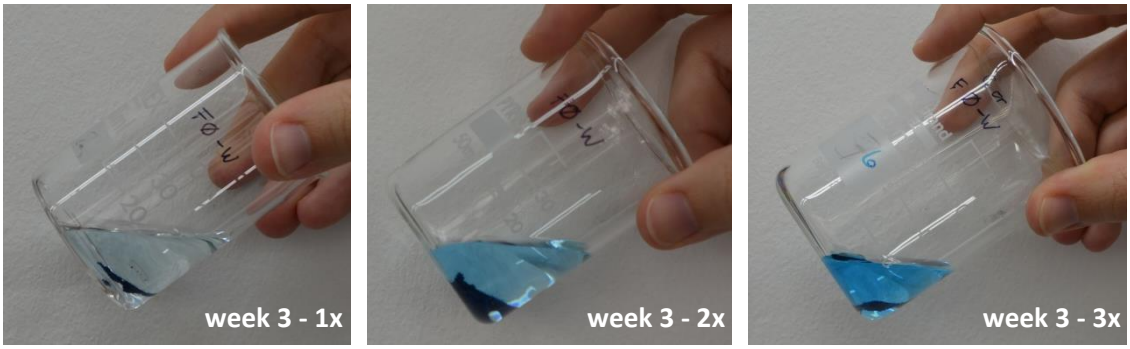


Figure 6.13. Washfastness results (beakers test) after repeated wetting and drying cycles for non-mordanted sample, dyed with Fisher indigo carmine at 45-50 °C (**F0-W**) from the storeroom scenario after week 3. The visibility of solubilised dye increased after each cycle.
© CTCTAH, University of Glasgow, Photos by Megan Creamer.

[205] Appendix 5.
[206] A photograph for 48h–1x does not exist, as no solubilised dye was shown during initial testing.

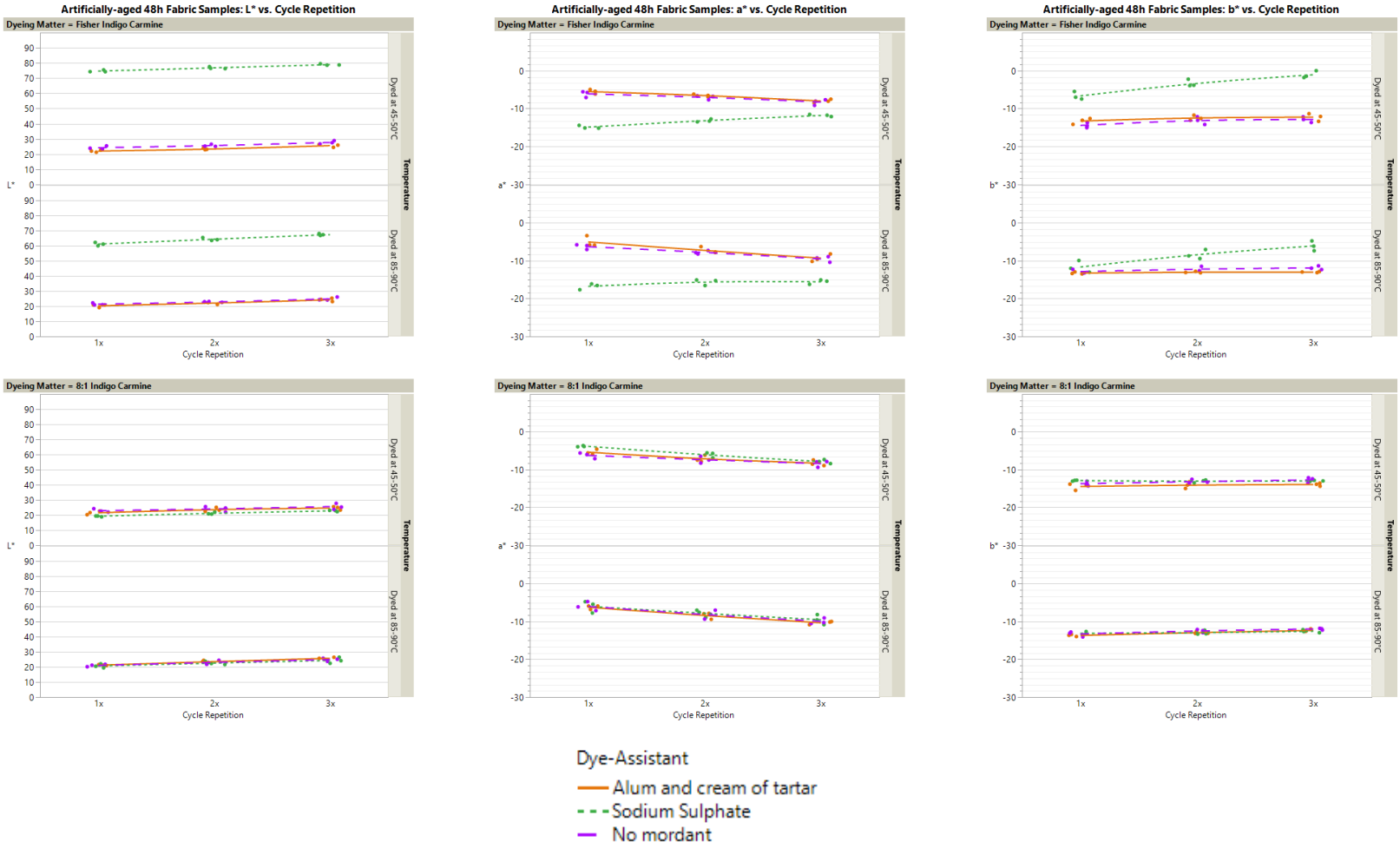


Figure 6.14. Colour measurement results for artificially-aged fabric samples (after 48 hours).
Most samples became lighter (+L*), greener (-a*), and less blue (+b*). Change in colour was significant.

6.4 Discussion

6.4.1 Colour Measurement

Studies on the effects of light over dyed textiles show that the spectral characteristics of a light source can influence lightfastness as much as the absorption potential of the dye-fibre system.[207,208] Throughout artificial ageing, colour change was noticeable, evidencing that different formulations of indigo carmine faded similarly under extreme conditions. However, the relation between each lighting scenario and fading could not be determined – possibly because photodegradation did not occur within the short time-span allocated. Longer periods of observation and harsher conditions are suggested to examine the impact of different lighting scenarios.[209,210]

Colourimetry for artificially-aged samples agreed with mentions on the dyestuff's lightfastness, which is comparable to turmeric.[211] This characteristic remains unfamiliar to conservation practitioners, which can be linked to a larger problem of disseminating information regarding indigo carmine's particularities. Awareness on the dye's photosensitivity would inform strategies to prevent photodegradation.[212]

6.4.2 Washfastness: Beakers Test

Graphed data shows that dye solubilisation decreased for most scenarios after the first week. However, this trend in visual colour-matching results was considered misleading after finding references related to issues on the identification of indigo carmine. Although it was known beforehand that indigo carmine solutions are unstable and tend to degrade to become yellowish or colourless,[213] it was not considered that this effect could be triggered by several photodegradation pathways,[214] or that chromophores could be present in deactivated states.[215] This means that more reliable techniques, which do not depend on the perception of the human eye, are required to objectively evaluate the possible presence of indigo carmine's deactivated states or degradation products in solution.

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207 Bowman and Reagan, 37, 42.
208 Millington, 155.
209 UV radiation in the barkcloth lab was expected to be high. Unfortunately, as the experiment progressed, it was noticed that UV radiation was limited. The experiment kept running as changing scenario would not allow for comparisons.
210 Appendix 5.
211 Troalen et al., 88.
212 Bowman and Reagan, 41.
213 de Keijzer et al., S92.
214 Hernández-Gordillo et al., 34.
215 Sousa et al., 1354.

After the 24-hour cycle of artificial ageing for fabric samples elapsed, it was noticed that some solutions tinted yellow, instead of blue. Other observations throughout this test included strong odors and increasing difficulty to wet samples in water. In-depth investigation outside the scope of this dissertation is required to explain these effects, which were perceived to increase with ageing and could potentially relate to the "formation of intermediates containing a chromophoric group."[216] Indigo carmine's breakdown products include formic, acetic, and oxalic acids,[217] meaning that more complex reactions could take place. If these yellow products were to be representative of the dyestuff's photodegradation, it is unlikely for conservators to perceive them during wet-cleaning treatments of soiled historical textiles.

6.4.3 Washfastness: Blotting Test

This test suggests that non-mordanted samples show more dye transfer; however, when correlating results with other tests in the experiment, it is not clear whether those samples are less resistant to washing. Overall, data was not consistent across replicates, formulations, or scenarios, so trends could not be determined; furthermore, dye solubilisation did not show a relation with dye transfer. The blotting test was therefore considered unreliable for evaluating dye transfer, leading to further questions about the representativeness of current washfastness tests used in textile conservation.

Based on the amount of factors that influence the visibility of signposts in current washfastness tests, it is thought that more control over variables during testing is required to inform decision-making for wet cleaning historical textiles. For example, the presence of an alkaline reserve in acid-free blotting paper can influence results because indigo carmine is pH sensitive and chromophores can deactivate on basic conditions. The use of cotton wool might be a more indicative tool for washfastness, although the use of cellulosic substrates disregards indigo carmine's affinity to proteinaceous fibres. In practice, considering the importance of affinity between specific dye-fibre systems, it would be more appropriate to complete washfastness tests over a substrate that is similar in nature to the fibres adjacent to indigo carmine dyed elements. This would respond to variations in the rate of diffusion between substrates. Checking colour movement at specific intervals can

[216] Galindo et al., 51.
[217] Sousa et al., 1354.

also prove useful,[218] as indigo carmine tends to become colourless. Finally, it is recommended to perform this test with the solution and drying method proposed for treatment, as this greatly influences the degree of dye transfer.

The relevance of washfastness tests involves bigger questions as to why textile conservators rely on this piece of information before completing wet cleaning treatments: Can dye bleed be objectively quantified? Is the method accessible in textile conservation practice? Do results allow for accurate inferences in behaviour? In which ways do these results inform our decision-making? All of these emphasise the importance of ethical sampling to avoid destructive techniques when the decision-making process can be informed by looking at conservation literature and studying the context or provenance for historical textiles. Conservators have to evaluate the likelihood of obtaining representative data from destructive sampling.

6.4.4 Additional Testing

Additional testing showed that the degree of dye loss escalates between repeating wetting and drying cycles. A relation with photodegradation may exist since artificially-aged samples showed more colour change between cycles than samples proceeding from the storeroom scenario. More importantly, this phase demonstrated that it is unlikely for solubilised dye to be excess dye, since it would have washed-off from the first time the samples were wetted. In opposition, blue tonalities became more intense as cycles were completed.

Exposure to water is certainly causing dye loss but this could be related to many degradation pathways. Although this preliminary study offered insight into indigo carmine's wet behaviour, a better understanding of the chemical reactions that are taking place is fundamental to inform decision-making in conservation practice. The dye's complex photochemistry should be studied to inform the treatment of historical textiles.

[218] Foskett and CTCTAH (unpublished), 19-20.

Figure 6.15. Beakers test showing positive results for solubilised dye on most samples, throughout additional testing.
© CTCTAH, University of Glasgow, Photo by author.

6.5 Conclusion

Null and unclear results did not allow for clarifying the relationship between photodegradation and washfastness. As in experiment A, lighter shades did not show dye solubilisation or transfer, which was attributed to the low dye concentration rather than to better fixing properties of dye-assistants. Furthermore, trends could not be established due inconsistency in results across replicates, formulations, or scenarios. This called for an evaluation of current washfastness tests used in textile conservation, exhorting that techniques prove unreliable unless more factors are controlled throughout testing. It is recommended that conservators perform washfastness tests with the solution and drying method to be used, as this greatly influences the degree of dye transfer

Additional testing showed increments in solubilised dye after each wetting and drying cycle. Significant dye loss was observed on artificially-aged samples, as opposed to unexposed storeroom samples. This suggests that a relation between indigo carmine's photodegradation and washfastness may exist, although it depends on more complex factors. The understanding of mechanisms of decay remains fundamental for informing conservation practice.[219]

[219] Quye et al., 9.

7. Experiment C: Wetting of Historical Samplers

7.1 Introduction

This experiment was designed following the findings of experiment B additional testing phase:

v. To assess if indigo carmine colouring matter from historical samplers shows different degrees of solubilisation after repeated cycles of wetting and drying.

The objectives included:

- To compare degree of dye solubilisation between rinsing cycles.
- To quantify colour change after each rinsing cycle.
- To discuss ethical issues regarding dye solubilisation.

This allowed verifying if the behaviour observed on replica samples throughout repeated wetting and drying cycles was comparable to the one on historical textiles with indigo carmine present. Besides objectively assessing if colour change was significant with each water rinse, it was expected to define if new colouring matter solubilised repeatedly. Two samplers presenting the characteristic staining caused by indigo carmine from the Karen Finch Reference Collection were selected because of their little soiling.[220]

Sampler 1783 was embroidered by Elizabeth Storherd, using silk threads on a woollen ground.[221] Blue haloes were visible near green embroidery threads. Sampler 1808 was embroidered by Hannah West, using silk threads on a linen ground. Although staining was spread throughout the sampler due to the predominant use of blue embroidery threads, blue haloes were more evident on the upper half.

7.2 Methodology

Data was collected between cycles using a Konika Minolta spectrophotometer. The tonality of the bath solutions was evaluated visually, as in experiment B. As part of the set-up, five sampling points per sampler were selected to be colour-measured, each one

[220] Appendix 7.
[221] Fibre identification was completed with optical microscopy.

measuring 3 mm in diameter. This matched the spectrophotometer aperture switch (Figures 7.2 and 7.3). A Melinex® sheet template was used to promote registering readings on the same location. The selection of sampling points included stained areas as well as indigo carmine threads in order to study whether stained areas released dye less readily or noticeably, as reported.[222]

The conditions for immersion and drying method were defined in advance: 500 mL tap water were used per rinse to allow for a shallow bath that evidenced dye solubilisation. Solubilised dye samples from each rinse were collected and kept in the freezer for future analysis with UV-Visible spectroscopy. After the allocated time for immersion elapsed, 500 mL tap water were poured over the object to remove superficial dye. Blotting paper was used to remove excess water from the sampler. Drying was completed by simultaneously using a cool hairdryer and the suction table to prevent dye transfer.

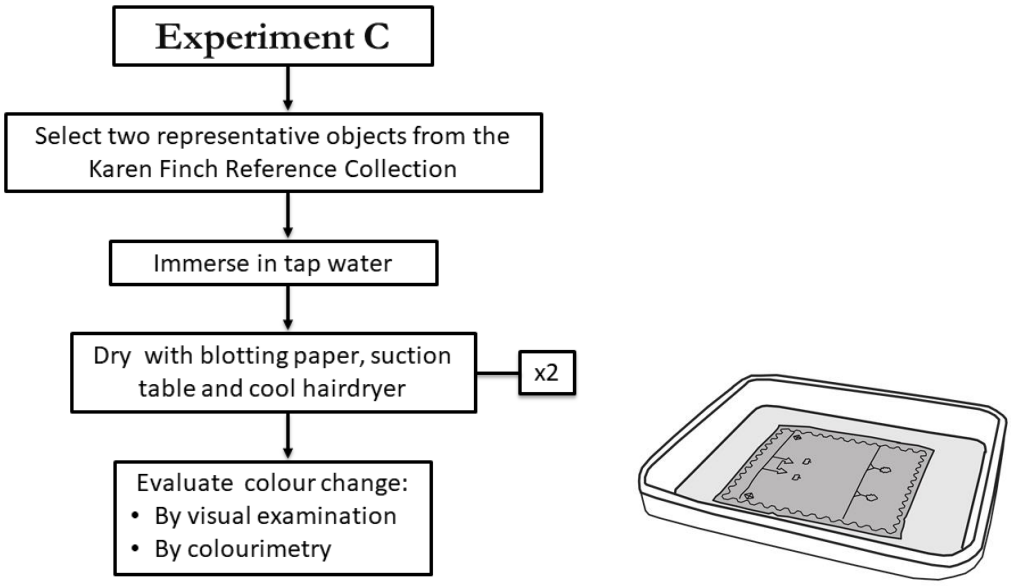

Figure 7.1. Summary of the methodology followed in experiment C

[222] Sahmel et al., 82.

Figure 7.2. Location of sampling points for Sampler 1783

Table 7.1. Sampling Points from Sampler 1783		
Sampling Point	**Type**	**Description**
1	Stain on wool	Wool ground slightly stained
2	Embroidery thread	Light green tree
3	Embroidery thread	Bright blue and green base of a tree
4	Stain on wool	Wool ground largely stained
5	Embroidery thread	Bright green bird with orange dots

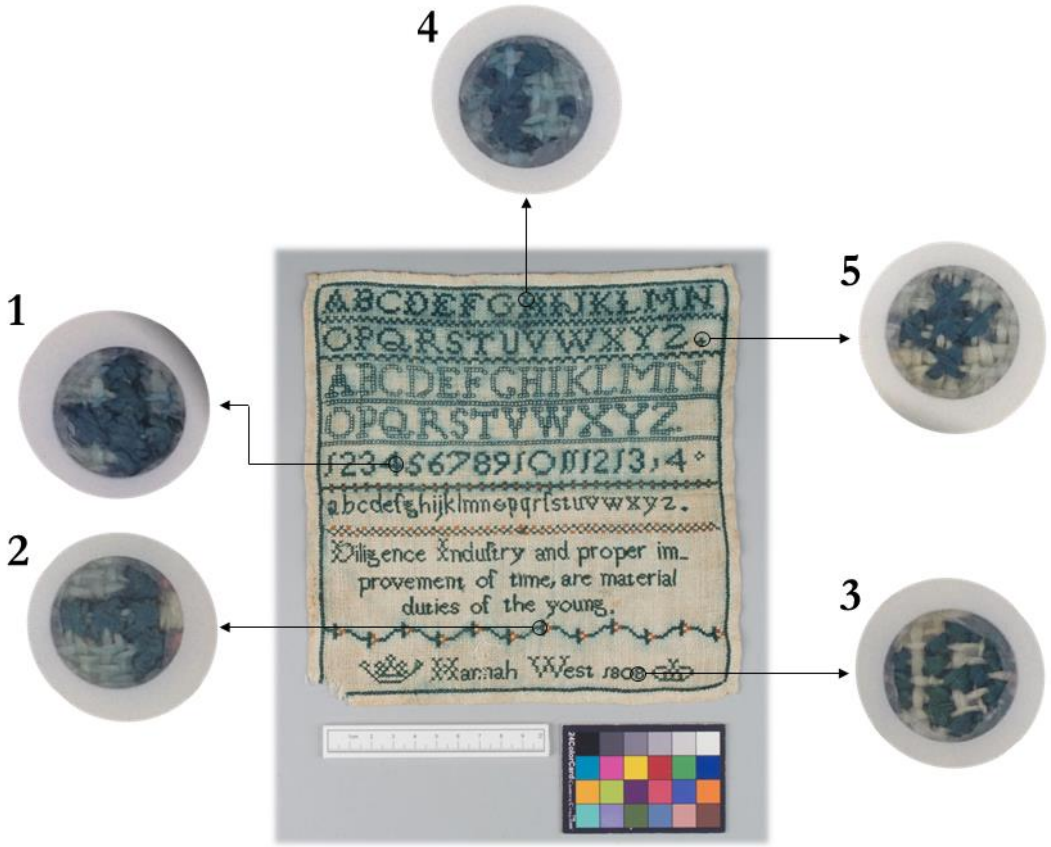

Figure 7.3. Location of sampling points for Sampler 1808

Table 7.2. Sampling Points from Sampler 1808		
Sampling Point	**Type**	**Description**
1	Embroidery thread	Section of number 4
2	Embroidery thread and stained linen	Stem of bottom flower divider
3	Embroidery thread	Last 8 from 1808
4	Embroidery thread and stained linen	Section of letter H
5	Embroidery thread	Dot after letter Z, unstained linen

7.3 Results

The immersion of samplers was completed under these conditions:

Table 7.3. Conditions During Immersion			
Conditions		**First Rinse**	**Second Rinse**
Sampler 1783	Initial pH[223]	7.5	7
	Final pH	6.5	7
	Total duration	25 minutes	25 minutes
	Temperature	22 °C	23 °C
	Relative humidity	49%	47%
Sampler 1808	Initial pH	7.5	7
	Final pH	7	7
	Total duration	10 minutes	10 minutes
	Temperature	23 °C	22 °C
	Relative humidity	49%	47%

Samples of each rinsing cycle were collected, with two different solutions for Sampler 1783 to show differences in dye release as time elapsed.

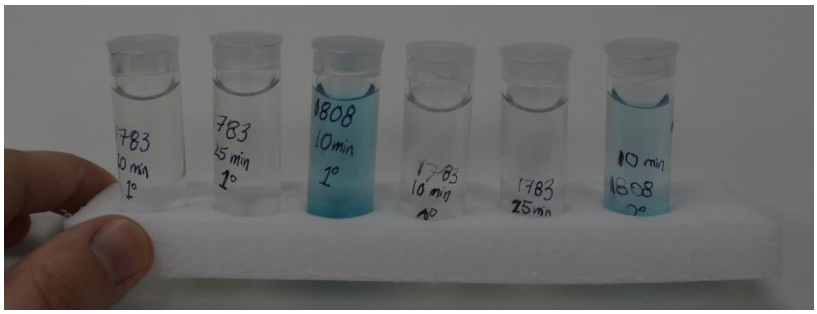

Figure 7.4. Collected samples of solubilised dye per rinsing cycle

The selected drying method proved useful for avoiding dye transfer to adjacent fibres. However, when the samplers were pressed with blotting paper, a considerable amount of blue dye migrated onto the paper substrate.

7.3.1 Eye Examination

Blue colouring matter was solubilised with each immersion. For both objects, the solution from the first rinse was slightly darker, presumably caused by the removal of soiling products. The solution from the second rinse was slightly less saturated, but of brighter blue tonality. Changes in pH after rinsing were not considered significant.

[223] As measured with pH indicator strips (Macherey-Nagel, 0-14 range)

Figures 7.5 and 7.6. Solubilised dye from Sampler 1783 after first (left) and second rinse (right)

Figures 7.7 and 7.8. Solubilised dye from Sampler 1808 after first (left) and second rinse (right)

Sampler 1783 did not exhibit significant changes other than the reduction of blue haloes (Table 7.5). Even though Sampler 1808 was exposed to water for a shorter time-period, blue dye was released continuously. The final condition of the object presented visible colour change towards duller greens (Table 7.6). The blue tonalities at the top of Sampler 1808 were the most altered, evidencing slight differences in colour on embroidery threads between the top and bottom section, which was not apparent before immersion.

Figures 7.9 and 7.10. Differences on initial dye release on Sampler 1783 (left) and 1808 (right)

Figures 7.11 and 7.12. Sampler 1783 before (left) and after completion of two rinsing cycles (right) Evidence of reduction of blue haloes
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Figures 7.13 and 7.14. Sampler 1808 before (left) and after completion of two rinsing cycles (right) Evidence of reduction of blue haloes and change in colour towards greener and duller tonalities
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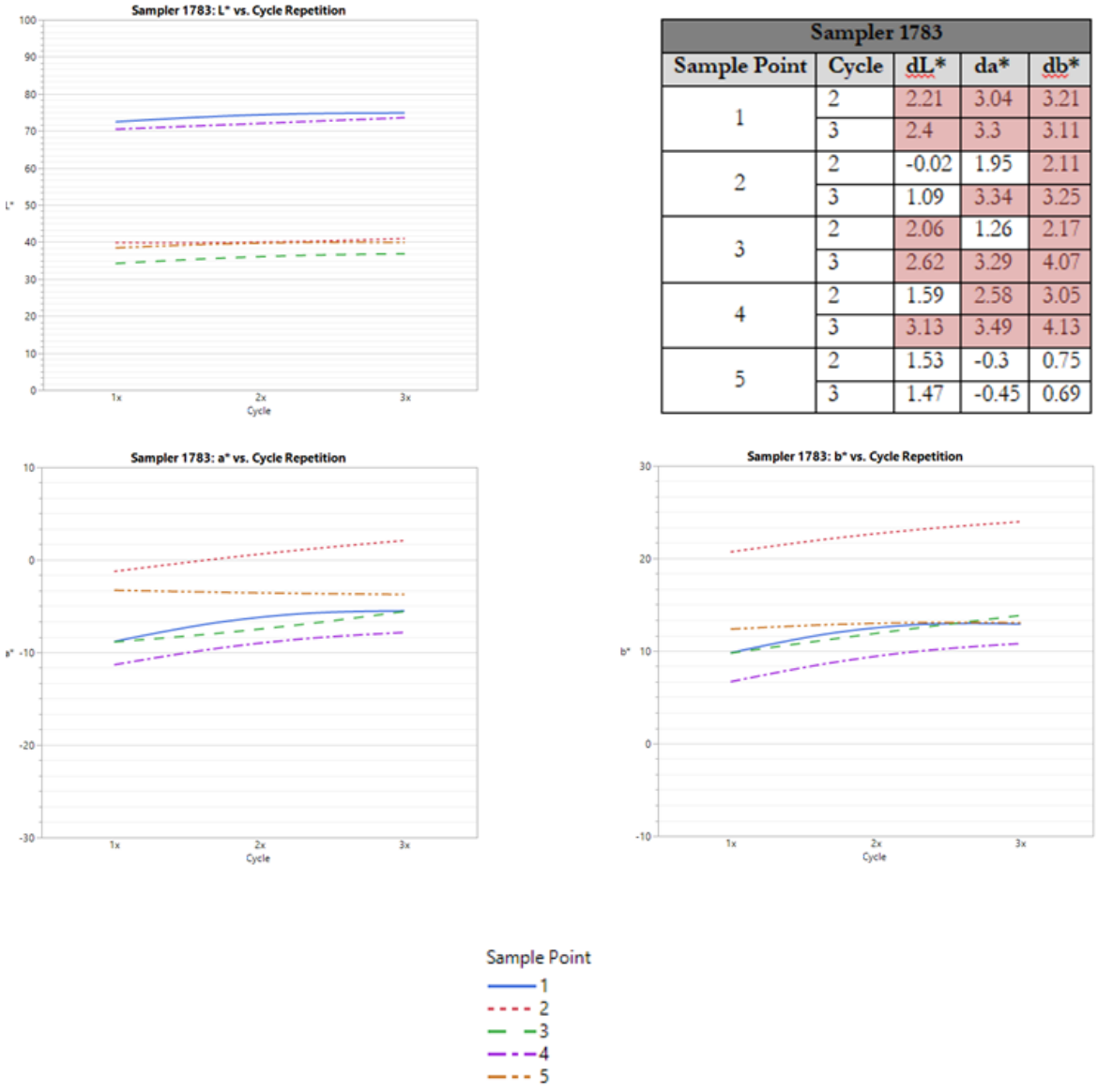
7.3.2 Colour Measurement

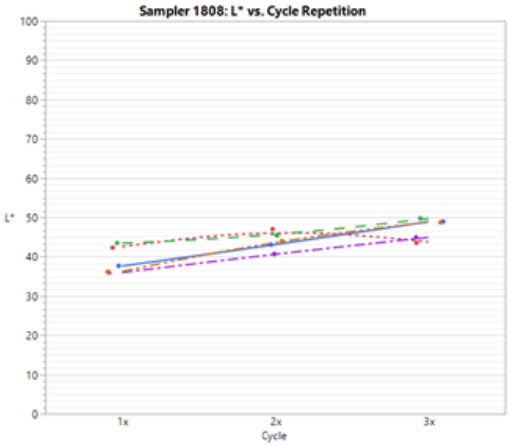
The colourimetric results presented a continuous progression towards lighter (+L*), less green (+a*) and less blue (+b*) tonalities for the majority of sampling points.[224] All sampling points showed significant colour change (e.g. Table 7.4), with the exception of point 5 in Sampler 1783 (bright green bird with orange dots), suggesting the unlikeliness of indigo carmine presence on those threads, and explaining why colour remained unaffected.

[224] Appendix 6.

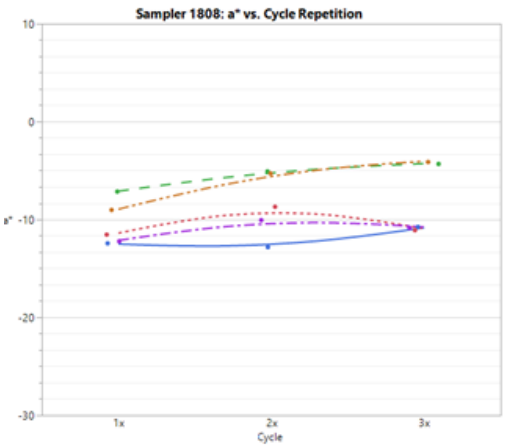


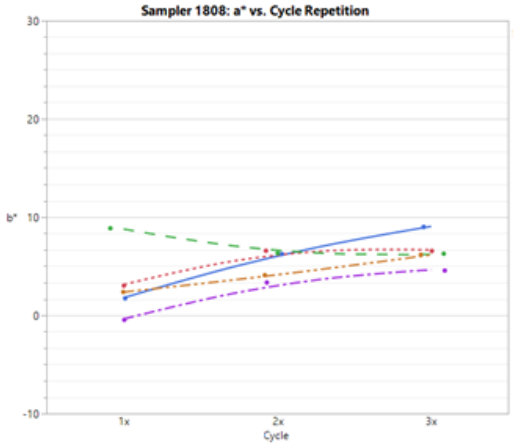
Sampler 1783				
Sample Point	Cycle	dL*	da*	db*
1	2	2.21	3.04	3.21
	3	2.4	3.3	3.11
2	2	-0.02	1.95	2.11
	3	1.09	3.34	3.25
3	2	2.06	1.26	2.17
	3	2.62	3.29	4.07
4	2	1.59	2.58	3.05
	3	3.13	3.49	4.13
5	2	1.53	-0.3	0.75
	3	1.47	-0.45	0.69

Figure 7.15. Colourimetry results for Sampler 1783, showing a continuous progression towards lighter (+L*), less green (+a*) and less blue (+b*) colours. The table shows that colour change (marked in red) is significant for all sampling points except 5 (bright green bird with orange dots).



Sampler 1808				
Sample Point	Cycle	dL*	da*	db*
1	2	5.38	-0.39	4.51
	3	11.29	1.67	7.28
2	2	4.73	2.84	3.55
	3	1.22	0.45	3.53
3	2	1.91	2.06	-2.52
	3	6.28	2.82	-2.58
4	2	4.73	2.16	3.8
	3	8.96	1.36	5.02
5	2	7.77	3.74	1.71
	3	12.53	4.9	3.8





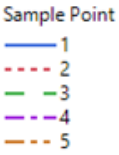
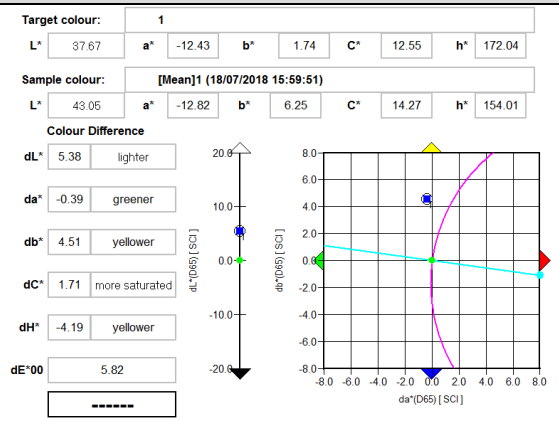
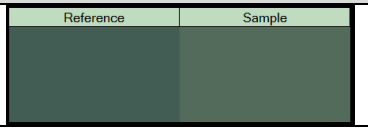


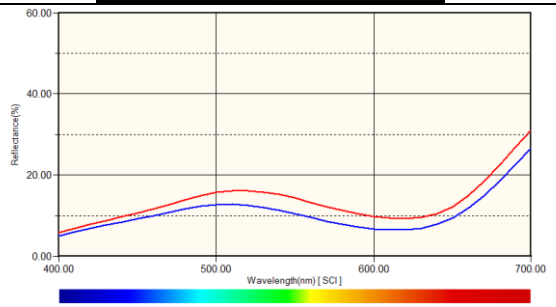
Figure 7.16. Colourimetry results for Sampler 1808, showing a continuous progression towards lighter (+L*), less green (+a*) and less blue (+b*) colours, with the exception of sampling point 3 (last 8 from 1808), which became bluer. The table shows that colour change (marked in red) is significant for all sampling points.

Table 7.4. Sampler 1808 – Sampling Point 1 (Section of number 4).

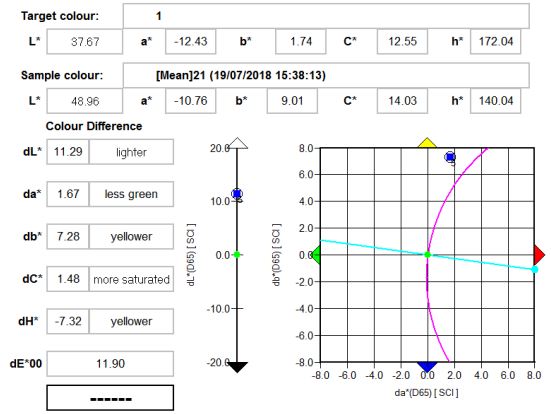
After first rinse

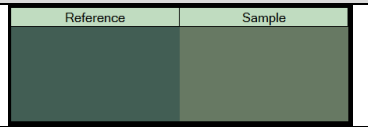


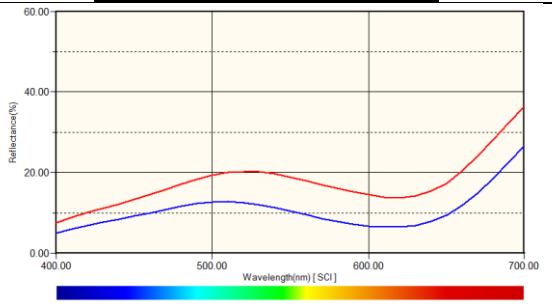




After second rinse







Results: Sampling point presents shifts towards lighter (+L*), less green (+a*) and less blue/yellower (+b*) colours after each rinsing cycle, in comparison to reference sample, which was measured before wetting cycles were completed (graphs at the left). Changes in the sampling point average colour are evident and increase after each rinse (figures at the top, right). Changes in spectral reflectance indicate an overall 10% increase in reflectance after second rinse, with a slight shift (~510 to 530 nm) in reflection from the blue range (450-495 nm) towards the green range (495-570 nm) (graphs at the bottom, right). Effects are cumulative.

Table 7.5. Sampler 1783 – Rinsing Cycles		
Before	**After first rinse**	**After second rinse**
		
Condition before wetting cycles.	Reduction of blue haloes around trees in the lower section of the sampler.	Further reduction of blue haloes around trees in the lower section of the sampler.

Table 7.6. Sampler 1808 – Rinsing Cycles		
Before	**After first rinse**	**After second rinse**
		
Condition before wetting cycles.	Overall reduction of blue haloes around embroidery threads on the top half of the sampler. The lower part looks slightly more stained, especially along the border.	Further reduction of blue haloes around embroidery threads on the top half of the sampler. The staining in the lower part was also reduced. Colour change towards greener and duller shades is evident throughout. The middle section of the sampler did not present as much dye solubilisation as the top and lower parts.
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7.4 Discussion

7.4.1 Eye Examination

Overall, indigo carmine elements behaved as expected: dye solubilisation in water occurred. However, no increase in the amount was observed between cycles. As concluded in previous experiments, it could be that specialised techniques – other than visual examination – are required to objectively quantify dye concentration; although it is also possible that the dyed fabric samples used throughout experiment A and B are not entirely representative of historical indigo carmine elements.

As in conservation practice, this experiment showed that each historical object responds differently, even though the same conditions were used during immersion. This was evidenced by the response to water exhibited by the samplers, where Sampler 1808 released dye faster and more readily than Sampler 1783. Although stain removal was not the focus of this dissertation, good results were achievable on Sampler 1783 without the need of chelators.[225]

Sampler 1808 was more uniform in tonality before completing the rinsing cycles whiles, at present, the top five lines show a different tonality to the lines corresponding to the lowercase alphabet, the verse, and the signature. This can be attributed to indigo carmine being used for both areas but mixed in different ratios, or with other dyes, for threads on the bottom part. It is possible that more constitutive matter was washed from the top section, where threads contained purer indigo carmine. This alteration provides evidence on the damages that repetitive wet cleaning can cause over indigo carmine elements.

As this experiment showed, lighter and yellower tonalities can also result from repeated washing. Linking back these results to reports on indigo carmine fading to become greener and yellower,[226] it is considered difficult to differentiate between the visual effects of fading and repeated cleaning. Therefore, determining the cause of degradation for decontextualized objects based solely on tonality may prove misleading.

[225] Sahmel et al.
[226] de Keijzer et al., S87.

7.4.2 Colour Measurement

Sampler 1808 showed more colour change than Sampler 1783. The step in colour change was larger after the first rinse for Sampler 1783, while Sampler 1808 suffered more significant changes after the second rinse was completed. A clear trend is indistinguishable on whether sampling points from stained areas or embroidery threads suffered from more dye loss.

It is likely that the proteinaceous (Sampler 1783) or cellulosic nature (Sampler 1808) of the ground fabric impacted on the degree of stain reduction. However, this aspect could not be quantified through this experiment. It was initially expected for staining on Sampler 1808 to be more superficial because cellulosic fibres have less affinity for indigo carmine. Therefore, dye should be releases with more ease. However, the results were obscured because dyeing matter in Sampler 1808 was less resistant to water than the one in Sampler 1783. This observation shows the complexity of dye-fibre systems and supports initial observations about indigo carmine presenting diverse behaviours, possibly dependant on dyeing formulations or degradation pathways.

7.4.3 Ethical Issues

Decision-making for wet cleaning objects with indigo carmine is theoretically more complex than initially thought, considering that colour change after aqueous treatments is noticeable by human perception. This opens discussion about acceptable colour change[227] and calls for thoughtful risk assessments to prevent loss in value. An agreed framework between heritage specialists is considered necessary to evaluate and assess the importance of context and colour associations for this type of objects.

The solubilisation of constitutive dyeing matter also needs to be addressed. The cumulative effects of repetitive wetting and drying cycles remain unclear. Further studies are needed to find if chemical changes during wet cleaning could make objects more susceptible to deterioration. More discussion is needed about whether tolerance for risk exists or aqueous treatments should be deemed unacceptable.

[227] Richardson and Saunders, 184-185.

7.5 Conclusion

This experiment allowed for research findings to be associated with some unexpected realities of wet cleaning indigo carmine elements. Direct experimentation with historical textiles showed similar results to the additional testing phase of experiment B, with the exception that increments in solubilised dye between cycles were not observed. Further study into the stability of the dye-fibre system and the chemical reaction that potentially increments dye solubilisation is required to suggest preventative measures and strategies for conservation purposes.

The risk of dye solubilisation and colour change during wet cleaning is undeniable for indigo carmine elements, although dye transfer can be controlled. This experiment supported the hypothesis that solubilised blue colouring matter is unlikely to be excess dye. This raises new ethical questions for conservators as it shows that traditional wet cleaning procedures for indigo carmine objects are presumably causing dye loss and changes in colour, which are irreversible and undesirable alterations.

It is suggested that conservators systematically examine the amount, location, and distribution of indigo carmine elements before proceeding with wet cleaning. The practice of isolating areas also gains importance for this kind of objects as localised cleaning offers a less interventive approach that could prevent some alterations. Alongside the treatment proposal for soiling removal, gathering this type information will allow for better risk assessments, as it will inform the decision-making process in order to balance time, costs, and benefits.

8. Conclusions

8.1 Evaluation of Project

This preliminary investigation contributed to the understanding of indigo carmine's variable behaviour during conservation wet cleaning. Assumptions about the dye's properties were reviewed and evaluated against documentary and material evidence, concluding that the practical expectations were overly simplistic. The methodological approach showed the importance of historical primary sources to gain insight into the inherent properties of this semi-synthetic dye. For the first time, a relation between indigo carmine's lightfastness and washfastness was revealed. In addition, the wet behaviour of replica samples was compared to historical samplers, demonstrating that solubilised blue matter is not excess dye. The experimental phase showed that material investigation of indigo carmine can inform decision-making for textile conservation practice.

The research question about whether indigo carmine shows variations according to inherent properties was explored by combining literature evidence and experimental observation. A dyeing method for indigo carmine on wool was adapted and recreated using historical dyeing recipes from the eighteenth and nineteenth-centuries, complemented with dye-chemistry literature. Dye transfer and solubilisation for replica samples were assessed experimentally, and results evaluated to inform textile conservation practice.

The research aim of identifying variations in historical dyeing practices of indigo carmine on wool was reached. However, patterns in the degree of solubilised dye could not be identified due to the complex relationship between numerous interconnected factors impacting on washfastness. Critical reflection on outcomes led to implementing new aims throughout the experimental phase.

8.2 Summary of Findings

Regarding the historical formulations, the review of recipes revealed that there was no consensus for one method of dyeing with indigo carmine, although trends can be identified. Awareness of the variabilities between historical materials was demonstrated to be crucial for understanding indigo carmine's properties, particularly with regards to its synthesis (degree of sulfonation) and use (dye concentration on the fibre).

The overall conclusion of this dissertation is that informed decision-making is needed, balancing the benefits of wet cleaning against the high likelihood of dye loss and colour change, which are irreversible and undesirable alterations. The experimental phase allowed for additional conclusions to be drawn:

- Historical accounts of indigo carmine indicate variations in the dye's properties and behaviour, depending on its manufacture and context. These differences were evident between modern-commercial and historically recreated indigo carmine. Therefore, meaningful experimental testing for historical indigo carmine should involve dye material of the right chemical composition.

- The condition of dyeing temperature relates to indigo carmine's washfastness. Threads from dye-baths without boiling temperatures are more likely to bleed. This inherent property has consequences on aqueous treatments. Unfortunately, it is not a property that can be determined visually.

- The degree of staining from dye bleed is influenced by the drying method. In conservation practice, controlling the rate of diffusion of solubilised dye into the fibres can be effective at preventing or reducing staining.

- Lighter shades of indigo carmine are less prone to staining from dye bleed than darker shades. This appears to be related to dye concentration.

- A relationship between indigo carmine's photodegradation and washfastness may exist, although the reasons are complex and not yet understood. This investigation is the first to evidence the influence of this factor.

The research outcomes raise new questions regarding use of visual signposts for bleeding in current conservation practice. The assessment of blue tonalities from solubilised dye on collected wash-bath solutions can be misleading since it relies on dye concentration, which is variable between objects. Likewise, the reliability of blotting tests to evaluate dye transfer depends on properly recreating the rate of diffusion, related to the dye-fibre system's affinity. Testing methods that use substrates of similar nature to the object of interest, as well as the solution and drying method to be used during the aqueous

conservation treatment, would provide a better opportunity to simulate dye transfer. This measure applies on washfastness tests for other fugitive dyes, which would allow textile conservators to gauge expectations for treatments with more certainty and assess risks objectively.

If photodegradation is closely related to washfastness, samples taken from the reverse of flat objects are not representative of the dye's sensitivity to water, since these fibres would have less exposure to light. Under this framework, it is worth questioning and re-evaluating the information drawn from washfastness tests with samples taken from the reverse of an object. This raises issues about the ethics of sampling in relation to the question asked, as analysis to determine chemical composition of the dye might be more pertinent than completing washfastness tests. As this study shows, learning about the degree of sulfonation or any clue relating to the temperature of the dye-bath would be more indicative of bleed. When analytical techniques are not accessible for conservation studios, professionals have to look more closely at context and material evidence.

8.3 Suggestions for Future Research

This dissertation showed that numerous avenues of research regarding indigo carmine remain unexplored. While the behaviour of the dye is clearer, a large number of questions remain unsolved. Investigation is encouraged on the following areas:

- Localised cleaning for stained objects and for isolating indigo carmine elements or adjacent areas of ground fabric. Agents for indigo carmine removal, such as enzymes and absorbent ashes, have been studied in the industrial sector, which could potentially be tailored for conservation.

- Differences in pH and dye concentration need to be better understood if chromophoric structures and dye-fibre thermodynamics change with pH variation.

- Washfastness for indigo carmine on other substrates, like silk, may be different.

- Evaluation with UV-visible spectroscopy: to quantitatively assess dye solubilisation. Indigo carmine in solution degrades quickly, so the researcher would require regular access to the equipment.

- Risk assessments: Correlate variables to evaluate impact and likelihood of bleeding. Cost-benefit analysis would allow for mitigating high-level and priority risks.

Bibliography

Unpublished Sources

Caycedo, Marguerite. "Identification of Fifteen First Priority Textile Dyes from the Schweppe Collection with Raman and Surface Enhanced Raman Spectroscopy." MSc dissertation, University of Amsterdam, 2012. https://esc.fnwi.uva.nl/thesis/centraal/files/f446931068.pdf Accessed May 17, 2018.

de Keijzer, Matthijs, Maarten R. van Bommel, Regina Hofmann-de Keijzer, and Regina Knaller. "The Early Synthetic Organic Dyestuffs: Indigo Carmine: Favored but Fading." In 29*th Meeting of Dyes in History and Archaeology, held at Gulbenkian Foundation, Lisbon, 12 November 2010*.

Foskett, Sarah and CTC-TAH. *Wet Cleaning Handbook*. MPhil in Textile Conservation, University of Glasgow, 2017.

Gabbutt, Freya. "Treatment Report CTC.210." MPhil in Textile Conservation, University of Glasgow, 2015.

Hunter, Michelle. "Let There Be Light? An Investigation into the Fading Characteristics of the Early Synthetic Dye Magenta." MPhil in Textile Conservation dissertation, University of Glasgow, 2016.

Kinti, Maria. "Treatment Proposal CTC.RF11." MPhil in Textile Conservation, University of Glasgow, 2014.

Knight, Beth. "Treatment Report CTC.246." MPhil in Textile Conservation, University of Glasgow, 2016.

Sato, Moe. "An Experimental Evaluation of Non-Ionic Surfactant Dehypon® LS54." MPhil in Textile Conservation dissertation, University of Glasgow, 2014.

Schmitt, Emma. "Treatment Report CTC.75." MPhil in Textile Conservation, University of Glasgow, 2013.

van Bommel, Maarten, and Enrica Fantini. "Unravelling the Colour Palette of 19th Century Furniture: Reconstruction and Analysis of Synthetic Dyes Used as Stains." In *31st Meeting of Dyes in History and Archaeology, held at Antwerp, Belgium, 2012*.

Wood, Susan. "A Preliminary Investigation into Green Dyed Embroidery Threads on Samplers During the Period 1780 to 1849 and their Susceptibility to Dye Bleeding." MA dissertation, Textile Conservation Centre, University of Southampton, 2006.

Primary Sources

Bancroft, Edward. *Experimental Researches Concerning the Philosophy of Permanent Colours*. Philadelphia: Thomas Dobson, 1814.

Bemiss, Elijah. *The Dyer's Companion, 3rd edition (1815),* edited by Rita J. Adrosko. New York: Dover Publications, 1973.

Berthollet, Claude-Louis. *Elements of the Art of Dyeing*, translated by William Hamilton. London: Stephen Couchman, 1791.

Berthollet, Claude-Louis, and Ammédée Berthollet. *Elements of the Art of Dyeing and Bleaching*, translated by Andrew Ure. London: Thomas Tegg, 1841.

Bird, Frederick. *The American Practical Dyer's Companion, Comprising a Description of the Principal Dye-Stuffs and Chemicals Used in Dyeing, Their Natures and Uses, Mordants, and How Made.* Philadelphia: Henry Carey Baird & Co, 1882.

Cooper, Thomas. *A Practical Treatise on Dyeing and Callicoe Printing.* Philadelphia: Thomas Dobson, 1815.

Crace-Calvert, Frederick. *Dyeing and Calico Printing*, edited by John Stenhouse and Charles Edward Groves. Manchester: Palmer & Howe, 1876.

Ferguson, Dufay, Hellot, Geoffery, Colbert, and de Julienne. *The Dier's Assistant in the Art of Dying Wool and Woolen Goods,* translated and edited by James Haigh. Philadelphia: James Humphreys, 1810.

Fernández, Luis. *Tratado Instructivo y Practico sobre el Arte de la Tintura: Reglas Experimentadas y Metódicas para tintar Sedas, Lanas, Hilos de Todas Clases y Esparto en Rama.* Madrid: Blas Román, 1778.

Hellot, Macquer, and le Pileur D'Apligny. *The Art of Dyeing Wool, Silk, and Cotton,* edited by R. Baldwin. London: Scott, Greenwood & Co, 1901.

Hummel, John James. *The Dyeing of Textile Fabrics.* London: Cassell & Company, 1888.

Love, Thomas. *The Art of Cleaning, Dyeing, Scouring, and Finishing, on the Most Approved English and French Methods.* London: Longman, Brown, Green, and Longmans, 1855.

Partridge, William. *A Practical Treatise on Dying of Woolen, Cotton, and Skein Silk with the Manufacture of Broadcloth and Cassimere* (1823)*,* edited by K.G. Ponting. Edington: Pasold Research Fund, 1973.

Smith, David. *The English Dyer.* Manchester: Palmer and Howe, 1882.

Secondary Sources

American Association of Textile Chemists and Colorists. *AATCC Technical Manual vol. 68*. North Carolina: AATCC, 1993.

Appelbaum, Barbara. *Conservation Treatment Methodology*. Boston: Butterworth-Heinemann, 2007.

Balfour-Paul, Jenny. *Indigo*. London: Archetype Publications, 2006.

Barnett, Jennifer. "Synthetic Organic Dyes, 1856–1901: An Introductory Literature Review of Their Use and Related Issues in Textile Conservation." *Studies in Conservation* 52 (2007): 67-77. doi: 10.1179/sic.2007.52.Supplement-1.67

Bowman, Janet Gilliland and Barbara Reagan. "Filtered and Unfiltered Lights and Their Effects on Selected Dyed Textiles." *Studies in Conservation* 28 (1983): 36-44. doi: 10.2307/1506105

Cardon, Dominique. *Natural Dyes: Sources, Tradition, Technology and Science*. London: Archetype Publications, 2007.

Cardon, Dominique. *The Dyer's Handbook: Memoirs of an 18th-Century Master Colourist*. Havertown: Oxbow Books, 2016.

Cartwright, Helen and Alain Colombini, "Detergent Monitoring during the Washing Process at the Textile Conservation Studios, Hampton Court Palace." In *ICOM-CC 10th Triennial Conference, Washington DC, 22-27 August 1993, Preprints*, edited by Janet Bridgland, 293-298. London: James & James, 1993.

de Keijzer, Matthijs, Maarten R. van Bommel, Regina Hofmann-de Keijzer, Regina Knaller and Edith Oberhumer. "Indigo Carmine: Understanding a Problematic Blue Dye." *Studies in Conservation* 57 (2012): S87-S95. doi: 10.1179/2047058412Y.0000000058

Duff, David and Roy Sinclair. *Giles's Laboratory Course in Dyeing*. Bradford: Society of Dyers and Colourists, 1989.

Duff, David, Roy Sinclair, and David Stirling, "The Fastness to Washing of Some Natural Dyestuffs." *Studies in Conservation* 22:4 (1977): 170-176. http://www.jstor.org/stable/1505833

El-Mansy, M. "Quantum Chemical Studies on Structural, Vibrational, Nonlinear Optical Properties and Chemical Reactivity of Indigo Carmine Dye." *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 183 (2017): 284-290. doi: 10.1016/j.saa.2017.04.047

Elnagar, Khaled, Sameh Reda, Harby Ahmed, and Shady Kamal. "Studying Irradiation Homogeneity in Light Aging for Historical Textile Conservation." *Fibers and Polymers* 14:9 (2013): 1581-1585. doi: 10.1007/s12221-013-1581-6

Feller, Robert. *Accelerated Ageing: Photochemical and Thermal Aspects*. Los Angeles: Getty Conservation Institute, 1994.

Finch, Karen and Greta Putnam. *Caring for Textiles*. London: Barrie & Jenkins, 1977.

Francis, Kathy. "Predicting the Drying Behavior of Textiles." In *AIC 20th Annual Meeting, Postprints vol. 2,* edited by Suzanne Thomassen-Krauss, Linda Eaton and Sara Lynn Reiter, 1-6. Buffalo: The Textile Specialty Group, 1992.

Galindo, Catherine, Patrice Jacques, and André Kalt. "Photochemical and Photocatalytic Degradation of an Indigoid Dye: a Case Study of Acid Blue 74 (AB74)." *Photochemistry and Photobiology A: Chemistry* 141 (2001): 47-56. doi: 10.1016/S1010-6030(01)00435-X

Gottsegen, Mark. "Lightfastness Testing of Artists' Materials Using ASTM D 4303 and the Blue Wools." In *AIC 32nd Annual Meeting, June 2004, Postprints vol. 1*, edited by Joseph Swider and Alison Murray, 26-36. Portland: Research and Technical Studies Specialty Group, 2012.

Gulmini, M., A. Idone, E. Diana, D. Gastaldi, D. Vaudan, and M. Aceto. "Identification of Dyestuffs in Historical Textiles: Strong and Weakpoints of a Non-invasive Approach." *Dyes and Pigments* 98 (2013): 136-145. doi: 10.1016/j.dyepig.2013.02.010

Hernández-Gordillo, Agileo, Vicente Rodríguez-González, Socorro Oros-Ruiz, and Ricardo Gómez. "Photodegradation of Indigo Carmine Dye by CdS Nanostructures Under Blue-light Irradiation Emitted by LEDs." *Catalysis Today* 266 (2016): 27-35. doi: 10.1016/j.cattod.2015.09.001

Hofenk de Graaff, Judith. *The Colourful Past: Origins, Chemistry and Identification of Natural Dyestuffs*. London: Abegg-Stiftung and Archetype Publications, 2004.

Kirby, Jo, Maarten van Bommel, and André Verhecken. *Natural Colourants for Dyeing and Lake Pigments: Practical Recipes and their Historical Sources*. London: Archetype Publications, 2014.

Klos, Agata. "Non-Invasive Methods in the Identification of Selected Writing Fluids from Late 19th and Early 20th Century." *CeROArt* (2014): 1-25.

Komboonchoo, Sunsanee and Thomas Bechtold, "Sorption Characteristics of Indigo Carmine as a Blue Colorant for Use in One-bath Natural Dyeing." *Textile Research Journal* 80 (2010): 734-743.

Lakshmi, Uma, Vimal Chandra Srivastava, Indra Deo Mall, and Dilip Lataye. "Rice Husk Ash as an Effective Adsorbent: Evaluation of Adsorptive Characteristics for Indigo Carmine Dye." *Journal of Environmental Management* 90 (2009): 710-720. doi: 10.1016/j.jenvman.2008.01.002

Landi, Sheila. *The Textile Conservator's Manual*. Oxford: Butterworth-Heinemann, 1992.

Lowengard, Sarah. "Colour Quality and Production: Testing Colour in Eighteenth-Century France." *Journal of Design History*, vol. 14, no. 2 (2001): 91-103.

Lowengard, Sarah. *The Creation of Colour in 18th-Century Europe*. Columbia: Columbia University Press, 2006.

Millington, K.R.. "Colorfastness." In *Engineering of High-Performance Textiles*, edited by Menghe Miao and John Xin. Kidlington: Woodhead Publishing, 2017.

Poulin, Jennifer. "A New Methodology for the Characterisation of Natural Dyes on Museum Objects Using Gas Chromatography-Mass Spectrometry." *Studies in Conservation* (2017): 1-26. doi: 10.1080/00393630.2016.1271097

Quye, Anita. "The Dyer's Handbook: Memoirs of an 18th-Century Master Colourist." *Textile History* 49:1 (2018): 135-136. doi: 10.1080/00404969.2018.1440799

Quye, Anita, and Jan Wouters. "An Application of HPLC to the Identification of Natural Dyes." In *10th Meeting of Dyes in History and Archaeology, held at the National Gallery, London 1991*, edited by Walton Rogers, 48-54. York: Textile Research Associates, 1991.

Quye, Anita, Kathryn Hallett, and Concha Herrero Carretero. '*Wroughte in gold and silk' Preserving the Art of Historic Tapestries*. Edinburgh: NMS Enterprises Limited, 2009.

Reponen, Tarja. "The Effects of Conservation Wet Cleaning on Standard Soiled Wool Fabric: Some Experimental Work." In *ICOM-CC 10th Triennial Conference, Washington DC, 22-27 August 1993, Preprints*, edited by Janet Bridgland, 321-326. London: James & James, 1993.

Rogerson, Cordelia and Paul Garside. "Increasing the Profile and Influence of Conservation - An Unexpected Benefit of Risk Assessments." *Journal of the Institute of Conservation*, 40:1 (2017): 34-48. doi: 10.1080/19455224.2016.121484

Sahmel, Katherine, Laura Mina, Ken Sutherland, and Nobuko Shibayama. "Removing Dye Bleed from a Sampler: New Methods for an Old Problem." In *AIC 40th Annual Meeting, May, Postprints vol. 22*, edited by Amanda Holden et al., 78-90. Albuquerque: The Textile Specialty Group, 2012.

Scharff, Annemette Bruselius. "Synthetic Dyestuffs for Textiles and Their Fastness to Washing (1999)." In *Changing Views of Textile Conservation,* edited by Mary Brooks, and Dinah Eastop. Los Angeles: Getty Conservation Institute, 2011.

Schmidt, Alfred. "Substitutes for Natural Indigo in Wool Dyeing and the Artificial Indigo." *Journal of the Society of Dyers and Colourists* 14:3 (1898): 63-74. doi: 10.1111/j.1478-4408.1898.tb00143.x

Schweppe, Helmut. *Practical Information for the Identification of Dyes on Historic Textile Materials*. Washington DC: Smithsonian Institution, 1988.

Shadi, Iqbal, Babur Chowdhry, Martin Snowden, and Robert Withnall. "Analysis of the Conversion of Indigo into Indigo Carmine Dye Using SERRS." *Chemical Communications* 12 (2004): 1436-1437. doi: 10.1039/B403601H

Shen, Baoen, M. Olbrich-Stock, J. Posdorfer and R.N. Schindler. "An Optical and Spectroelectrochemical Investigation of Indigo Carmine." *International Journal of Research in Physical Chemistry and Chemical Physics* 173:2 (1991): 251-255.

Sousa, Micaela, Catarina Miguel, Isa Rodrigues, Jorge Parola, Fernando Pina, Sergio Seixas de Meloc, and Maria Melo. "A Photochemical Study on the Blue Dye Indigo: From Solution to Ancient Andean Textiles." *Photochemical & Photobiological Sciences* 7 (2008): 1353-1359. doi: 10.1039/b809578g

Sullivan MX, Barnett Cohen, and W. Mansfield Clark. "Electrode Potentials of Indigo Sulphonates, Each in Equilibrium with Its Reduction Product." *Studies on Oxidation-Reduction IV* 38:30 (1923): 1669-1718. doi: 10.2307/4576820

Tarrant, Naomi. *Remember Now Thy Creator: Scottish Girls' Samplers, 1700-1872*. Edinburgh: Society of Antiquaries of Scotland, 2014.

Taylor, G.W. "Identification of Dyes on Early William Morris Embroideries from Castle Howard." *Textile History* 16:1 (1985): 97-102. doi: 10.1179/004049685793701197

Timár-Balázsy, Ágnes. "Wet Cleaning of Historical Textiles: Surfactants and Other Wash Bath Additives." *Reviews in Conservation, IIC* 1 (2000): 46-64.

Timár-Balázsy, Ágnes and Dinah Eastop, *Chemical Principles of Textile Conservation.* Oxford: Butterworth-Heinemann, 1998.

Timár-Balázsy, Ágnes, György Mátéfy, and Sandor Csányi. "Effect of Stains and Stain Removal Methods on Historical Textiles." In *ICOM-CC 10th Triennial Conference, Washington DC, 22-27 August 1993, Preprints*, edited by Janet Bridgland, 330-335. London: James & James, 1993.

Troalen, LG, Röhrs, S, Calligaro, T, Pacheco, C, Kunz, S, del Hoyo-Meléndez, JM & Hulme, AN. "A Multi-analytical Approach Towards the Investigation of Subarctic Athapaskan Colouring of Quillwork and its Sensitivity to Photo-degradation." *Microchemical Journal* 126 (2016): 83-91. doi: 10.1016/j.microc.2015.11.053

Trotman, S.R. and H. Horner. "The Action of Sulphuric Acid in Dyeing Wool with Acid Dyes." *Journal of the Society of Dyers and Colourists* 50 (1934): 65-72. doi: 10.1111/j.1478-4408.1934.tb01814.x

Valldeperas-Morell J. and F. Carrillo-Navarrete. "Colour Fastness." In *Understanding and Improving the Durability of Textiles,* edited by Patricia Annis. Cambridge: Woodhead Publishing, 2012, 82-103.

Van Stralen, Trudy. *Indigo, Madder & Marigold: A Portfolio of Colors from Natural Dyes*. Colorado: Interweave Press, 1993.

Websites

Douma, Michael. "Prussian Blue" in *Pigments Through the Ages*. WebExhibits, 2001. http://www.webexhibits.org/pigments/indiv/recipe/prussblue.html Accessed June 24, 2018.

Grossman, DM. "Errors Caused by Using Joules to Time Laboratory and Outdoor Exposure Tests" in *Technical Bulletin LU-8030*. Q-Lab Corporation, 2011. https://www.q-lab.com/products/q-sun-xenon-arc-test-chambers/q-sun-xe-1 Accessed June 27, 2018.

Jensen, William. "The Symbol for pH" in *Ask the Historian.* Chemical Education Today, 2004. https://pubs-acs-org.ezproxy.lib.gla.ac.uk/doi/pdf/10.1021/ed081p21 Accessed July 24, 2018.

Konica Minolta Inc. "Color Discrimination Threshold of the Human Eye" in *Konica Minolta Measuring Instruments,* 2018. https://www.konicaminolta.com/instruments/knowledge/color/part5/02.html Accessed August 2, 2018.

Konika Minolta Inc. "Portable Spectrophotometer CM-2300d" in *Specifications – Konika Minolta,* 2018. https://www.konicaminolta.eu/en/measuring-instruments/products/colour-measurement/spectrophotometers-portable/cm-2300d/specifications.html Accessed July 30th, 2018.

Q-Lab Corporation. "A Choice of Filters for Q-SUN Xenon Test Chambers" in *Technical Bulletin LX-5060*, 2014. https://www.q-lab.com/products/q-sun-xenon-arc-test-chambers/q-sun-xe-1 Accessed June 26, 2018.

Q-Lab Corporation. "Q-SUN Xenon Test Chambers" 2018. https://www.q-lab.com/products/q-sun-xenon-arc-test-chambers/q-sun-xe-1 Accessed June 26, 2018.

Quill, Jeffery, Greg Fedor, Patrick Brennan and Eric Everett. "Quantifying the Indoor Light Environment" in *Technical Bulletin LX-5026*, Q-Lab Corporation, 2007. https://www.q-lab.com/products/q-sun-xenon-arc-test-chambers/q-sun-xe-1 Accessed June 26, 2018.

Sappi Fine Paper North America. "Defining and Communicating Color: The CIELAB System." 2013. https://cdn-s3.sappi.com/s3fs-public/sappietc/Defining%20and%20Communicating%20Color.pdf Accessed July 30, 2018.

Appendices

Appendix 1: Glossary

acid dye: an anionic dye that dissociates in aqueous solution to give a negatively charged coloured ion, characterised by substantivity for protein fibres and often applied from an acid dyebath.[228]

alum: potassium aluminium sulfate, $KAl(SO_4)_2 \cdot 12H_2O$. Salt used extensively in dyeing as a mordant.

black panel thermometer: (BPT) an uninsulated temperature measuring device which has a sensing unit coated with black to absorb most of the radiant energy encountered in lightfastness testing. It provides an estimate of the maximum temperature that specimens/samples may attain during artificial ageing because it is not practical to measure the surface of specimens/samples. The units indicate the absorbed irradiance minus the heat dissipated by conduction and convection.[229] Not to be confused with the black standard thermometer.

chelating agent: also called sequestrants. Organic acids or salts with a high degree of ionization, used to sequester metal ions. Working properties are pH sensitive.[230]

chromophore: colour-bearing group in the dye's molecular structure.

colour change: a change in hue, chroma, or lightness.

colourfastness: the ability of the original colour of the finished textile to resist any challenges that it may normally encounter during its manufacture and working lifetime.[231] It includes its resistance to change in any of its colour characteristics and to transfer colour to adjacent materials.[232]

cream of tartar: potassium hydrogen tartrate, $KC_4H_50_6$. A salt commonly used as a dye-assistant with alum as a mordant to brighten colours. Its use has been considered unnecessary when dyeing with demineralised or distilled water since its effect depends partly on the presence of traces of ions (mainly iron) found in tap water.[233] Cream of tartar is said to "brighten the colours, protect the fibres and/or help the absorption of the mordants.[234]

cyclododecane: waxy solid that sublimes at room temperature. Used in conservation as a temporary consolidant, fixative, and masking material. One of its uses in textile conservation is as a confining or isolating layer to prevent staining.

depth of shade: usually given in a percentage to show the relation between the weight of the dyestuff in relation to the fabric.

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[228] Duff and Sinclair, 159.
[229] AATCC, 33, 35.
[230] Timár-Balázsy and Eastop, 222-223.
[231] Millington, 155.
[232] AATCC, 159.
[233] Kirby et al., 49.
[234] Ferreria et al., 330.

dye: a colourant applied to or formed in a substrate, via the molecular dispersed state, which exhibits some degree of permanence.[235]

dye transfer: the movement of a dye from one part of a material to another.[236] If desirable, it is called levelling, if undesirable, it is called staining or dye bleed.

dye solubilisation: the movement or release of a dye from one part of a material to a solution.

excess dye: colouring matter that is superficially-bound to the fibres, as opposed to dye that is absorbed by the textile substrate.

exhaustion: process of transfer of dye from the dyebath to the fibre, commonly expressed quantitatively as a percentage.[237] In an ideal scenario, no dye is left in the bath (100% dye exhaustion).

Glauber's salts: sodium sulfate. Salt used to prevent rapid or uneven fixation of indigo carmine.[238]

irradiance: radiant power per unit area as a function of wavelength, expressed as watts per square meter (W/m^2).[239]

irradiation: the time integral of irradiance expressed in joules per square meter (J/m^2).[240]

levelness: the property of dyeing in the same depth all over the textile material and showing complete penetration of the dye. Levelness is ensured by using good agitation and controlling the rate of dyeing.[241]

liquor ratio: the volume of dyeing liquor used in relation to the fibre weight.[242]

migration: see dye transfer. Also applies to pigments.

mordant: metal salt which links permanently with the molecular structure of fibres and dyes when dissolved in water. Colours produced by mordant dyeing vary greatly depending on the mordant used.[243]

oil of vitriol: refers to sulfuric acid, used in the eighteenth century.

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[235] AATCC, 301.
[236] Duff and Sinclar, 164.
[237] Ibid, 6.
[238] Bird, 343.
[239] AATCC, 33.
[240] Ibid.
[241] Duff and Sinclair, 6.
[242] Ibid, 9.
[243] Balfour-Paul, 115.

pH: the negative logarithm of the effective hydrogen ion concentration or hydrogen ion activity in gram equivalents per litre used in expressing both acidity and alkalinity on a scale whose values run 0-14 with 7 representing neutrality, numbers less than 7 increasing acidity, and numbers greater than 7 increasing alkalinity.[244]

radiant energy: energy travelling through space in the form of photons or electromagnetic waves of various lengths.[245]

rate of dyeing: the rate at which a dye is absorbed by a substrate under specified conditions.[246]

Saxon blue or green: first name given to indigo carmine.

scouring: freeing textile materials or wool sheepskins from natural or other non-fibrous constituents by treatment with aqueous solutions or organic solvents.[247]

semi-synthetic: produced by humans through chemical alteration of a natural material.

skitteriness: an undesirable speckled effect arising from differences in colour between adjacent fibres or portions of the same fibre.[248]

spectrophotometer: an instrument, usually photoelectric, for measuring the reflectance or transmittance of light (or other radiation) by an object at a particular wavelength in the spectrum.[249]

transfer: (in textile processing or testing) movement of a chemical, dye, or pigment between fibres within a substrate or between substrates.[250]

ultraviolet radiation: radiant energy for which the wavelengths of the monochromatic components are smaller than those for visible radiation and more than about 100 nm.[251]

visible radiation: any radiant energy capable of causing a visual sensation. The lower limit is usually taken between 380 and 400 nm and the upper limit between 760 and 780 nm.[252]

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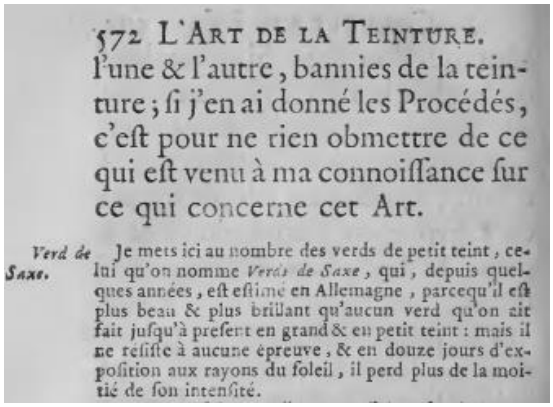
[244] AATCC, 107.
[245] Ibid, 179.
[246] Duff and Sinclair, 164.
[247] Ibid, 165.
[248] Ibid.
[249] Ibid, 166.
[250] AATCC, 301.
[251] Ibid, 179-180.
[252] Ibid, 180.

Appendix 2. Historical Dyeing Recipes

The following section provides a brief summary of the key points identified through the review of nineteen historical dyeing recipes. The provenance of each resource and the pages where the information was found are also indicated. A succinct image for each historical text is included to show ease of reading/understanding the information.[253]

1. Hellot (1750) Provenance: Archive.org & Getty Research Institute.

Hellot, Jean. *L'Art de Teinture des Laines et des Etoffes des Laines*. Paris: Imprimerie Royale, 1750.



572 L'ART DE LA TEINTURE.
l'une & l'autre, bannies de la teinture; ſi j'en ai donné les Procédés, c'eſt pour ne rien obmettre de ce qui eſt venu à ma connoiſſance ſur ce qui concerne cet Art.

Verd de Saxe. Je mets ici au nombre des verds de petit teint, celui qu'on nomme *Verd de Saxe*, qui, depuis quelques années, eſt eſtimé en Allemagne, parcequ'il eſt plus beau & plus brillant qu'aucun verd qu'on ait fait juſqu'à preſent en grand & en petit teint: mais il ne réſiſte à aucune épreuve, & en douze jours d'expoſition aux rayons du ſoleil, il perd plus de la moitié de ſon intenſité.

- Entry in French. Mentions low fastness of the dye; optional use of cobalt, orpiment and antimony; and use of alum and cream of tartar as Dye-assistants (p. 572).
- Sarah Lowengard studied further this dyer's experiment. [254] Hellot tested Saxon green to find if it was better than the available dyes of good quality. The examination consisted on removing the blue dye from Roederer's green (Saxon green) samples by using only fresh water. The report indicated that the colour production was not the standard method for dyeing indigo as the samples responded differently to expectations.

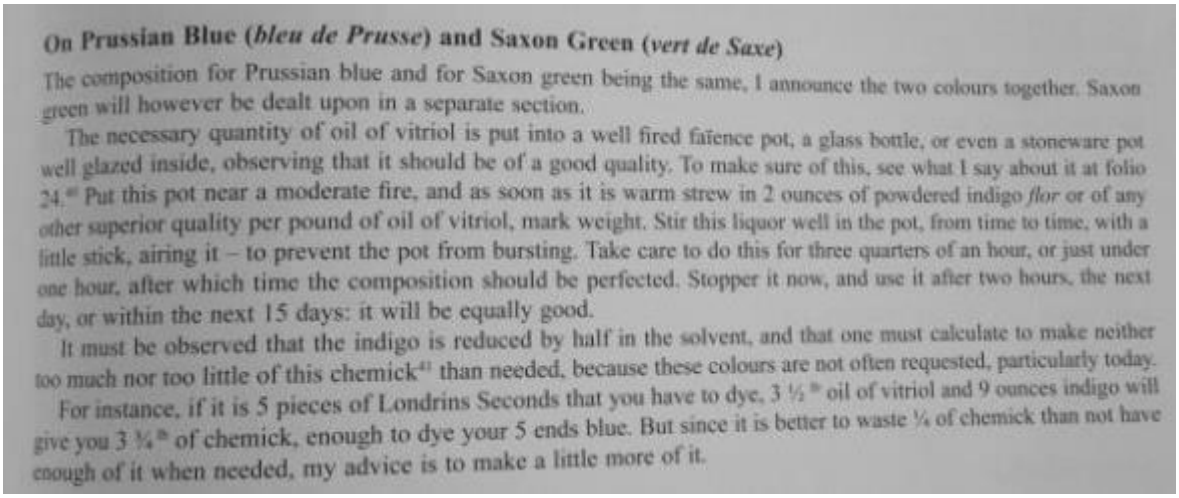
1. Hellot (1750)	
Ratio: (4:1)	Dye-assistants: alum and cream of tartar
Temperature: boiling	Other: Unusual for inclusion of orpiment (As_2S_3), a strong reducing agent. Mentions brusque reaction.

[253] Kirby et al., 47. Translations in dyeing recipes can lead to confusion since sometimes translators were not aware about the particularities of the subject.
[254] Jean Hellot, *Vert de Saxe, imite par le Sr. Roederer de Strasbourg*, 26 February 1749, and related papers dated 9 April 1749, 1 January 1750, AN F12 2259, as cited in Lowengard 2001, 91-103.

2. Paul Gout (1768)

Gout, Paul. *Memoirs on Dyeing* (1762) as cited in Cardon, Dominique. *The Dyer's Handbook. Memoirs of an 18th-Century Master Colourist.* Oxford: Oxbow Books, 2016.

- Transcript of Prussian Blue (in reality, Saxon blue) (p. 63) and Saxon greens (p. 64).



On Prussian Blue (*bleu de Prusse*) and Saxon Green (*vert de Saxe*)

The composition for Prussian blue and for Saxon green being the same, I announce the two colours together. Saxon green will however be dealt upon in a separate section.

The necessary quantity of oil of vitriol is put into a well fired faïence pot, a glass bottle, or even a stoneware pot well glazed inside, observing that it should be of a good quality. To make sure of this, see what I say about it at folio 24.[40] Put this pot near a moderate fire, and as soon as it is warm strew in 2 ounces of powdered indigo *flor* or of any other superior quality per pound of oil of vitriol, mark weight. Stir this liquor well in the pot, from time to time, with a little stick, airing it – to prevent the pot from bursting. Take care to do this for three quarters of an hour, or just under one hour, after which time the composition should be perfected. Stopper it now, and use it after two hours, the next day, or within the next 15 days: it will be equally good.

It must be observed that the indigo is reduced by half in the solvent, and that one must calculate to make neither too much nor too little of this chemick[41] than needed, because these colours are not often requested, particularly today.

For instance, if it is 5 pieces of Londrins Seconds that you have to dye, 3 ½ ℔ oil of vitriol and 9 ounces indigo will give you 3 ¼ ℔ of chemick, enough to dye your 5 ends blue. But since it is better to waste ¼ of chemick than not have enough of it when needed, my advice is to make a little more of it.

- Information related to indigo carmine was unfortunately lost as some pages of the manuscript were cut off (pp. 63, 86). The book includes a photograph of a real fabric sample for Bleu de Prusse.
- Cardon explains the difference between vitriols (p. 98).
- Cardon explicitly acknowledges that Saxon blue was called Prussian blue by some dyers (pp. 86, 107-110).

2. Paul Gout (1768)	
Ratio: (6:1) and (8:1)	Dye-assistants: alum and cream of tartar
Temperature: boiling and below boiling	Other: Mention of risk of pot bursting.

3. Luis Fernández (1778) Provenance: Google Books & Biblioteca de la Abadía de Montserrat.

Fernández, Luis. *Tratado Instructivo y Practico sobre el Arte de la Tintura: Reglas Experimentadas y Metódicas para tintar Sedas, Lanas, Hilos de Todas Clases y Esparto en Rama.* Madrid: Blas Román, 1778.

CAPITULO X.

INSTRUCCION PARA preparar el Añil para tintar Lanas de los colores azules, y verdes de Saxonia.

1 SE ponen en una limeta, ò redoma de vidrio seis libras de Azeyte de Vitriolo, y doce onzas de Añil de flor molido en seco, y se menea todo junto de forma que el dicho Añil se incorpore con el Azeyte: despues se tapa la redoma con la curiosidad posible, para que no se exhale la virtud, y fortaleza de este espiritu.

- Entry in Spanish. Explains how to prepare indigo to dye wool with Saxon blue and Saxon green (pp. 168-171). He suggests that the solution should rest for three days and be used within 6 months. The dyeing instructions include diluting the extract, boiling and stirring the wool for half an hour in this dyeing solution, and adding alum and "rasuras" (cream of tartar?).

3. Luis Fernández (1778)	
Ratio: (8:1)	Dye-assistants: Alum and "rasuras"
Temperature: Boiling	Other: The solution should rest for three days.

4. Berthollet (1791) Provenance: Archive.org & Public Library of India.

Berthollet, Claude-Louis. *Elements of the Art of Dyeing*, translated by William Hamilton. London: Stephen Couchman, 1791.

THE colour dyed by means of a folution of indigo in fulphuric or vitriolic acid has received the appellation of *faxon blue*, from having been difcovered at Groffenhayn in Saxony, by counfellor Barth, about the year 1740. This difcovery was kept fecret for a time, but by degrees it got abroad. At firft the folution was not made with indigo alone; but alumine, antimony, and other mineral fubftances were previoufly digefted in the fulphuric acid, the indigo was added afterwards, and when the folution was finifhed, it was employed for dyeing.

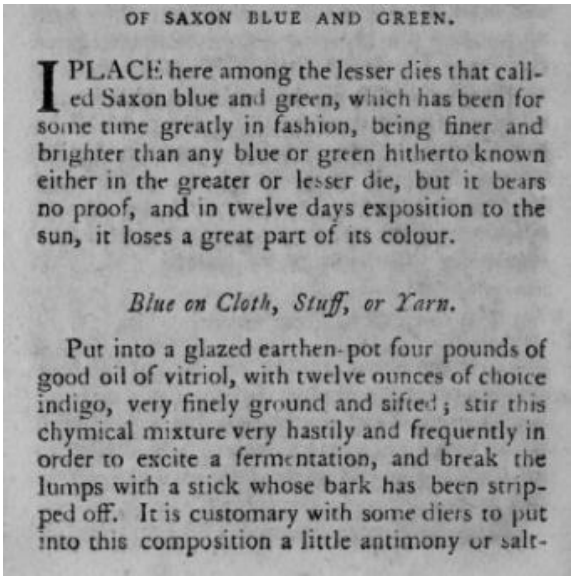
Bergman made many experiments on this procefs, and he thinks, that if it has hitherto afforded only a fading colour, it has been becaufe the acid ufed was too weak.

- "Of Saxon Blue" (pp. 98-102). This entry is very specific about the duration and the preferred temperature during the creation of the extract. It is unusual for sometimes adding potash. It mentions the specific gravity of sulfuric acid and talks about the fading of light shades. "Prussian Blue" is still mentioned as the obtained colour.
- Detailed description for dyeing Saxon green (pp. 312-316). It mentions that "cloth dyed blue in the bath with alum and tartar, has a less vivid, but more durable colour, than when it is dyed blue in a bath with water, without any other addition" (p. 313).
- He suggests the use of a pound and a quarter of the solution of indigo for each piece of cloth of eighteen ells which is to be dyed. Different to Cooper's recipe.
- Discusses the faults of Saxon blue and Saxon green (pp. 317-319).
- Special mention to English blue and English green, which are obtained as variations of indigo carmine (p. 319).

4. Berthollet (1791)	
Ratio: (4:1) and (3:1)	Dye-assistants: Alum and cream of tartar / No mordant
Temperature: Boiling and cold	Other: Unusual for sometimes adding potash. Mentions specific gravity of sulfuric acid. Talks about fading of light shades. Prussian Blue is still mentioned as the obtained colour.

5. Ferguson et al (1810) Provenance: Archive.org & Getty Research Institute

Ferguson, Dufay, Hellot, Geoffery, Colbert, and de Julienne. *The Dier's Assistant in the Art of Dying Wool and Woolen Goods,* translated and edited by James Haigh. Philadelphia: James Humphreys, 1810.



OF SAXON BLUE AND GREEN.

I PLACE here among the lesser dies that called Saxon blue and green, which has been for some time greatly in fashion, being finer and brighter than any blue or green hitherto known either in the greater or lesser die, but it bears no proof, and in twelve days exposition to the sun, it loses a great part of its colour.

Blue on Cloth, Stuff, or Yarn.

Put into a glazed earthen-pot four pounds of good oil of vitriol, with twelve ounces of choice indigo, very finely ground and sifted; stir this chymical mixture very hastily and frequently in order to excite a fermentation, and break the lumps with a stick whose bark has been stripped off. It is customary with some diers to put into this composition a little antimony or salt-

- They categorize Saxon blue and Saxon green as lesser dyes (p. 242).
- They mention that temperature can affect the colour and make it greener (p. 243). The entry also mentions specific measurements and sequence of processes.

5. Ferguson et al (1810)	
Ratio: (5:1) and (8:1)	Dye-assistants: Alum, cream of tartar and else
Temperature: Below boiling	Other: Mentions that other dyers add antimony and that temperature can affect the colour and make it greener.

6. Bancroft (1814) Provenance: Archive.org & Harvard University

Bancroft, Edward. *Experimental Researches Concerning the Philosophy of Permanent Colours*. Philadelphia: Thomas Dobson, 1814.

> **The powerful action of sulphuric acid upon indigo, and the very bright lively blue colour thereby produced, had been observed by chemists long ago, but no person seems to have applied this colour upon cloth as a dye, until about the year 1740, when it was done by Counsellor Barth, at Grossenhayn, in Saxony. In addition to the indigo and sulphuric acid, he employed crude antimony and lapis caliminaris, (and as some say, alum), mixing them with the oil of vitriol first, and adding the indigo afterwards: but these additions being found useless, were after some time discontinued.**

- The action of sulfuric acid upon indigo had already been observed by chemists, but that Counsellor Barth was the first one to apply it to cloth (p. 168).
- Production of "great heat" during the extract preparation (p. 168).
- He talks about a "triple combination" with oxygen to explain the chemical reaction. He mentions that indigo will not be fast when treated with sulfuric acid, especially if boiling water and soap are used (p. 170).
- He defends Poerner's suggestion for the 4:1 ratio in opposition to Bergman's 8:1 ratio (p. 171). Also mentions that the indigo extract should be left for 48 hours in a warm situation for it to dissolve and that indigo should be finely powdered.
- The addition of chalk dyes Saxon blue more slowly (p. 172).
- First one to mention the term "sulphate of indigo" (pp. 172-173):

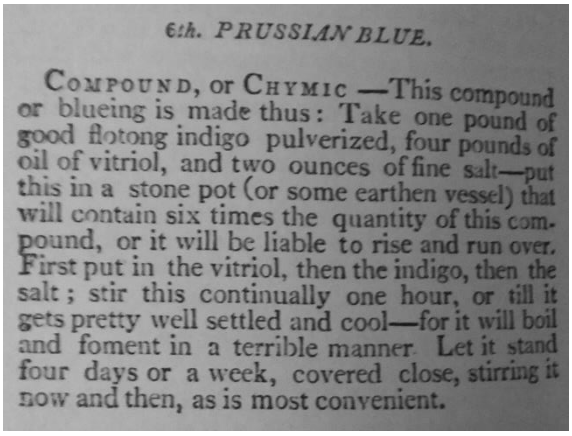
> **The solution of indigo by sulphuric acid, is usually called by dyers chemical blue. It ought, however, according to the new nomenclature, to be termed sulphate of indigo; a name by which I shall continue to distinguish it.* When applied to wool, the blue colour is much more permanent than it is in a fluid state; for though a little manganese, added to the sulphate of indigo, instantly destroys its colour,† wool, which had been previously dyed blue with some of the same preparation, was not discoloured by the action of manganese, dissolved in sulphuric acid.**

- Unusual for mentioning occasional additions of potash, orpiment, or manganese (pp. 172-175). Comment about impurities in indigo. Mentions the undesired effect of nitric acid, which is sometimes present in sulfuric acid (pp. 177-178).
- Uses ratio of 6:1 for calico (p. 199).

6. Bancroft (1814)	
Ratio: (4:1), (6:1) and (8:1)	Dye-assistants: Not specified
Temperature: Not specified	Other: First one to mention 'sulphate of indigo'.

7. Elijah Bemiss (1815) Provenance: The University of Glasgow Library

Bemiss, Elijah. *The Dyer's Companion, 3rd edition (1815),* edited by Rita J. Adrosko. New York: Dover Publications, 1973.



6th. PRUSSIAN BLUE.

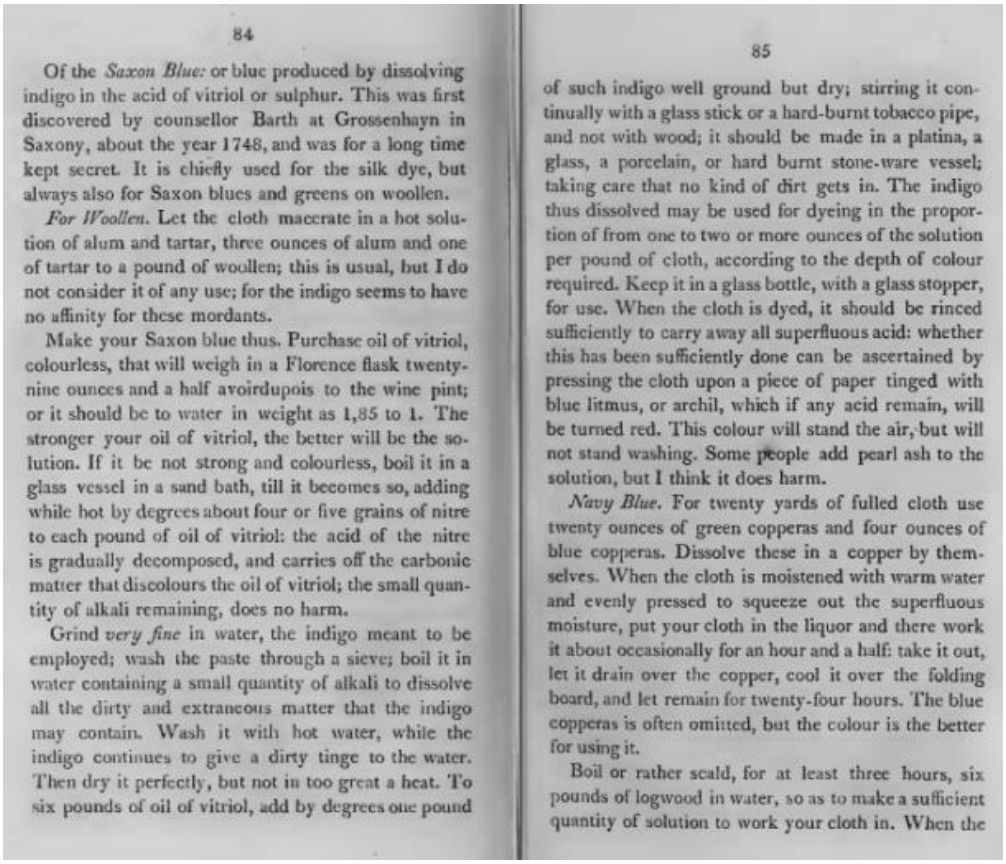
COMPOUND, or CHYMIC —This compound or blueing is made thus: Take one pound of good flotong indigo pulverized, four pounds of oil of vitriol, and two ounces of fine salt—put this in a stone pot (or some earthen vessel) that will contain six times the quantity of this compound, or it will be liable to rise and run over. First put in the vitriol, then the indigo, then the salt; stir this continually one hour, or till it gets pretty well settled and cool—for it will boil and foment in a terrible manner. Let it stand four days or a week, covered close, stirring it now and then, as is most convenient.

- The term "Prussian Blue" (pp. 14-15) is used to refer to indigo carmine. He mentions a recipe using indigo, lime stone (calcium oxide or calcium carbonate), and oil of vitriol (sulfuric acid). It is worth noting that both alkaline and acid materials are used, creating a redox reaction.
- Explains several recipes to dye blue and green over silk and cotton, using variations of indigo carmine (pp. 57-60).
- Tries to explain the behaviour of Prussian Blue (pp. 72-75).
- 'On Blue Dyeing' (pp. 107-179), explains differences between the great and lesser dye (indigo and woad versus logwood). He mentions the materials and utensils needed for dyeing. He explains the easiness of making deep blues as opposed to light blues. He talks about 'the theory of the invisible change of the blue dye', fastness, and the choice of salts. Common indigo vats and indigo carmine dyeing are not clearly differentiated throughout the text.
- Overall, this source does not seem as reliable as others.

7. Elijah Bemiss (1815)	
Ratio: (4:1) and (6:1)	Dye-assistants: salt
Temperature: Boiling	Other: Unusual for inclusion of lime stone.

8. Thomas Cooper (1815) Provenance: Archive.org & Getty Research Institute

Cooper, Thomas. *A Practical Treatise on Dyeing and Callicoe Printing.* Philadelphia: Thomas Dobson, 1815.



84

Of the *Saxon Blue:* or blue produced by dissolving indigo in the acid of vitriol or sulphur. This was first discovered by counsellor Barth at Grossenhayn in Saxony, about the year 1748, and was for a long time kept secret. It is chiefly used for the silk dye, but always also for Saxon blues and greens on woollen.

For Woollen. Let the cloth macerate in a hot solution of alum and tartar, three ounces of alum and one of tartar to a pound of woollen; this is usual, but I do not consider it of any use; for the indigo seems to have no affinity for these mordants.

Make your Saxon blue thus. Purchase oil of vitriol, colourless, that will weigh in a Florence flask twenty-nine ounces and a half avoirdupois to the wine pint; or it should be to water in weight as 1,85 to 1. The stronger your oil of vitriol, the better will be the solution. If it be not strong and colourless, boil it in a glass vessel in a sand bath, till it becomes so, adding while hot by degrees about four or five grains of nitre to each pound of oil of vitriol: the acid of the nitre is gradually decomposed, and carries off the carbonic matter that discolours the oil of vitriol; the small quantity of alkali remaining, does no harm.

Grind *very fine* in water, the indigo meant to be employed; wash the paste through a sieve; boil it in water containing a small quantity of alkali to dissolve all the dirty and extraneous matter that the indigo may contain. Wash it with hot water, while the indigo continues to give a dirty tinge to the water. Then dry it perfectly, but not in too great a heat. To six pounds of oil of vitriol, add by degrees one pound

85

of such indigo well ground but dry; stirring it continually with a glass stick or a hard-burnt tobacco pipe, and not with wood; it should be made in a platina, a glass, a porcelain, or hard burnt stone-ware vessel; taking care that no kind of dirt gets in. The indigo thus dissolved may be used for dyeing in the proportion of from one to two or more ounces of the solution per pound of cloth, according to the depth of colour required. Keep it in a glass bottle, with a glass stopper, for use. When the cloth is dyed, it should be rinced sufficiently to carry away all superfluous acid: whether this has been sufficiently done can be ascertained by pressing the cloth upon a piece of paper tinged with blue litmus, or archil, which if any acid remain, will be turned red. This colour will stand the air, but will not stand washing. Some people add pearl ash to the solution, but I think it does harm.

Navy Blue. For twenty yards of fulled cloth use twenty ounces of green copperas and four ounces of blue copperas. Dissolve these in a copper by themselves. When the cloth is moistened with warm water and evenly pressed to squeeze out the superfluous moisture, put your cloth in the liquor and there work it about occasionally for an hour and a half: take it out, let it drain over the copper, cool it over the folding board, and let remain for twenty-four hours. The blue copperas is often omitted, but the colour is the better for using it.

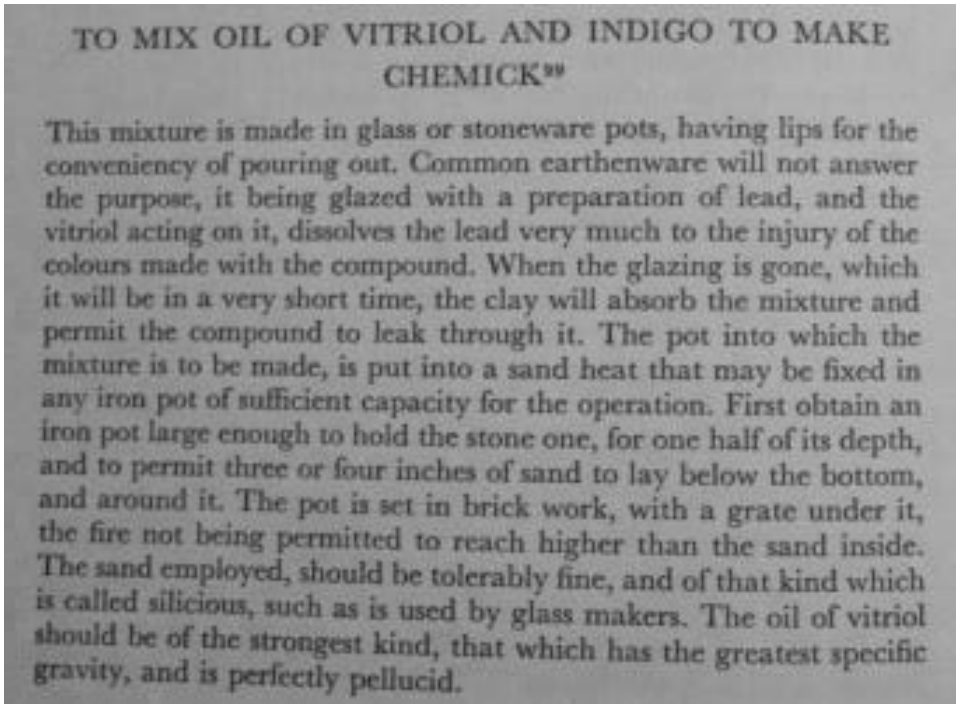
Boil or rather scald, for at least three hours, six pounds of logwood in water, so as to make a sufficient quantity of solution to work your cloth in. When the

- Reliable source. Precisions about the oil of vitriol (sulfuric acid) to be used (p. 24).
- Precise quantification of the materials needed to make Saxon blue (pp. 84-85). Mentions the importance of using concentrated sulfuric acid and includes a brief introduction to the history of the dye. Dye-assistants (alum and cream of tartar) have no affinity with the indigo powder. Mentions that the dye will not be resistant to washing.
- Useful comparison between recipes. Cooper provides his opinion on the matter by criticising some aspects of Homassel's procedure (pp. 186-192).

8. Thomas Cooper (1815)	
Ratio: (6:1) and (8:1)	Dye-assistants: alum and cream of tartar
Temperature: Boiling or below boiling	Other: Mentions that the mordants have no affinity with the indigo powder. Also points out that the green tinge is caused by impurities from the indigo powder, not the acid.

9. William Partridge (1823) Provenance: The University of Glasgow Library

Partridge, William. *A Practical Treatise on Dying of Woolen, Cotton, and Skein Silk with the Manufacture of Broadcloth and Cassimere* (1823), edited by K.G. Ponting. Edington: Pasold Research Fund, 1973.

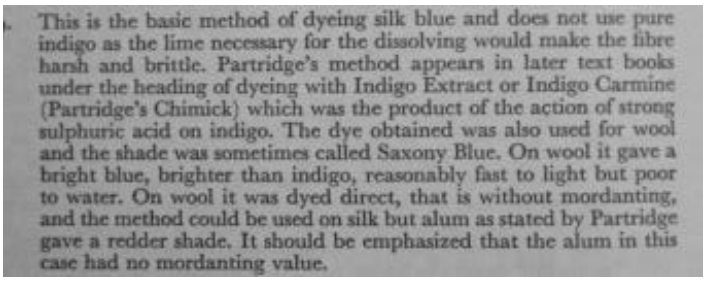


TO MIX OIL OF VITRIOL AND INDIGO TO MAKE CHEMICK[99]

This mixture is made in glass or stoneware pots, having lips for the conveniency of pouring out. Common earthenware will not answer the purpose, it being glazed with a preparation of lead, and the vitriol acting on it, dissolves the lead very much to the injury of the colours made with the compound. When the glazing is gone, which it will be in a very short time, the clay will absorb the mixture and permit the compound to leak through it. The pot into which the mixture is to be made, is put into a sand heat that may be fixed in any iron pot of sufficient capacity for the operation. First obtain an iron pot large enough to hold the stone one, for one half of its depth, and to permit three or four inches of sand to lay below the bottom, and around it. The pot is set in brick work, with a grate under it, the fire not being permitted to reach higher than the sand inside. The sand employed, should be tolerably fine, and of that kind which is called silicious, such as is used by glass makers. The oil of vitriol should be of the strongest kind, that which has the greatest specific gravity, and is perfectly pellucid.

- 'On the mordants and dying drugs used by the dyers in England, on wool and woolen cloth' (pp. 99-101). Besides explaining mordants, he mentions "chemick" (p. 99). He also says "when the crystals of blue vitriol have the least tinge of green, they are not good, as they contain more or less iron, and approximate to a mixture of iron and copper salts, instead of being entirely of copper" (pp. 100-101).
- Description of the process to make chemick (indigo carmine) (pp. 104-106). Notice that "the oil of vitriol should be of the strongest kind, that which has the greatest specific gravity, and is perfectly pellucid" (p. 104). He mentions that the ratio should be 4:1 sulfuric acid to indigo powder (p. 105).
- Variations on recipes for blue and green colours using chemick (indigo carmine) are mentioned in pp. 173-175, 177-178, 202, 210-211, 218. The recipes tend to include alum, cream of tartar and boiling.
- The editor provides insight into terminology on note 99: "Partridge would appear to be giving a recipe for manufacturing what was to be known as Indigo Extract, and he later gives several recipes for its use. Indigo extract, sometimes called Indigo Carmine, gave a bright blue easily dyed from a simple dyebath without mordant but it was not a fast dye" (p. 240).

- Note 159 is also important (p. 250). The editor mentions that the use of alum is not necessary:

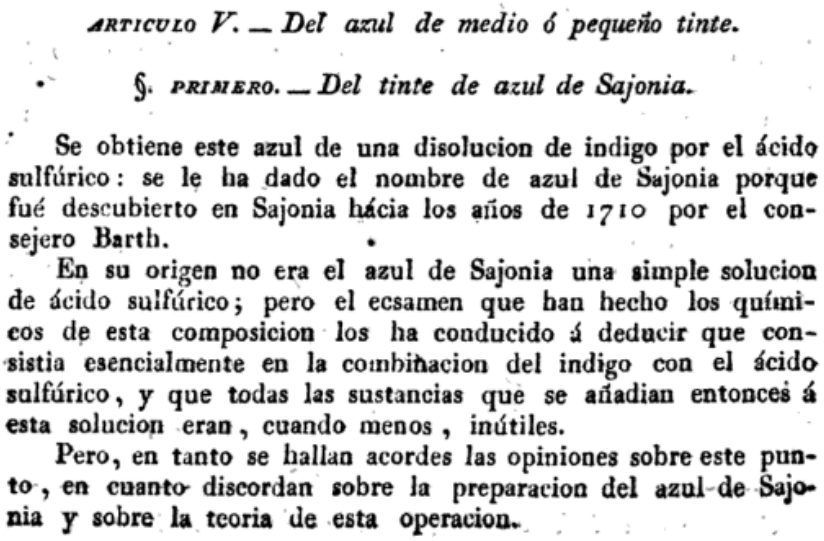


This is the basic method of dyeing silk blue and does not use pure indigo as the lime necessary for the dissolving would make the fibre harsh and brittle. Partridge's method appears in later text books under the heading of dyeing with Indigo Extract or Indigo Carmine (Partridge's Chimick) which was the product of the action of strong sulphuric acid on indigo. The dye obtained was also used for wool and the shade was sometimes called Saxony Blue. On wool it gave a bright blue, brighter than indigo, reasonably fast to light but poor to water. On wool it was dyed direct, that is without mordanting, and the method could be used on silk but alum as stated by Partridge gave a redder shade. It should be emphasized that the alum in this case had no mordanting value.

9. William Partridge (1823)	
Ratio: (4:1)	Dye-assistants: alum and cream of tartar / No mordant
Temperature: Boiling	Other: Mentions that the ratio of sulfuric acid (4:1) is sufficient; otherwise, the fibres might be damaged. The editor mentions that the use of alum is not necessary.

10. J.B. Vitalis (1829) Provenance: Google Books & Biblioteca del Ateneo de Barcelona.

Vitalis, Jean Baptiste. (1829) *Química Aplicada a la Tintura y Blanqueo de la Lana, Seda, Lino, Cáñamo y Algodón y al Arte de Imprimir o Pintar las Telas,* translated by J.R. Trullas. Barcelona: José Rubio, 1829.



ARTICULO V. — Del azul de medio ó pequeño tinte.

§. PRIMERO. — Del tinte de azul de Sajonia.

Se obtiene este azul de una disolucion de indigo por el ácido sulfúrico: se le ha dado el nombre de azul de Sajonia porque fué descubierto en Sajonia hácia los años de 1710 por el consejero Barth.

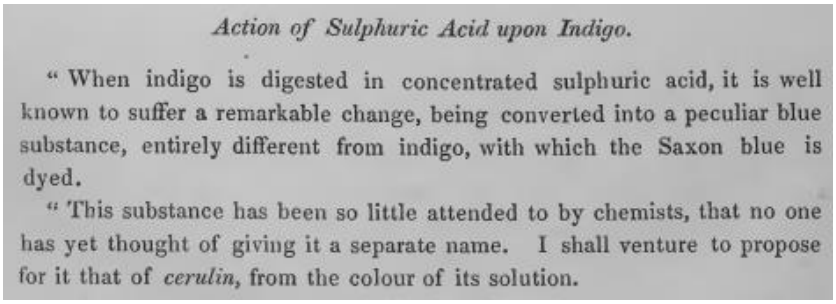
En su origen no era el azul de Sajonia una simple solucion de ácido sulfúrico; pero el ecsamen que han hecho los químicos de esta composicion los ha conducido á deducir que consistia esencialmente en la combinacion del indigo con el ácido sulfúrico, y que todas las sustancias que se añadian entonces á esta solucion eran, cuando menos, inútiles.

Pero, en tanto se hallan acordes las opiniones sobre este punto, en cuanto discordan sobre la preparacion del azul de Sajonia y sobre la teoria de esta operacion.

- Entry in Spanish, translated from French (pp. 148-152). Overall, a confusing entry because it mentions several recipes from different dyers (often contradicting) without going into much detail.
- Explains that chemists have found that any additions to the sulfuric acid and indigo powder are useless. Compares formulations that used by renowned dyers.
- Unusual for the inclusion of potash (which is regarded as an optional measure). Also mentions that some dyers added tin.

10. J.B. Vitalis (1829)	
Ratio: (8:1)	Dye-assistants: alum and cream of tartar / No mordant
Temperature: Below boiling and cold	Other: Unusual for inclusion of potash (optional). Also mentions addition of tin. Mentions that any additions to the sulfuric acid and indigo powder are useless.

11. Berthollet & Berthollet (1841) Provenance: Archive.org & Getty Research Institute. Berthollet, Claude-Louis, and Ammédée Berthollet. *Elements of the Art of Dyeing and Bleaching*, translated by Andrew Ure. London: Thomas Tegg, 1841.



Action of Sulphuric Acid upon Indigo.

"When indigo is digested in concentrated sulphuric acid, it is well known to suffer a remarkable change, being converted into a peculiar blue substance, entirely different from indigo, with which the Saxon blue is dyed.

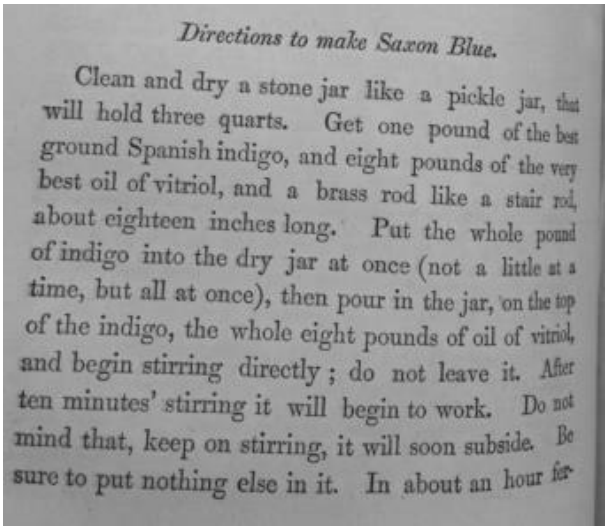
"This substance has been so little attended to by chemists, that no one has yet thought of giving it a separate name. I shall venture to propose for it that of *cerulin*, from the colour of its solution.

- Very similar to Berthollet's (1791), with some additions. "Of Saxon Blue" (pp. 303-306) often cites the work of Bergmann, chemist: "Bergmann conceived that the Saxon blue owed its little permanence merely to the too feeble concentration of the acid which he employed for dissolving it. But his trials must have led him into a mistake in this respect" (p. 306).
- Mentions specific cares that should be taken while preparing the extract, such as tempering the heat and controlling the concentration of the sulfuric acid (p. 306).
- "A small quantity of alkali may have good effects, but a greater would be injurious, since the alkali possesses the property of dissolving the blue molecules precipitated from the sulphuric acid" (p. 306).
- Describes process for Saxon green (pp. 421-425) which is supposed to have "more brightness, but less permanence" (p. 421). The established date for the invention of Saxon blue is different (1750, instead of 1740) (pp. 421).
- The notes (pp. 482-483), written by the translator, include some interesting observations about the "action of sulphuric acid upon indigo". For example, that indigo carmine should not be confused with cerulean blue.

11. Berthollet & Berthollet (1841)	
Ratio: (4:1) and (8:1)	Dye-assistants: Alum and cream of tartar / No mordant.
Temperature: Boiling, below boiling and cold.	Other: Unusual for suggesting addition of alkalis. Mentions the generation of great heat during the preparation of the extract.

12. Thomas Love (1855) Provenance: The University of Glasgow Library, Special Collections (Sp Coll Ferguson Ai-c.61). Use of images by permission of University of Glasgow Library, Special Collections.

Love, Thomas. *The Art of Cleaning, Dyeing, Scouring, and Finishing, on the Most Approved English and French Methods*. London: Longman, Brown, Green, and Longmans, 1855.



Directions to make Saxon Blue.

Clean and dry a stone jar like a pickle jar, that will hold three quarts. Get one pound of the best ground Spanish indigo, and eight pounds of the very best oil of vitriol, and a brass rod like a stair rod, about eighteen inches long. Put the whole pound of indigo into the dry jar at once (not a little at a time, but all at once), then pour in the jar, on the top of the indigo, the whole eight pounds of oil of vitriol, and begin stirring directly; do not leave it. After ten minutes' stirring it will begin to work. Do not mind that, keep on stirring, it will soon subside. Be sure to put nothing else in it. In about an hour fer-

- 'Remarks on Indigo in its Pure State / Directions to make Saxon Blue' (pp. 78-79). Explains how indigo powder is not soluble in water unless it is treated. Mentions that Saxon blue provides the "prettiest of light blues in silks", that differences in preparation exist between recipes, and the directions to prepare Saxon blue (for silk).
- Mentions the importance of avoiding damp air (p. 79).
- Explains how to prepare Saxon greens for silk-dyeing (pp. 91-93).
- Mentions different ways in which white worsted damask (wool) can be dyed blue with Saxon blue variations (pp. 173-179).

12. Thomas Love (1855)	
Ratio: (8:1)	Dye-assistants: No mordant
Temperature: Not specified	Other: Saxon blue process is described for silk. Mentions the importance of avoiding damp air.

13. David Smith (1860) Provenance: Archive.org & American Libraries.

Smith, David. *The Dyer's Instructor, Comprising Practical Instructions in the Art of Dyeing Silk, Cotton, Wool, and Worsted and Woollen Goods*. Philadelphia: Henry Carey Baird, 1860.

No. 60.

20 lbs. OF WOOL.—SAXONY BLUE.

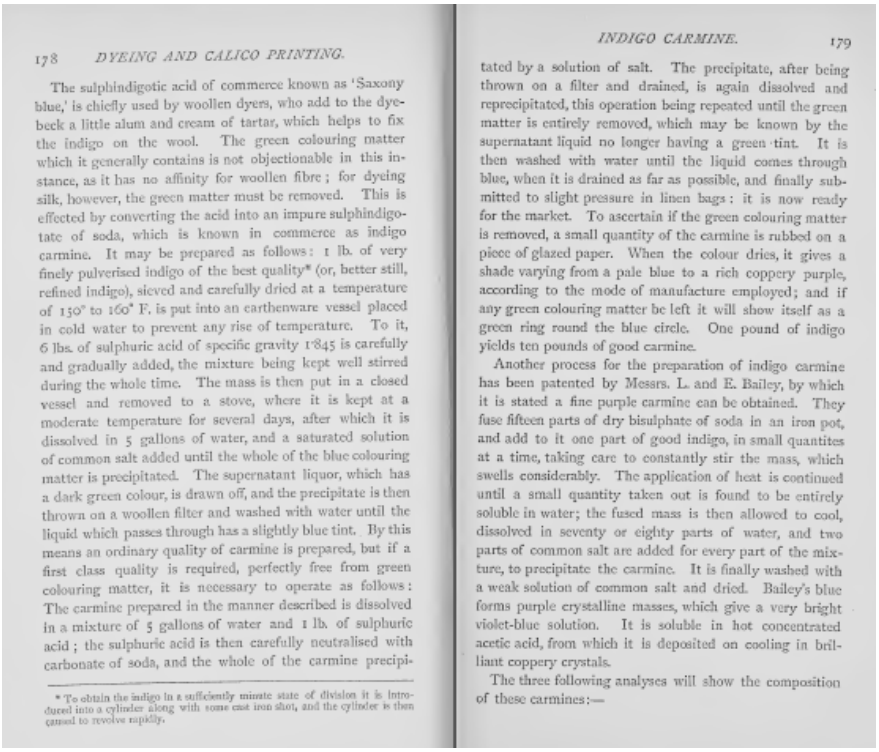
Dye with 1 pint of Liquid Extract.
1 lb. of Argol.
2 lbs. of Alum.
Boil twenty minutes.

- Smith's instructions are titled by shade and colour rather than by dyeing matter. It is possible that the "liquid extract" does not always refer to indigo carmine.
- Extremely brief recipe for Saxony Blue on Wool (No. 60) (p. 47).
- Unclear recipes that apparently use indigo carmine (pp. 109-110). Throughout the manual, many more recipes using "liquid extract" can be found.

13. David Smith (1860)	
Ratio: Not specified	Dye-assistants: Alum
Temperature: Boiling	Other: Instructions titled by shade and colour

14. Crace-Calvert (1876) Provenance: Archive.org & Getty Research Institute.

Crace-Calvert, Frederick. *Dyeing and Calico Printing*, edited by John Stenhouse and Charles Edward Groves. Manchester: Palmer & Howe, 1876.



178 DYEING AND CALICO PRINTING.

The sulphindigotic acid of commerce known as 'Saxony blue,' is chiefly used by woollen dyers, who add to the dye-beck a little alum and cream of tartar, which helps to fix the indigo on the wool. The green colouring matter which it generally contains is not objectionable in this instance, as it has no affinity for woollen fibre; for dyeing silk, however, the green matter must be removed. This is effected by converting the acid into an impure sulphindigotate of soda, which is known in commerce as indigo carmine. It may be prepared as follows: 1 lb. of very finely pulverised indigo of the best quality* (or, better still, refined indigo), sieved and carefully dried at a temperature of 130° to 160° F. is put into an earthenware vessel placed in cold water to prevent any rise of temperature. To it, 6 lbs. of sulphuric acid of specific gravity 1·845 is carefully and gradually added, the mixture being kept well stirred during the whole time. The mass is then put in a closed vessel and removed to a stove, where it is kept at a moderate temperature for several days, after which it is dissolved in 5 gallons of water, and a saturated solution of common salt added until the whole of the blue colouring matter is precipitated. The supernatant liquor, which has a dark green colour, is drawn off, and the precipitate is then thrown on a woollen filter and washed with water until the liquid which passes through has a slightly blue tint. By this means an ordinary quality of carmine is prepared, but if a first class quality is required, perfectly free from green colouring matter, it is necessary to operate as follows: The carmine prepared in the manner described is dissolved in a mixture of 5 gallons of water and 1 lb. of sulphuric acid; the sulphuric acid is then carefully neutralised with carbonate of soda, and the whole of the carmine precipi-

* To obtain the indigo in a sufficiently minute state of division it is introduced into a cylinder along with some cast iron shot, and the cylinder is then caused to revolve rapidly.

INDIGO CARMINE. 179

tated by a solution of salt. The precipitate, after being thrown on a filter and drained, is again dissolved and reprecipitated, this operation being repeated until the green matter is entirely removed, which may be known by the supernatant liquid no longer having a green tint. It is then washed with water until the liquid comes through blue, when it is drained as far as possible, and finally submitted to slight pressure in linen bags: it is now ready for the market. To ascertain if the green colouring matter is removed, a small quantity of the carmine is rubbed on a piece of glazed paper. When the colour dries, it gives a shade varying from a pale blue to a rich coppery purple, according to the mode of manufacture employed; and if any green colouring matter be left it will show itself as a green ring round the blue circle. One pound of indigo yields ten pounds of good carmine.

Another process for the preparation of indigo carmine has been patented by Messrs. L. and E. Bailey, by which it is stated a fine purple carmine can be obtained. They fuse fifteen parts of dry bisulphate of soda in an iron pot, and add to it one part of good indigo, in small quantites at a time, taking care to constantly stir the mass, which swells considerably. The application of heat is continued until a small quantity taken out is found to be entirely soluble in water; the fused mass is then allowed to cool, dissolved in seventy or eighty parts of water, and two parts of common salt are added for every part of the mixture, to precipitate the carmine. It is finally washed with a weak solution of common salt and dried. Bailey's blue forms purple crystalline masses, which give a very bright violet-blue solution. It is soluble in hot concentrated acetic acid, from which it is deposited on cooling in brilliant coppery crystals.

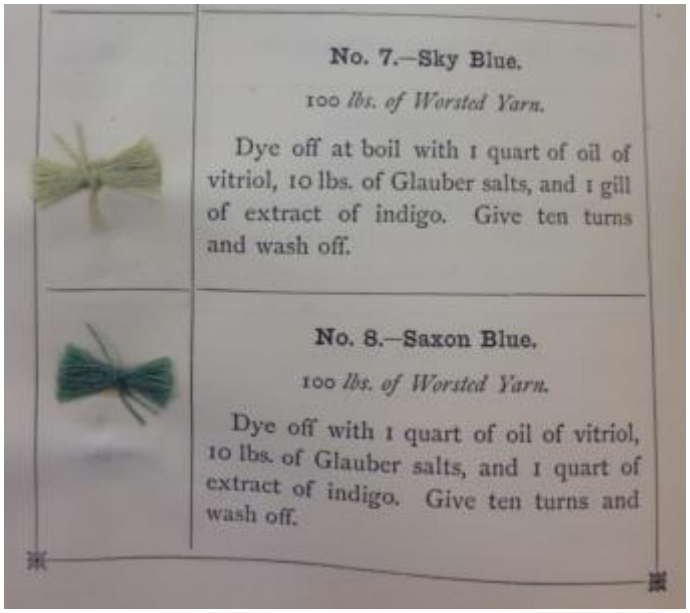
The three following analyses will show the composition of these carmines:—

- He makes a distinction between two different indigosulphonic acids: sulphopurpuric acid (4:1) and sulphindigotic acid (10:1 or 12:1) (175-176). He provides chemical formulae for these compounds (177), which include the presence of nitrogen.
- He mentions that the purple mass produced "is thrown into forty or fifty parts of water" (175). Then, he dilutes it with hydrochloric acid. Also unusual for adding soda carbonate or acetate to the solution for increased solubility.
- He describes the process for creating an "ordinary quality of carmine" and one that is first class as it is "perfectly free from green colouring matter" by neutralising with carbonate of soda (178).
- Unusual for trying to describe chemical reactions.

14. Crace-Calvert (1876)	
Ratio: (4:1, 6:1, 10:1 and 12:1)	Dye-assistants: Alum and cream of tartar
Temperature: Not specified	Other: Unusual for trying to describe chemical reactions.

15. David Smith (1882) Provenance: The University of Glasgow Library, Special Collections (Sp Coll RB 5095, acquisition number VX29/122). Use of images by permission of University of Glasgow Library, Special Collections.

Smith, David. *The English Dyer.* Manchester: Palmer and Howe, 1882.



No. 7.—Sky Blue.

100 *lbs. of Worsted Yarn.*

Dye off at boil with 1 quart of oil of vitriol, 10 lbs. of Glauber salts, and 1 gill of extract of indigo. Give ten turns and wash off.

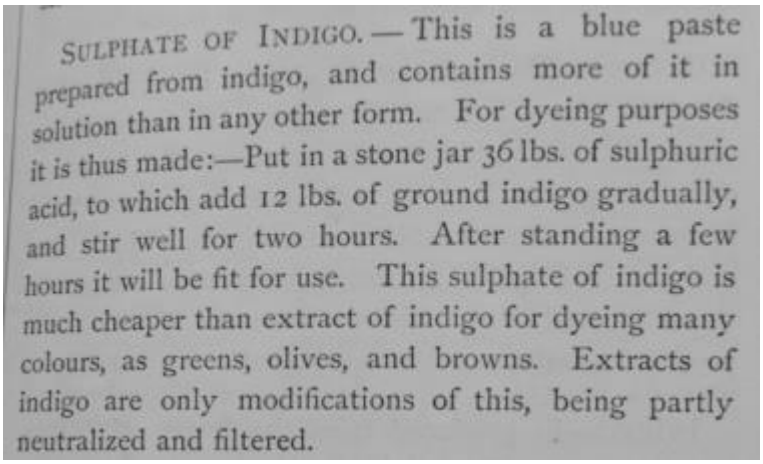
No. 8.—Saxon Blue.

100 *lbs. of Worsted Yarn.*

Dye off with 1 quart of oil of vitriol, 10 lbs. of Glauber salts, and 1 quart of extract of indigo. Give ten turns and wash off.

- Useful manual to see the colours achieved on an industrial scale, considering that fading might have occurred. Sky Blue and Saxon Blue recipes (p. 82). It was noted that both samples left an opaque mark (due to grease or acidic content) in the immediate following page. The causes behind this effect could be explored in future work.
- Light Green, Apple Green (p. 92), Drab – Red Shade, Drab – Blue Shade, Red Lavender, and Blue Lavender (p. 100). Use of extract of indigo (referring to indigo carmine, as clarified in p. 253) mixed with other dyes in order to obtain diverse colours.
- The process for dyeing Saxon blue is explained for silk (p. 158). The recipe includes nitrate of iron and yellow prussiate of potash, which would create a chemical compound different to indigo disulfonic acid. The process for obtaining different shades of green is also explained (p. 174).
- Sky Blue from Extract of Indigo (p. 165). An interesting process in which the extract of indigo is dyed onto wool and then discharged to dye silk in the same liquor.
- Description of alum (p. 250), prepared from alumina clays and alum stones. The entry mentions that the purest alum is obtained in the Roman States.

- Description of sulphate of indigo and its relation with extract of indigo (p. 253). The ratio used is 3:1 sulfuric acid to indigo powder. Mentions economic value.



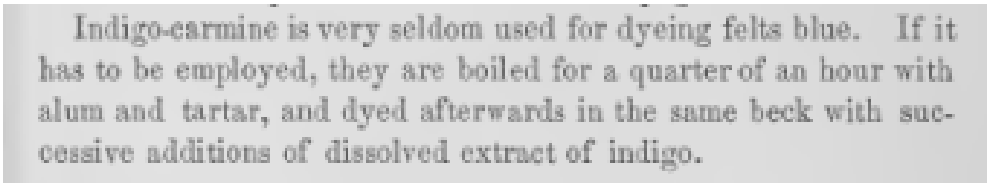
SULPHATE OF INDIGO.—This is a blue paste prepared from indigo, and contains more of it in solution than in any other form. For dyeing purposes it is thus made:—Put in a stone jar 36 lbs. of sulphuric acid, to which add 12 lbs. of ground indigo gradually, and stir well for two hours. After standing a few hours it will be fit for use. This sulphate of indigo is much cheaper than extract of indigo for dyeing many colours, as greens, olives, and browns. Extracts of indigo are only modifications of this, being partly neutralized and filtered.

- Brief mention about the different types of vitriol (p. 258).
- More information is provided in this edition, in comparison to the one from 1860.

15. David Smith (1882)	
Ratio: (3:1)	Dye-assistants: Sodium sulfate (Glauber salt)
Temperature: Boiling and below boiling	Other: Unusual for including potash and iron for dyeing silk with the Saxon blue recipe.

16. Frederick J. Bird (1882) Provenance: Archive.org & Getty Research Institute.

Bird, Frederick J. *The American Practical Dyer's Companion, Comprising a Description of the Principal Dye-Stuffs and Chemicals Used in Dyeing, Their Natures and Uses, Mordants, and How Made.* Philadelphia: Henry Carey Baird & Co, 1882.



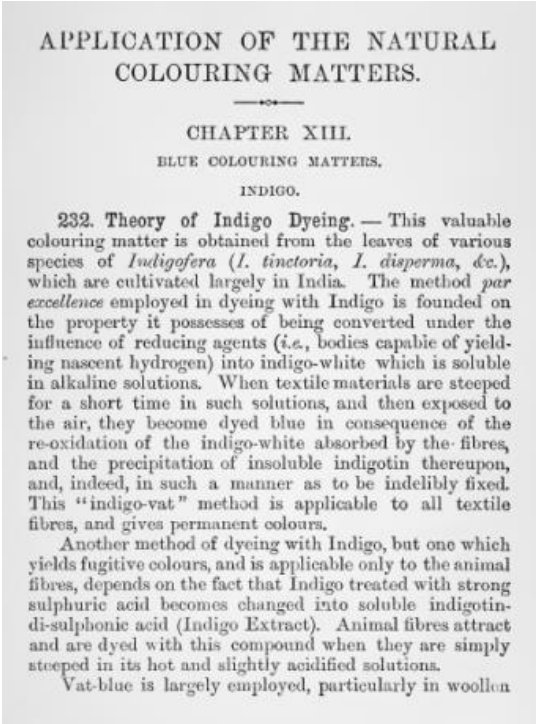
Indigo-carmine is very seldom used for dyeing felts blue. If it has to be employed, they are boiled for a quarter of an hour with alum and tartar, and dyed afterwards in the same beck with successive additions of dissolved extract of indigo.

- Includes a sample of cotton thread dyed green with indigo carmine and else (p. 214). Throughout his manual, indigo carmine / indigo extract is regularly mixed with other dyes.
- About blue felts (p. 233). Includes boiling and using alum and cream of tartar as dye-assistants.
- Explains key terms in the glossary, such as chemic (p. 369).

16. Frederick J. Bird (1882)	
Ratio: Not specified	Dye-assistants: Alum and cream of tartar
Temperature: Boiling	Other: Very brief

17. J.J. Hummel (1888) Provenance: Archive.org & Getty Research Institute

Hummel, John James. *The Dyeing of Textile Fabrics*. London: Cassell & Company, 1888.



APPLICATION OF THE NATURAL COLOURING MATTERS.

CHAPTER XIII.

BLUE COLOURING MATTERS.

INDIGO.

232. **Theory of Indigo Dyeing.** — This valuable colouring matter is obtained from the leaves of various species of *Indigofera* (*I. tinctoria*, *I. disperma*, *&c.*), which are cultivated largely in India. The method *par excellence* employed in dyeing with Indigo is founded on the property it possesses of being converted under the influence of reducing agents (*i.e.*, bodies capable of yielding nascent hydrogen) into indigo-white which is soluble in alkaline solutions. When textile materials are steeped for a short time in such solutions, and then exposed to the air, they become dyed blue in consequence of the re-oxidation of the indigo-white absorbed by the fibres, and the precipitation of insoluble indigotin thereupon, and, indeed, in such a manner as to be indelibly fixed. This "indigo-vat" method is applicable to all textile fibres, and gives permanent colours.

Another method of dyeing with Indigo, but one which yields fugitive colours, and is applicable only to the animal fibres, depends on the fact that Indigo treated with strong sulphuric acid becomes changed into soluble indigotin-di-sulphonic acid (Indigo Extract). Animal fibres attract and are dyed with this compound when they are simply steeped in its hot and slightly acidified solutions.

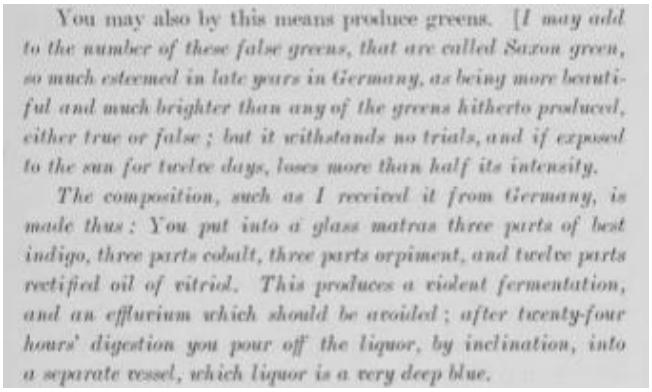
Vat-blue is largely employed, particularly in woollen

- Hummel was a professor at the University of Leeds, making this manual a useful and reliable source.
- Explains how indigo becomes soluble in water but yields fugitive colours (pp. 295-296). Indigo powder for indigo carmine should be ground in the dry state.
- Several terms referring to indigo carmine (pp. 317-318). He mentions the "sour extract" containing free sulfuric acid and how no addition is required in this case. Differences in colour attributed to temperature (p. 276); highlights the importance of adding sodium sulfate to the dye-bath for levelling. More sulfuric acid is needed in the dye-bath when sodium sulfate is used to achieve full colouring power.
- Mentions indigo carmine's application on silk.
- He mentions indigo carmine as a dye that shows evident differences in fastness to light depending on its constitution (p. 489), in comparison to indigo.

17. J.J. Hummel (1888)	
Ratio: Not specified	Dye-assistants: Sodium sulfate / No mordant / Alum
Temperature: Boiling and below boiling	Other: Highlights importance of temperature.

18. Hellot et al (1901) Provenance: Archive.org & Claire T. Carney Library, University of Massachusetts Dartmouth Collection.

Hellot, Macquer, and le Pileur D'Apligny. *The Art of Dyeing Wool, Silk, and Cotton,* edited by R. Baldwin. London: Scott, Greenwood & Co, 1901.



You may also by this means produce greens. [*I may add to the number of these false greens, that are called Saxon green, so much esteemed in late years in Germany, as being more beautiful and much brighter than any of the greens hitherto produced, either true or false; but it withstands no trials, and if exposed to the sun for twelve days, loses more than half its intensity.*

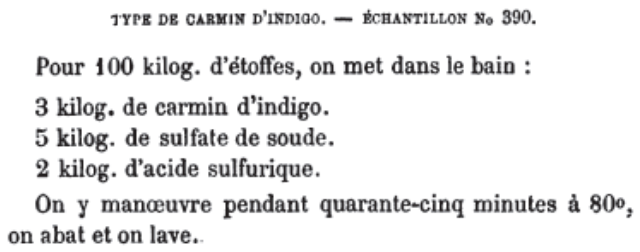
The composition, such as I received it from Germany, is made thus: You put into a glass matras three parts of best indigo, three parts cobalt, three parts orpiment, and twelve parts rectified oil of vitriol. This produces a violent fermentation, and an effluvium which should be avoided; after twenty-four hours' digestion you pour off the liquor, by inclination, into a separate vessel, which liquor is a very deep blue.

- This entry is a compilation of recipes from the past centuries - may be outdated. Explains the difference between true or false dyes, referring mainly to fading (p. 9). Important note as to why Saxon blue is a 'lesser dye' (p. 436).
- Explains how to identify if indigo is of good quality (p. 47).
- Blue liquor (indigo and potash) is added into a solution of vitriol (sulfuric acid) (p. 67), then lime (calcium oxide) is added. Done in cold weather. The recipe is not clearly named as Saxon blue.
- Referring to the preparation: "This blue is enlivened, that is to say, rendered more bright and beautiful, by immersing the stuff which has been just dyed in hot water, because then the colouring atoms which adhered to the fibres of the wool only superficially are carried off" (p. 79).
- They provide a recipe for Saxon green that may include the use of cobalt or antimony (p. 211). They mention the use of alum and cream of tartar.
- 'Of Saxon Blue' (p. 435). Only for dyeing cotton or linen and mentions. Fades when exposed to the air.

18. Hellot et al (1901)	
Ratio: (4:1)	Dye-assistants: Alum and cream of tartar / No mordant
Temperature: Boiling	Other: Unusual for inclusion of lime stone, as well as orpiment, and cobalt which could cause a redox reaction.

19. Théophile Grison (1908) Provenance: Archive.org & American Libraries.

Grison, Théophile. *La Teinture au Dix-Neuvieme Siecle en ce Qui Concerne la Laine et les Tissus ou la Laine Est Predominante.* Paris: H. Dunod et E. Pinat, 1908.



TYPE DE CARMIN D'INDIGO. — ÉCHANTILLON No 390.

Pour 100 kilog. d'étoffes, on met dans le bain :

3 kilog. de carmin d'indigo.
5 kilog. de sulfate de soude.
2 kilog. d'acide sulfurique.

On y manœuvre pendant quarante-cinq minutes à 80°, on abat et on lave.

- Entry in French. Very clear ratios of the materials needed (p. 78).
- Indigo carmine still suggested as a dye at the beginning of the 20th century (p. 133). He uses sodium chloride as mordant.
- Alum and cream of tartar used as Dye-assistants for green hues (p. 137).
- Explains preparation of common indigo (pp. 229-231).

19. Théophile Grison (1908)	
Ratio: (3:2)	Dye-assistants: Sodium sulfate / Sodium chloride / Alum and cream of tartar
Temperature: Below boiling	Other: Unusual ratio. Alum and cream of tartar are only used for green hues.

Appendix 3. Additional Information on the Preparation of Samples

1. Labelling Used for Samples

The following labelling convention was used:

i. *Dye-assistants (3 variables):* Refers to alum and cream of tartar (**A** for threads; **D** for fabric), sodium sulfate (**B** for threads; **E** for fabric), and without use of mordant (**C** for threads; **F** for fabric). Dyed thread and fabric samples can be differentiated throughout this dissertation by looking at this letter.

ii. *Dyeing matter (2 variables):* Refers to Fisher indigo carmine (**0**) and to the 8:1 indigo carmine prepared with sulfuric acid and indigo powder in 8:1 ratio (**8**) (w/w). It is expected that there are different degrees of sulfonation in the dyeing matter, although the ratio of sulfuric acid to indigo for Group **0** is not specified by the supplier.

iii. *Temperature (2 variables)*: Refers to a boiling dye-bath at 85-90 °C (**Y**) and a moderate temperature dye-bath at 45-50 °C (**W**). Correspondingly, red and blue colours are used for visual differentiation of graphed data.

In Experiment A (Dyeing Conditions and Washfastness), a code was added to samples to signal variables in *Drying* after wet cleaning. Hence, the last letter corresponds to absorption with blotting paper and pressure with glass weights (**B**) or evaporation with a fan pointed directly for air circulation (**H**). As an example of labelling, 2* B8-Y-H indicates the second replicate (**2***) of an embroidered fabric sample in which the thread was dyed with sodium sulfate (**B**) as dye-assistant, 8:1 ratio of sulfuric acid to indigo powder (**8**) as dyeing matter, at boiling temperature of 85-90 °C (**Y**). After wet cleaning, the sample was dried with a fan (**H**).

Similarly, a code was added to samples from Experiment B (Photodegradation and Washfastness) to signal variables in *Scenario.* This Greek letter is used at the beginning of the label and corresponds to the different lighting scenarios to which samples were exposed: storeroom (**α**), barkcloth lab (**β**), first-year workroom (**γ**) and artificial ageing (**δ**). As an example of labelling, β 1* D0-W is the first replicate (**1***) of a fabric sample located in the barkcloth lab (**β**), mordanted with alum and cream of tartar (**D**), and dyed with Fisher indigo carmine (**0**) at a temperature of 45-50 °C (**W**).

2. Calculations for Experiment A

Some assumptions were made for the recreation of indigo carmine samples since many variables could impact on the final product. The following calculations show a simplified view of the process. The approach is purely theoretical with educated guesses; the presence of anomalies in the recreation of samples is possible.

Preparation for dyeing:

Step 1. The molarity of each compound was calculated.

- Sulfuric Acid: 98 g/mol H_2SO_4
- Indigo (I): 262 g/mol $C_{16}H_{10}N_2O_2$
- Fisher indigo carmine: 466 g/mol $C_{16}H_8N_2O_8S_2Na_2$ (Na is a counter ion)
- 8:1 indigo carmine (inferred): 420 g/mol $C_{16}H_8N_2O_8S_2$ (Possibly $2H^+$)

Step 2. Based on Cooper's recipe,[255] it was defined that 2 oz of indigo carmine solution (IC) were required per pound of cloth. The corresponding equivalencies to the international metric system were made.

$$\frac{2\ oz\ IC}{1\ lb\ wool} \times \frac{1\ lb}{453.6\ g\ wool} \times \frac{28.35\ g\ wool}{1\ oz\ IC} = \frac{0.125\ g\ IC}{g\ wool} = \frac{0.25\ g\ IC}{2\ g\ wool}$$

This means that for every 2 g cloth, 0.25 g of IC solution is needed.

Step 3. Based on this calculation, 1.5 g IC were required to dye 6 skeins of 2 g each. By mixing 1g of indigo powder with sulfuric acid, a 100% conversion of indigo to indigo carmine is theoretically confirmed:

$$2g\ IC\ \times \frac{mol\ IC}{420\ g} = 0.00476\ mol\ IC\ extract = 1.24g\ indigo$$

$$1g\ indigo \times \frac{mol\ indigo}{262\ g\ indigo} \times \frac{2\ mol\ H2SO4}{mol\ indigo} \times \frac{98\ g\ H2SO4}{mol\ H2SO4} = 0.75g\ H2SO4$$

[255] Cooper, 85.

Step 4. The quantity needed for 8:1 indigo carmine replica mixed at different proportions with sulfuric acid was calculated.

$$8{:}1\ IC\ (8) = 2g\ indigo \times \frac{mol\ indigo}{262\ g\ indigo} \times \frac{mol\ IC}{mol\ indigo} \times \frac{420\ g\ ICextract}{mol\ IC} = \frac{3.2\ g\ IC}{150\ ml\ dilute}$$
$$= \frac{0.021\ g}{ml}$$

Considering that 0.25-0.27 g of IC solution is needed per 2 g wool and that 2 g of colouring matter were to be used consistently, it was concluded that the following quantities were needed for preparation and dyeing:

Table 1. Quantities Required for Dyeing

Dyeing Matter	Indigo	H_2SO_4	Indigo carmine	Diluted in	Quantity
0 – Fisher indigo carmine	None	None	2 g	150 mL	11.25 mL / beaker
8 – 8:1 indigo carmine	2 g	8.7 mL	(converted matter)	150 mL	12.85 mL / beaker

Preparation of wash-bath solution:

A midpoint between the cmc values of Dehypon ® LS54 (0.4-0.59 g/l) was selected based on previous findings using the Wilhemly plate method.[256] Since the samples were not soiled, 1x cmc was considered sufficient to observe any changes on indigo carmine's sensitivity to water.

Concentration: 1x cmc = 0.5 g/l
= 1 mL/2 litres of deionised water

It was assumed that the density of Dehypon ® LS54 is 1g/mL.
100 mL of wash-bath solution were used per tray. The pH of the solution was 7.5, as measured with pH strips.

[256] Sato, 83.

3. Calculations for Experiment B

Preparation for dyeing:

The calculations from experiment A were repeated. Since it was observed that dye exhaustion was not completed during experiment A, the quantities were not modified, despite dyeing a heavier sample (3.5 g per piece of wool fabric). The new dyeing matter for experiment B were prepared as follows:

Table 2. Quantities Required for Dyeing

Dyeing Matter	Indigo	H_2SO_4	Indigo carmine	Diluted in	Quantity
0 – Fisher indigo carmine	None	None	2 g	150 mL	11.25 mL / beaker
8 – 8:1 indigo carmine	2 g	8.7 mL	(converted matter)	150 mL	12.85 mL / beaker

Appendix 4. Bleeding During Wet Cleaning By Stages for Experiment A

Tray	Date	Time	Temperature (°C)	RH (%)	pH[257]	Replicate	Key	Replicate	Key	Soaking	Washing	Rinsing	Drying
1	June 1st	14:10	25-27	48-50	7.5	1	A0-Y-H	1	A0-Y-B	No	No	No	No
1	June 1st	14:10	25-27	48-50	7.5	2	A0-Y-H	2	A0-Y-B	No	No	No	No
1	June 1st	14:10	25-27	48-50	7.5	3	A0-Y-H	3	A0-Y-B	No	No	No	No
2	June 1st	15:00	25-27	48-50	7.5	1	A0-W-H	1	A0-W-B	No	No	No	No
2	June 1st	15:00	25-27	48-50	7.5	2	A0-W-H	2	A0-W-B	No	No	No	No
2	June 1st	15:00	25-27	48-50	7.5	3	A0-W-H	3	A0-W-B	No	No	No	No
5	June 4th	9:20	25-27	46-50	7.5	1	A8-Y-H	1	A8-Y-B	No	No	No	No
5	June 4th	9:20	25-27	46-50	7.5	2	A8-Y-H	2	A8-Y-B	No	No	No	No
5	June 4th	9:20	25-27	46-50	7.5	3	A8-Y-H	3	A8-Y-B	No	No	No	No
6	June 4th	9:50	25-27	46-50	7.5	1	A8-W-H	1	A8-W-B	No	No	No	No
6	June 4th	9:50	25-27	46-50	7.5	2	A8-W-H	2	A8-W-B	No	No	No	No
6	June 4th	9:50	25-27	46-50	7.5	3	A8-W-H	3	A8-W-B	No	No	No	No
9	June 4th	14:30	25-27	46-50	7.5	1	C0-Y-H	1	C0-Y-B	No	No	No	No
9	June 4th	14:30	25-27	46-50	7.5	2	C0-Y-H	2	C0-Y-B	No	No	No	No
9	June 4th	14:30	25-27	46-50	7.5	3	C0-Y-H	3	C0-Y-B	No	No	No	No
10	June 4th	15:00	25-27	46-50	7.5	1	C0-W-H	1	C0-W-B	No	No	No	No
10	June 4th	15:00	25-27	46-50	7.5	2	C0-W-H	2	C0-W-B	No	No	No	No
10	June 4th	15:00	25-27	46-50	7.5	3	C0-W-H	3	C0-W-B	No	No	No	No
13	June 5th	9:50	23-25	38-40	7.5	1	C8-Y-H	1	C8-Y-B	No	No	No	No
13	June 5th	9:50	23-25	38-40	7.5	2	C8-Y-H	2	C8-Y-B	No	No	No	No
13	June 5th	9:50	23-25	38-40	7.5	3	C8-Y-H	3	C8-Y-B	No	No	No	No
14	June 5th	10:20	23-25	38-40	7.5	1	C8-W-H	1	C8-W-B	No	No	No	No
14	June 5th	10:20	23-25	38-40	7.5	2	C8-W-H	2	C8-W-B	No	No	No	No
14	June 5th	10:20	23-25	38-40	7.5	3	C8-W-H	3	C8-W-B	No	No	No	No

[257] As measured with pH strips (Macherey-Nagel, 0-14 range).

Tray	Date	Time	Temperature (°C)	RH (%)	pH	Replicate	Key	Replicate	Key	Soaking	Washing	Rinsing	Drying
15	June 29th	13:50	25-27	47-49	7.5	1	B0-W-H	1	B0-W-B	No	No	No	No
15	June 29th	13:50	25-27	47-49	7.5	2	B0-W-H	2	B0-W-B	No	No	No	No
15	June 29th	13:50	25-27	47-49	7.5	3	B0-W-H	3	B0-W-B	No	No	No	No
16	June 29th	14:20	25-27	47-49	7.5	1	B0-Y-H	1	B0-Y-B	No	No	No	No
16	June 29th	14:20	25-27	47-49	7.5	2	B0-Y-H	2	B0-Y-B	No	No	No	No
16	June 29th	14:20	25-27	47-49	7.5	3	B0-Y-H	3	B0-Y-B	No	No	No	No
17	June 29th	14:50	25-27	47-49	7.5	1	B8-W-H	1	B8-W-B	No	No	No	1-B8-W-B
17	June 29th	14:50	25-27	47-49	7.5	2	B8-W-H	2	B8-W-B	No	No	No	No
17	June 29th	14:50	25-27	47-49	7.5	3	B8-W-H	3	B8-W-B	No	No	No	3-B8-W-B
18	June 29th	15:20	25-27	47-49	7.5	1	B8-Y-H	1	B8-Y-B	No	No	No	No
18	June 29th	15:20	25-27	47-49	7.5	2	B8-Y-H	2	B8-Y-B	No	No	No	No
18	June 29th	15:20	25-27	47-49	7.5	3	B8-Y-H	3	B8-Y-B	No	No	No	No

Appendix 5: Additional Data for Experiment B

1. Artificial Ageing

Artificial ageing was completed in a Q-SUN Xe1 Xenon Test Chamber through four cycles of 24-hours. A specialty glass 'Window – Q' was used as a filter to simulate sunlight coming through the window.[258] Recommended standard testing conditions were used, exposing samples to an irradiance of 1.1 w/m^2 at 420 nm.[259] The temperature was maintained at 63 °C, as measured by the black panel sensor, which indicates the maximum temperature in the chamber.[260] This parameter was set to encourage the acceleration of colour change promoted by infrared radiation.[261] The equipment does not allow for environmental simulation so relative humidity was not controlled. It was decided not to use blue wool standards because the study focused on the relation between washfastness and lightfastness, rather than on the fading rate.[262]

Figure 1. Q-Sun Xe1 Xenon Test Chamber with fabric tray on the inside
© CTCTAH, University of Glasgow, 2018. Photo by author.

[258] Q-Lab Corporation, "A Choice of Filters for Q-SUN Xenon Test Chambers" in *Technical Bulletin LX-5060*, 2014. https://www.q-lab.com/products/q-sun-xenon-arc-test-chambers/q-sun-xe-1 (accessed June 26, 2018).
[259] AATCC, 36.
[260] Q-Lab Corporation, "Q-SUN Xenon Test Chambers" 2018. https://www.q-lab.com/products/q-sun-xenon-arc-test-chambers/q-sun-xe-1 (accessed June 26, 2018).
[261] Mark Gottsegen, "Lightfastness Testing of Artists' Materials Using ASTM D 4303 and the Blue Wools," in *AIC 32nd Annual Meeting, June 2004, Postprints vol. 1*, ed. Joseph Swider and Alison Murray, 26-36 (Portland: Research and Technical Studies Specialty Group, 2012) 31.
[262] Ibid, 35.

It is important to mention that the xenon lamp produces infrared radiation so chiller units would need to be used to keep the temperature at lower settings; otherwise, temperature is restricted to high temperatures by the characteristics of the equipment. There is currently no way to provide an equivalency between the total energy absorbed by the samples and the amount of lux, as this last unit is useful in terms of human vision but excludes radiation on the infrared and ultraviolet range, which are key for defining the spectral sensitivity of materials.[263]

Tables 1 and 2 show the periodical recordings of total energy elapsed after each 24-hour cycle was completed. As a preventive measure, woven fabric strips were held with pins on one end to avoid samples from turning due to air circulation inside the chamber.

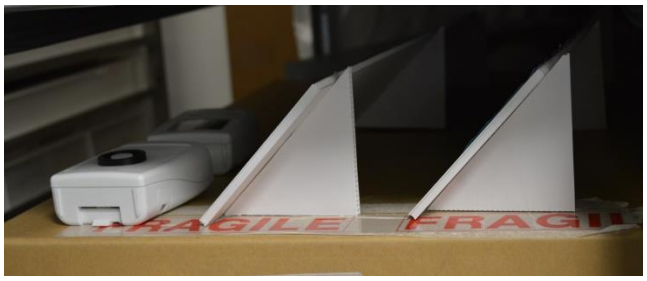
Table 1. Applied Energy during Artificial Ageing of Thread Samples		
Hours	**Total Energy Elapsed (kJ/m²)**	**Total Energy in Cycle (kJ/m²)**
0	32676	0
24	32771	95
48	32870	99
72	32962	92
96	33056	94

Table 2. Applied Energy during Artificial Ageing of Fabric Samples		
Hours	**Total Energy Elapsed (kJ/m²)**	**Total Energy in Cycle (kJ/m²)**
0	33056	0
24	33152	96
48	33247	95
72	33342	95
96	33437	95

[263] Jeffery Quill et al., "Quantifying the Indoor Light Environment" in *Technical Bulletin LX-5026*, Q-Lab Corporation, 2007. https://www.q-lab.com/products/q-sun-xenon-arc-test-chambers/q-sun-xe-1 (accessed June 26, 2018).

2. Monitoring of Lighting Scenarios

The monitoring of lighting scenarios took place from June 25th to July 16th, 2018. Originally, the experiment was designed to be run for four weeks but the results did not reveal changes worth of interpretation so the monitoring concluded earlier than planned. All lighting scenarios were monitored with Hanwell ML400 LuxBug and Humbug data loggers, with readings recorded every 15 minutes. Spot readings for UV were taken on Mondays, between 12:00-16:00, using a UVmeter (Elsec 763 UV Light Monitor).



Figures 2 and 3. Scenario α – Storeroom

Figures 4 and 5. Scenarios γ – First-Year Workroom (left) and β – Barkcloth Lab (right)

Lighting scenario α - Storeroom

Light source: UV filtered artificial light (tubular fluorescent lamps – HO 49 W/865, Lumilux T5 HO), although the storeroom is usually dark.

Chosen to simulate the conditions in which historical textiles are stored. The room was dark most of the time, with occasional low levels of exposure. The room has no entry of natural light and lights tend to be off, except when objects from the Karen Finch Reference Collection are retrieved. The rack was placed on an open shelf of the Storeroom, on Level 3.

Table 3. Lighting conditions in α – Storeroom			
	Week 1	**Week 2**	**Week 3**
Amount of visible light present (lux)	8.6	8.8	10.2
UV present (uW/lumen)	0	0	0
UV total amount (mW/M²)	0.3	0.4	0.3
Relative Humidity (%)	32-55		
Temperature (°C)	24-28		

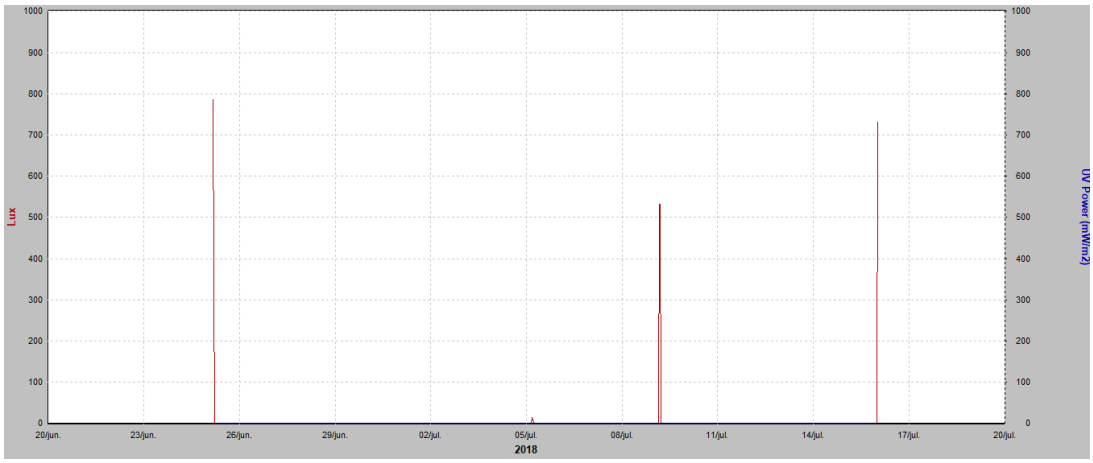


Figure 6. Luxbug Graph for α – Storeroom

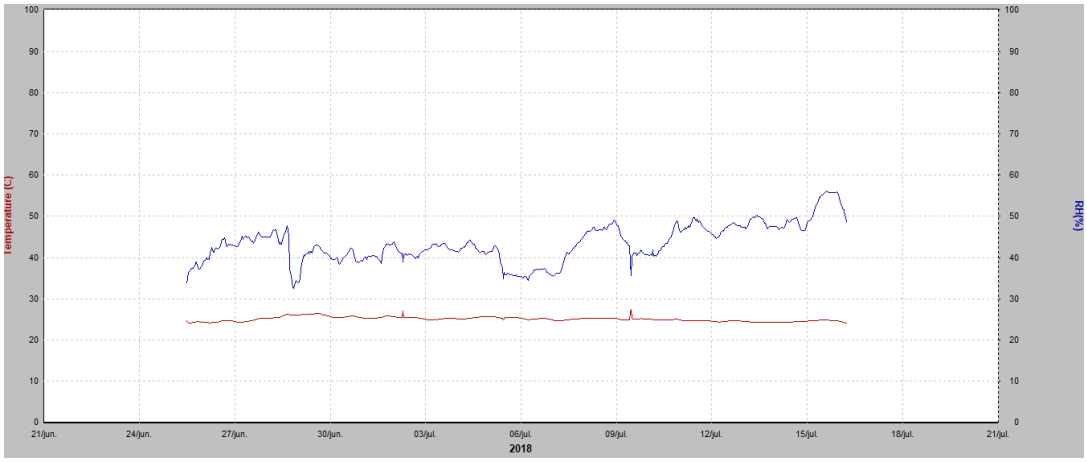


Figure 7. Temperature and Relative Humidity Graph for α – Storeroom

Lighting scenario β – Barkcloth Lab

Light source: Unfiltered diffused natural light and UV filtered fluorescent artificial light. Chosen to simulate indoor conditions with exposure to natural light. It is likely that samplers displayed in residences have been subject to similar conditions. The rack was placed on a north-facing windowsill of the Barkcloth Lab, on Level 5.

Table 4. Lighting conditions in β – Barkcloth Lab			
	Week 1	**Week 2**	**Week 3**
Amount of visible light present (lux)	1980	1651	4684
UV present (uW/lumen)	8	9	5
UV total amount (mW/M²)	18.8	14.6	26
Relative Humidity (%)	40-65		
Temperature (°C)	20-30		

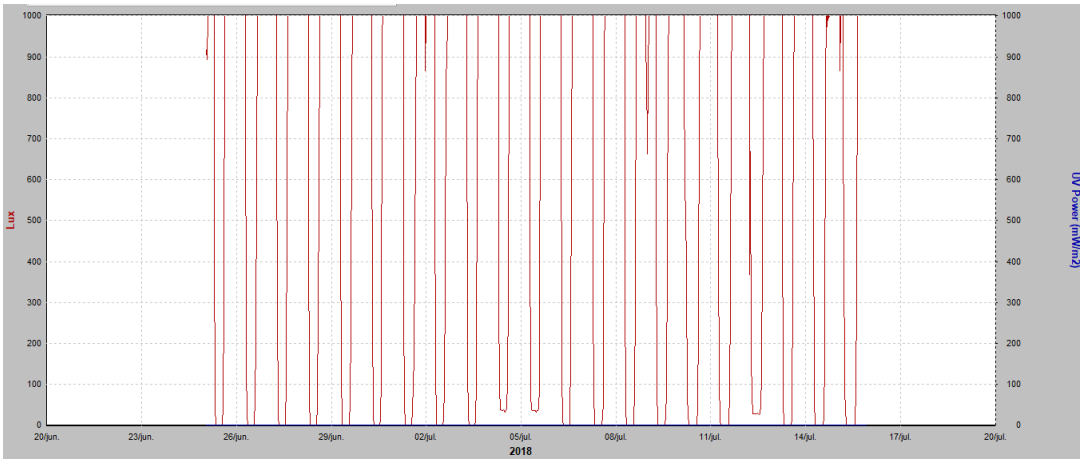


Figure 8. Luxbug Graph for β – Barkcloth Lab

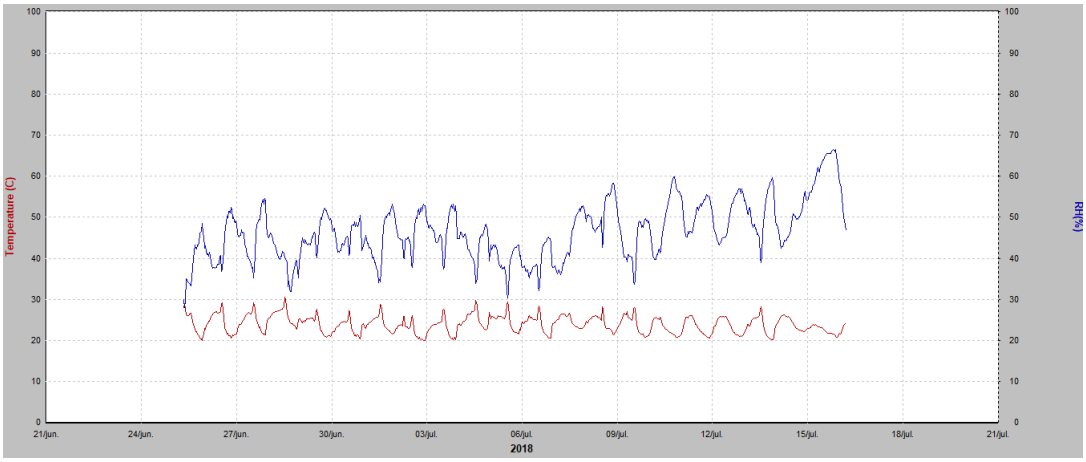


Figure 9. Temperature and Relative Humidity Graph for β – Barkcloth Lab

Lighting scenario γ – First-Year Workroom

Light source: UV filtered, diffused natural light and artificial light (tubular fluorescent lamps – HO 49 W/865, Lumilux T5 HO).

Chosen to simulate the conditions in which historical textiles might be examined and treated. Periodic exposure to light is expected but UV rays should be filtered. The rack was placed on a bench of the First Year Workroom, on Level 3.

Table 5. Lighting conditions in γ – First-Year Workroom			
	Week 1	**Week 2**	**Week 3**
Amount of visible light present (lux)	628	743	748
UV present (uW/lumen)	0	0	0
UV total amount (mW/M²)	0.6	0.7	0.6
Relative Humidity (%)	22-60		
Temperature (°C)	22-30		

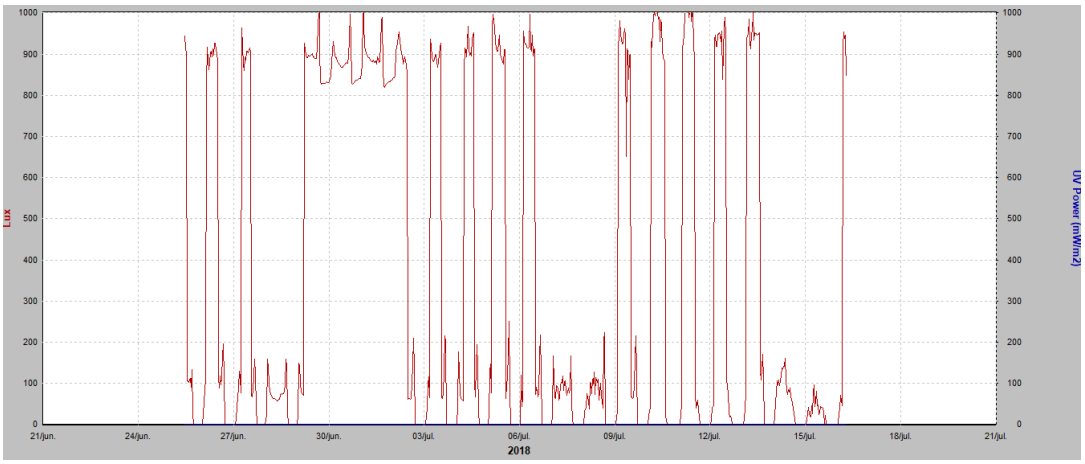


Figure 10. Luxbug Graph for γ – First-Year Workroom

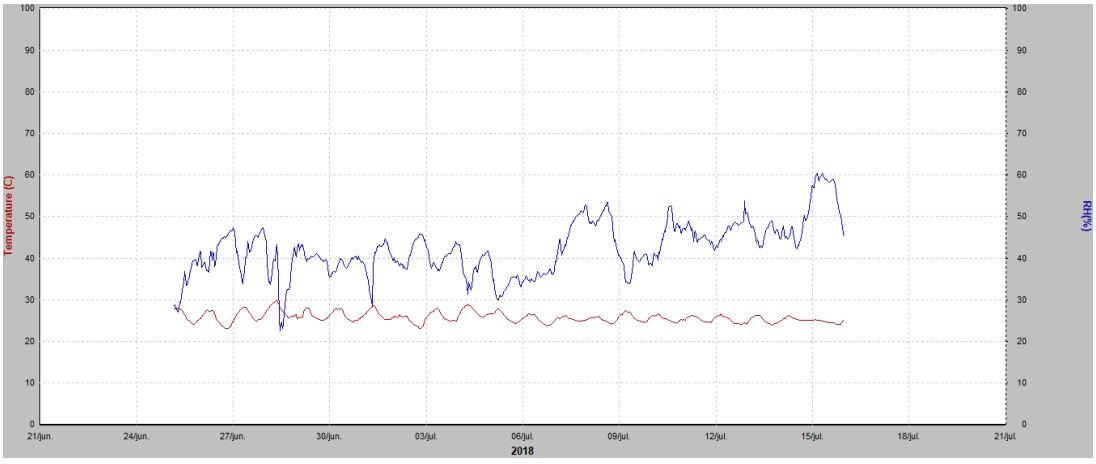


Figure 11. Temperature and Relative Humidity Graph for γ – First-Year Workroom

3. Colour Measurement Results

Figure 12. Artificial Ageing - Thread Samples

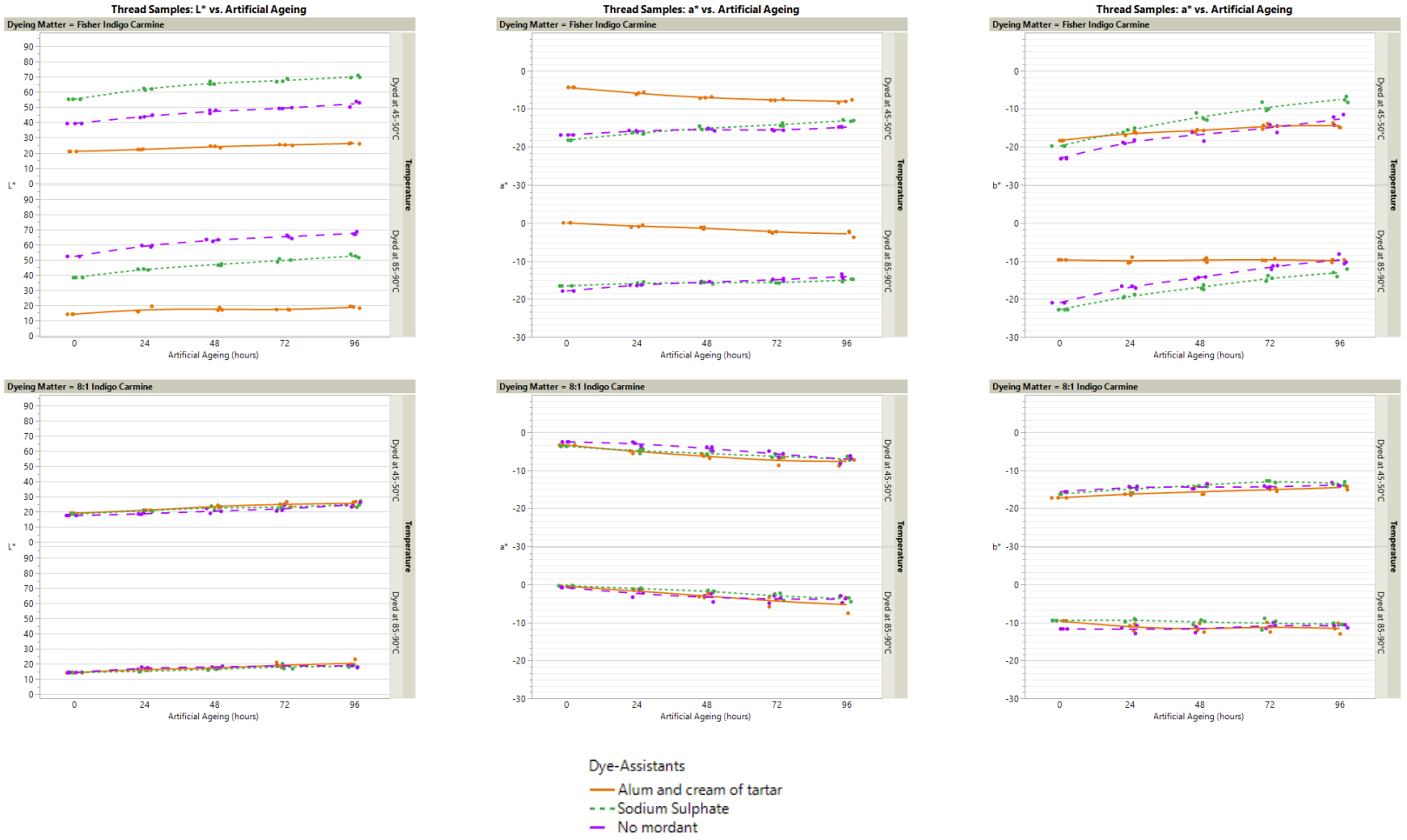


Figure 13. Artificial Ageing - Fabric Samples

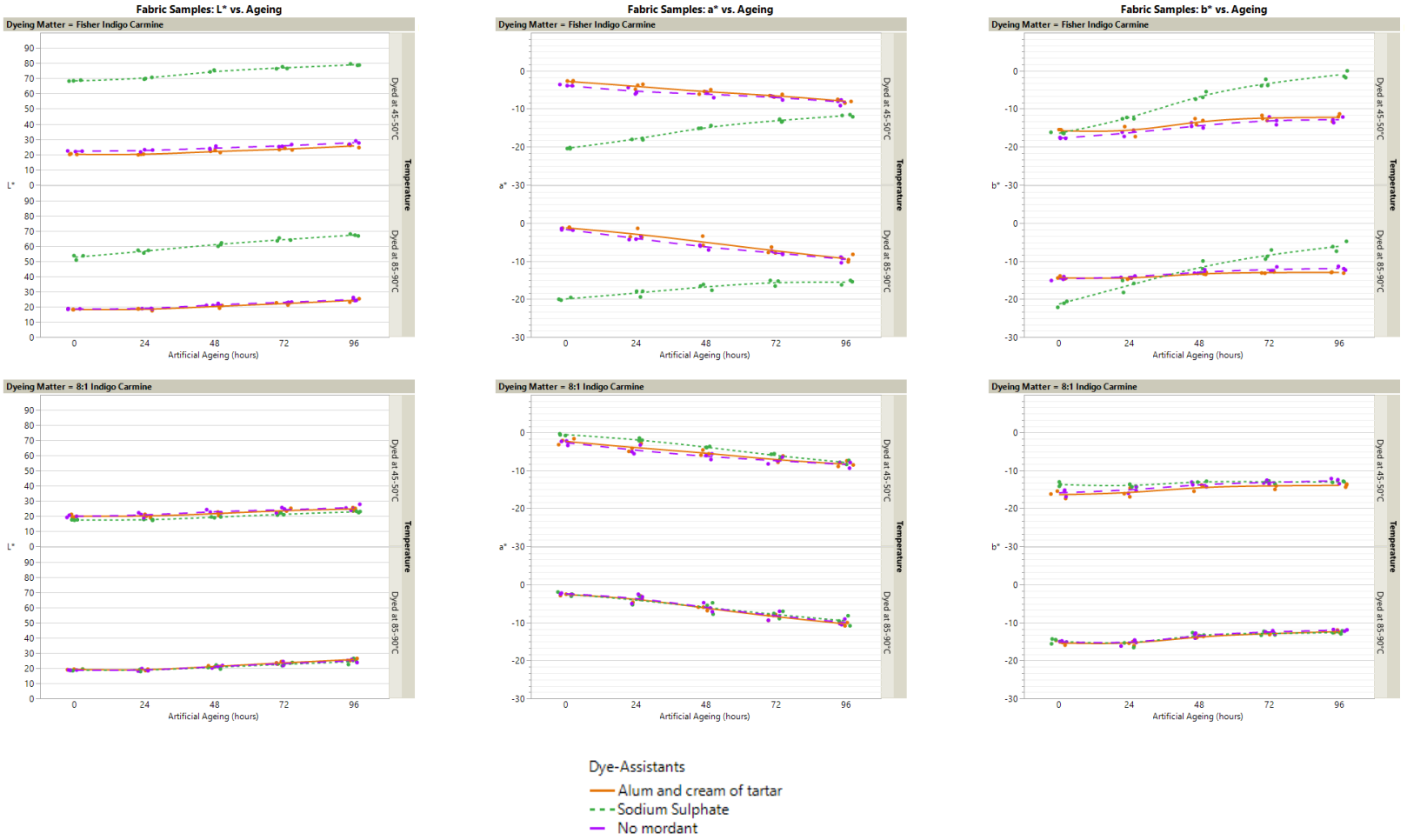


Figure 14. <u>Lighting Scenario - Storeroom</u>

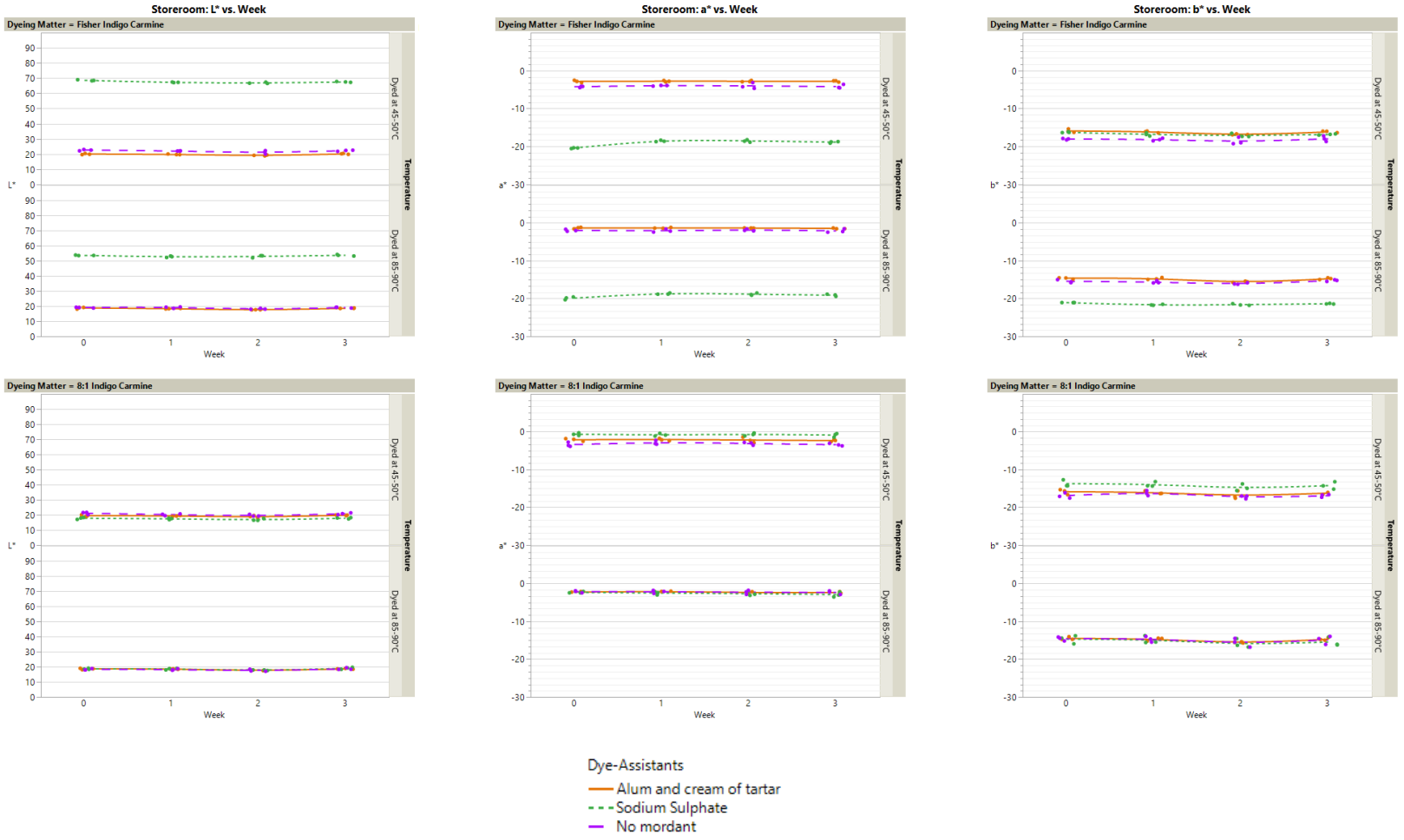


Figure 15. **Lighting Scenario - Barkcloth Lab**

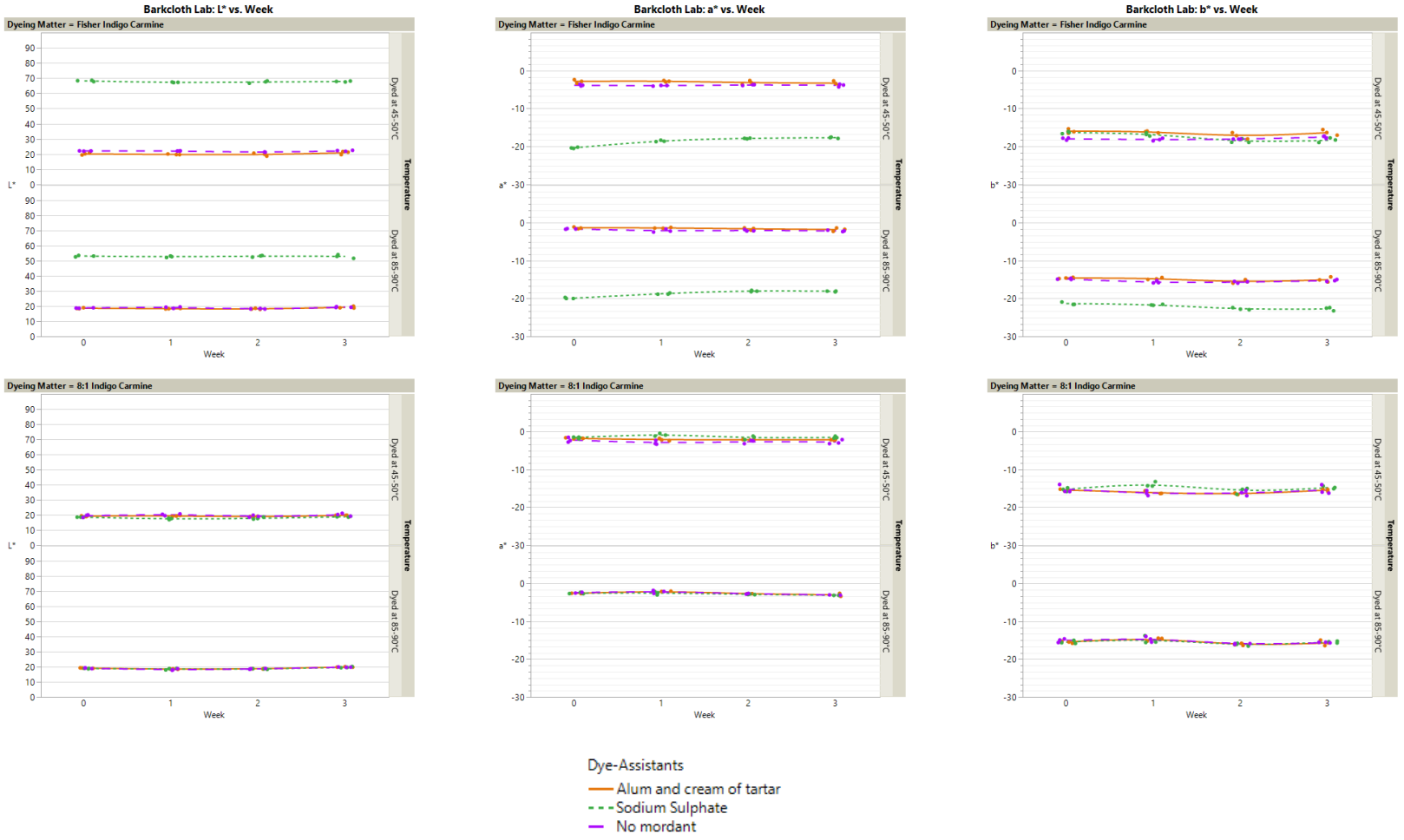


Figure 16. **Lighting Scenario – First-Year Workroom**

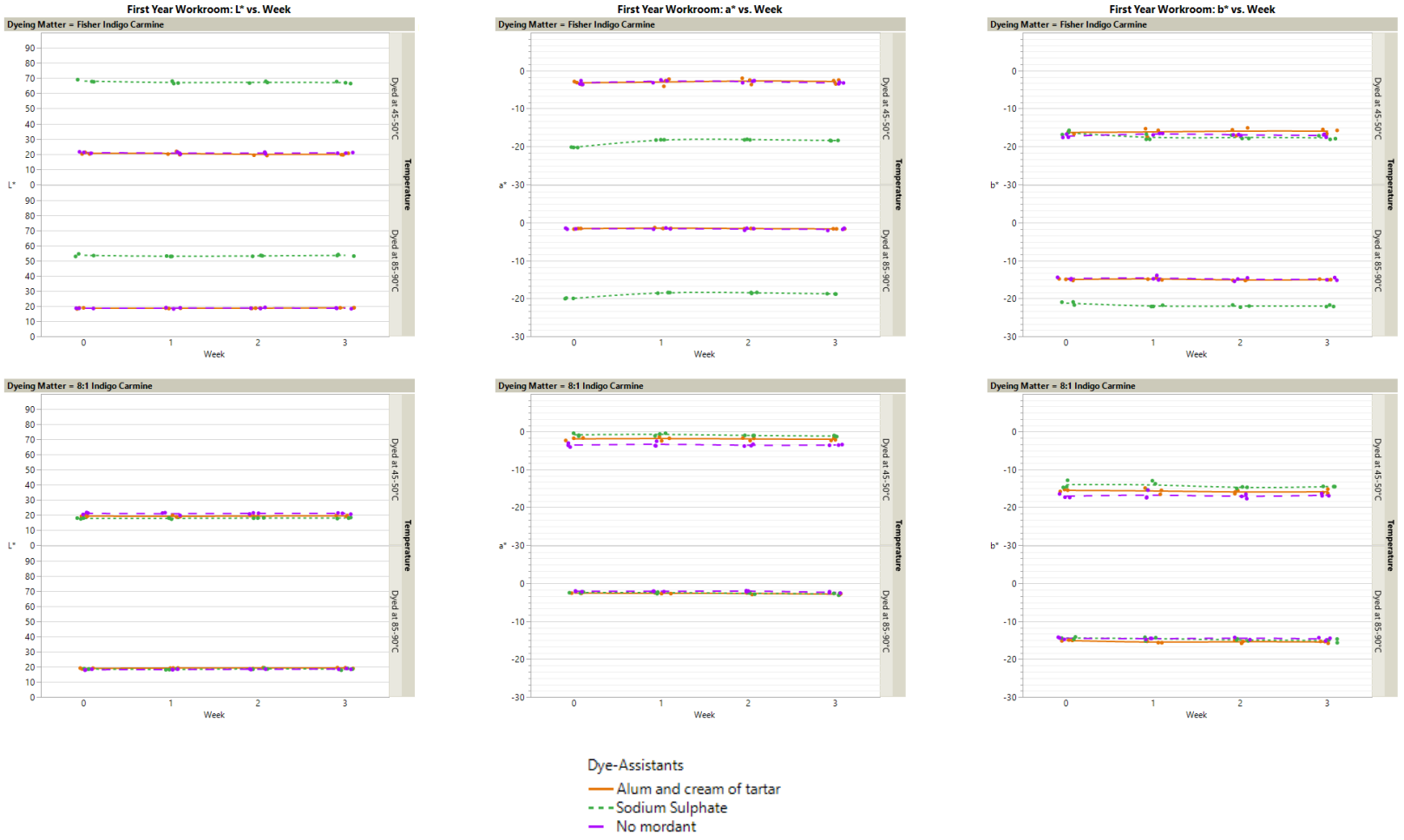


Figure 17. Artificial Ageing – Fabric Samples 48h (Repeating Cycles)

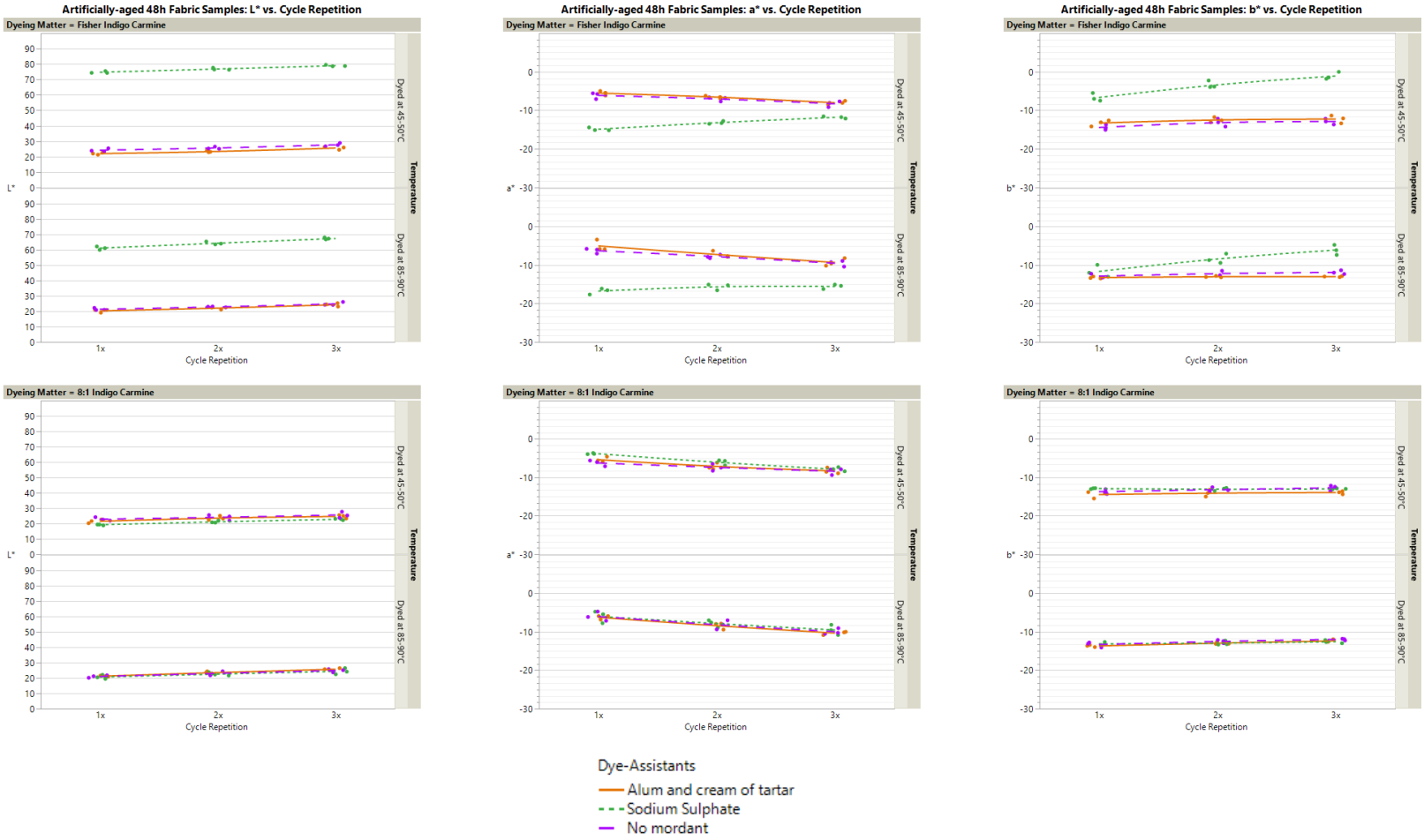
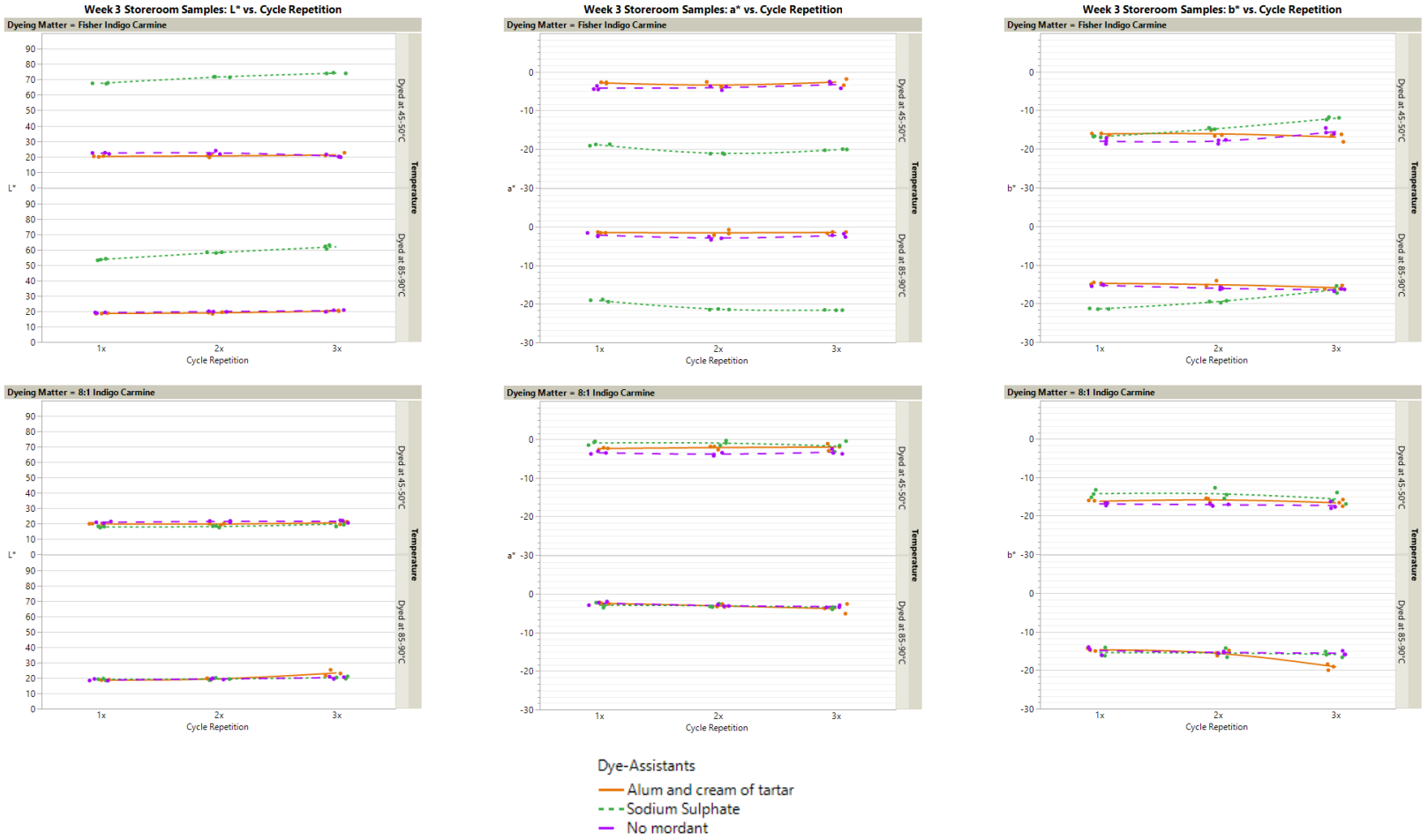
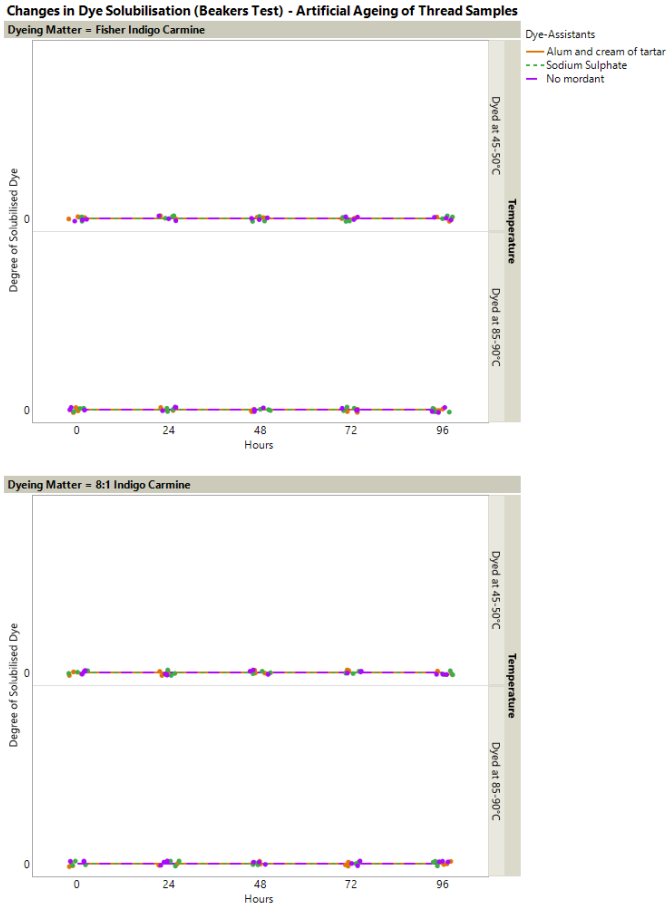


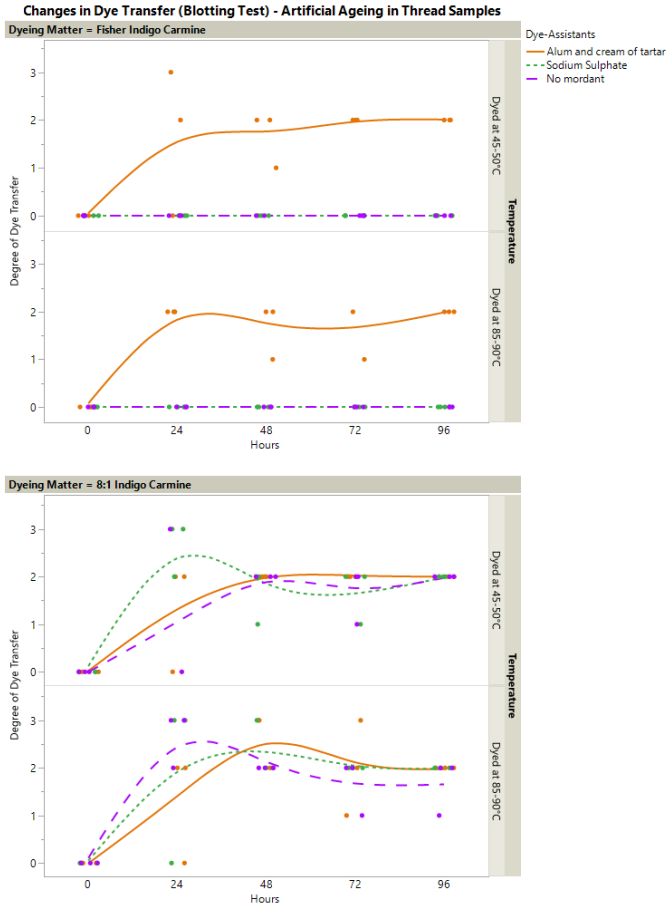
Figure 18. **Lighting Scenario - Storeroom – Week 3 (Repeating Cycles)**



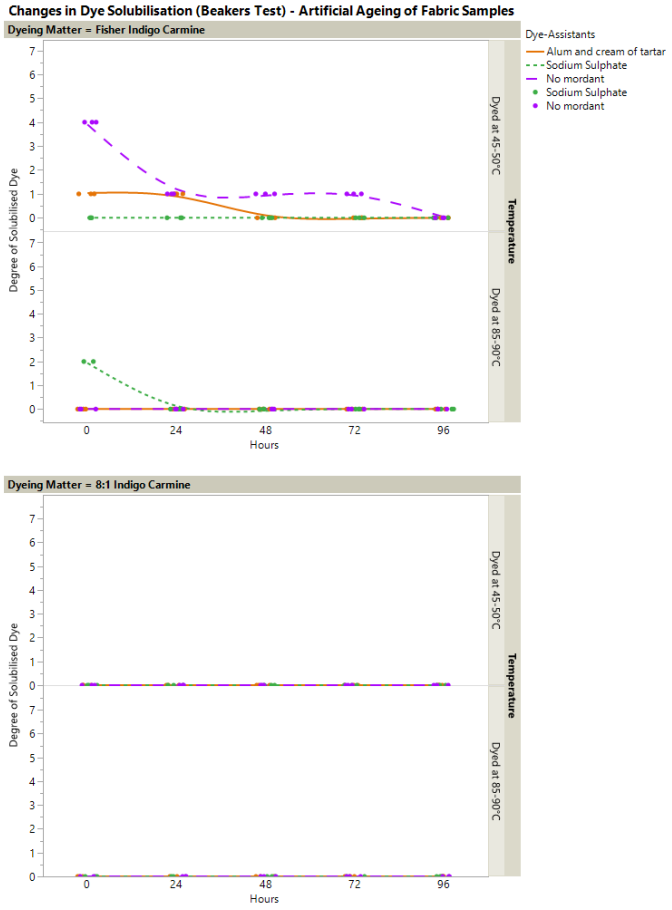
4. Washfastness Results for Beakers and Blotting Test

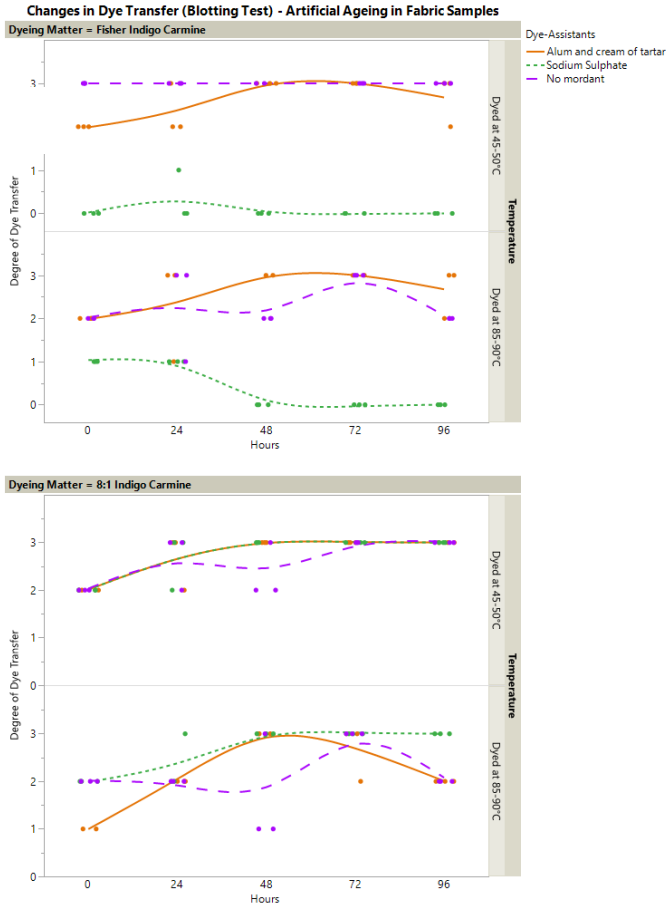
Figures 19 and 20. Artificial Ageing of Thread Samples





Figures 21 and 22. Artificial Ageing of Fabric Samples





Figures 23 and 24. Ageing of Storeroom Samples

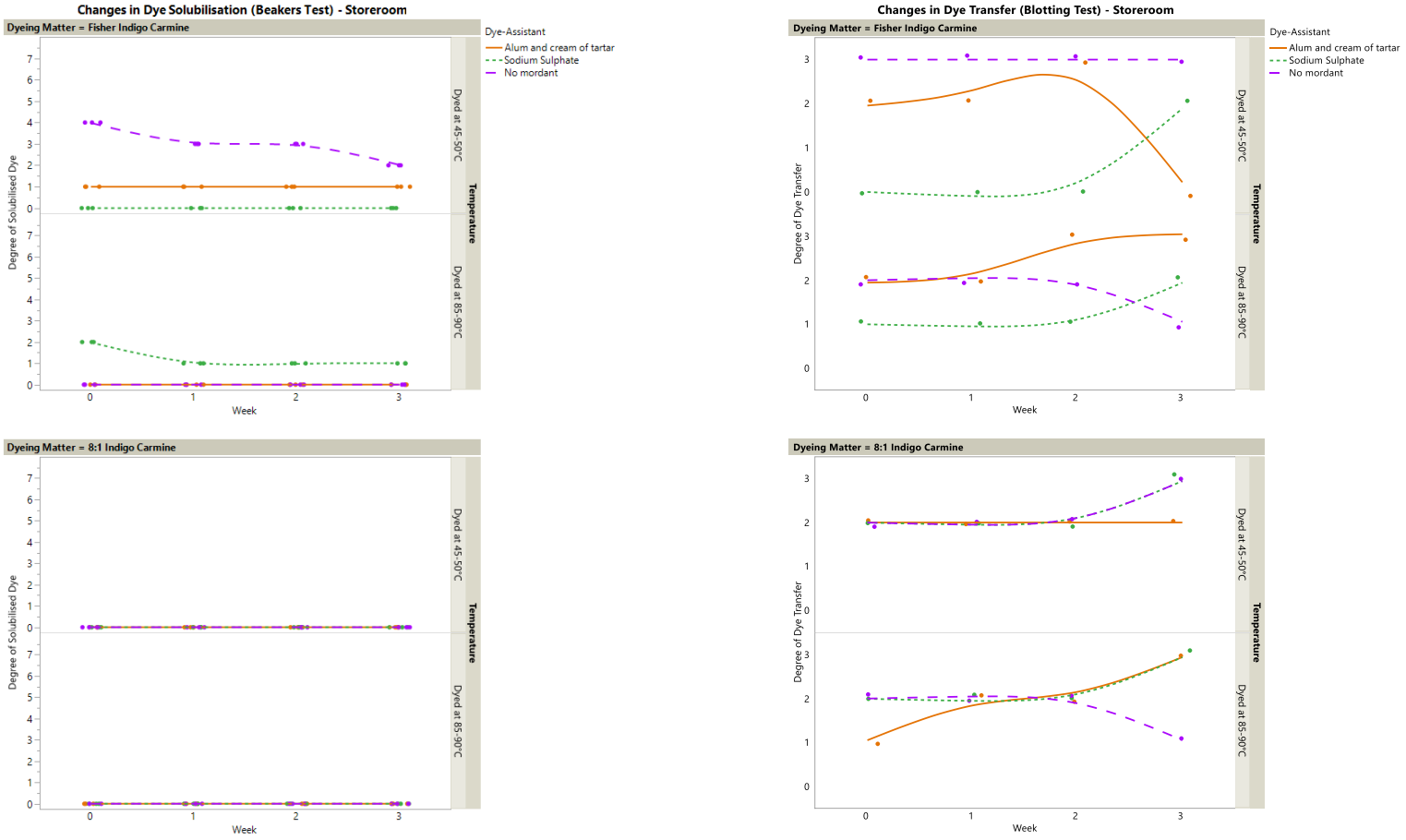
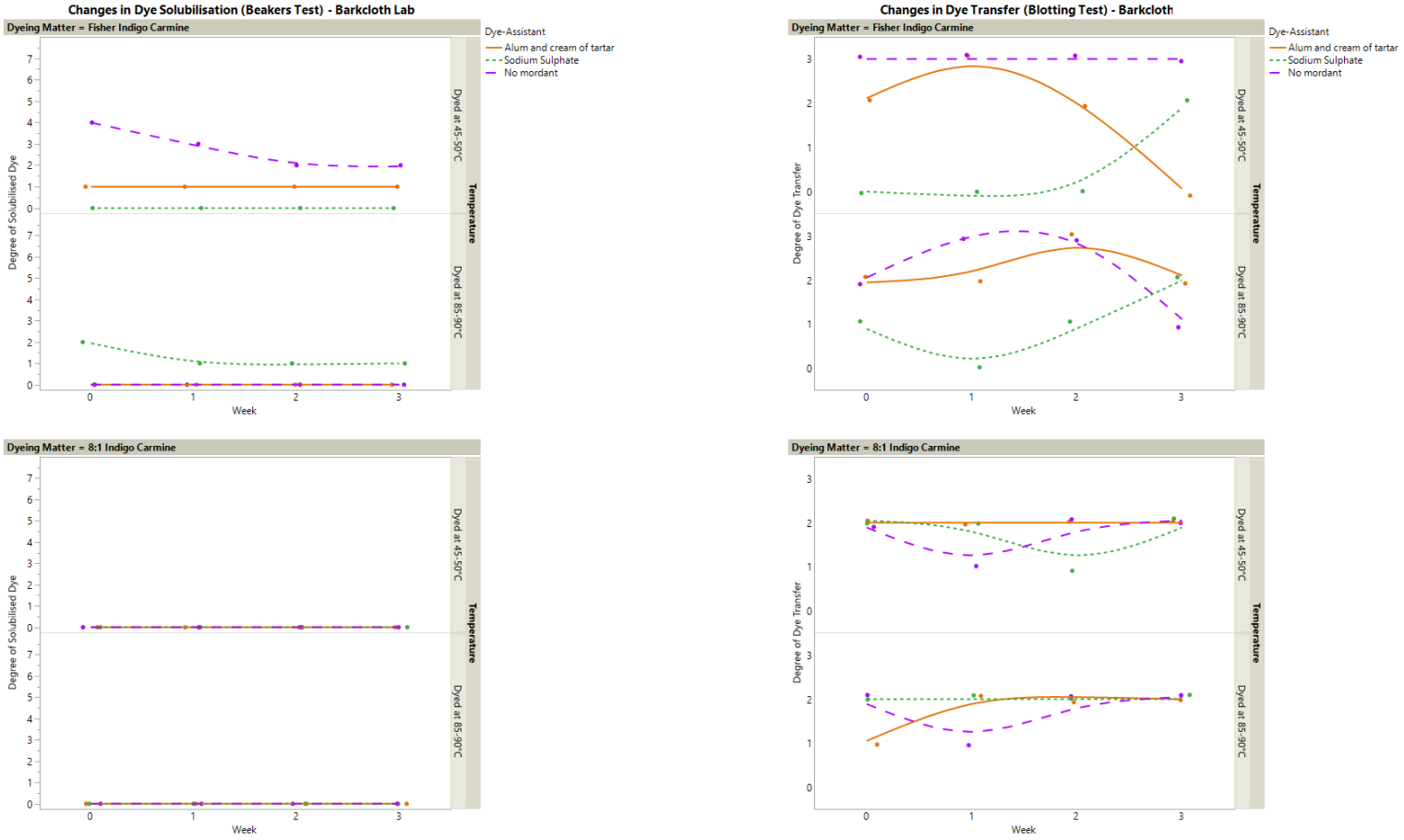
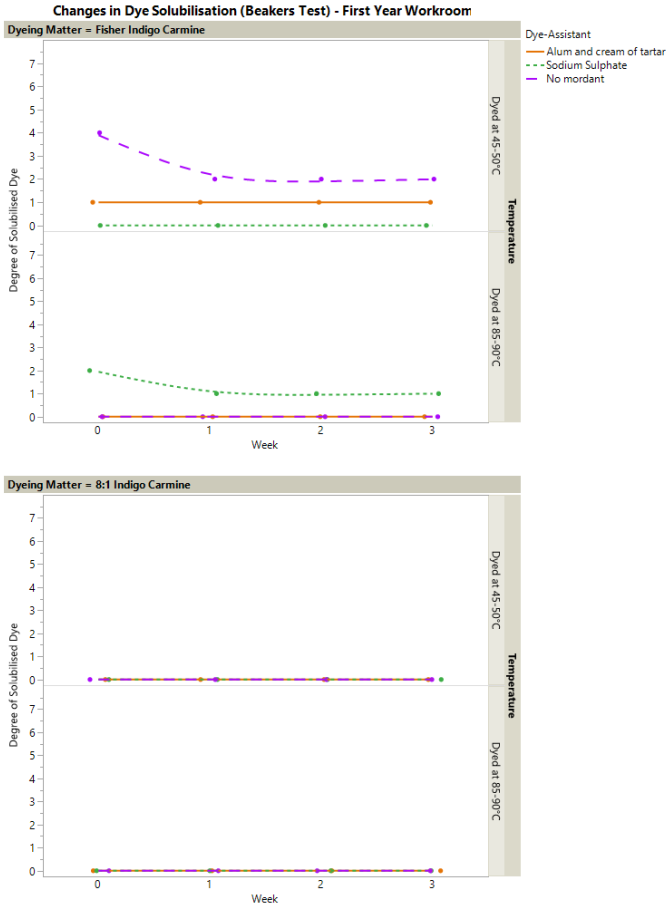


Figure 25 and 26. Ageing of Barkcloth Samples



Figures 27 and 28. Ageing of First-Year Workroom Samples



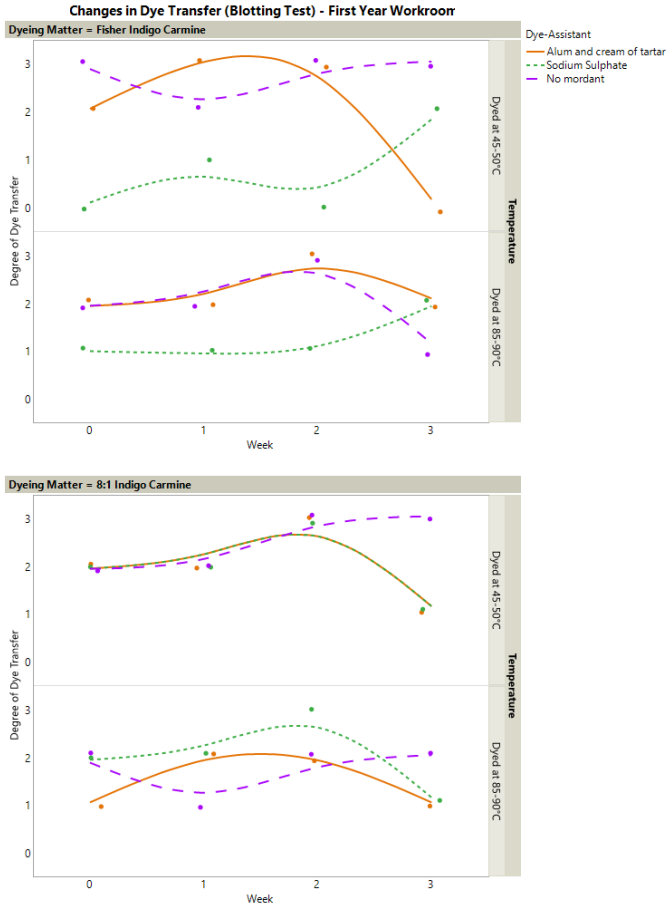
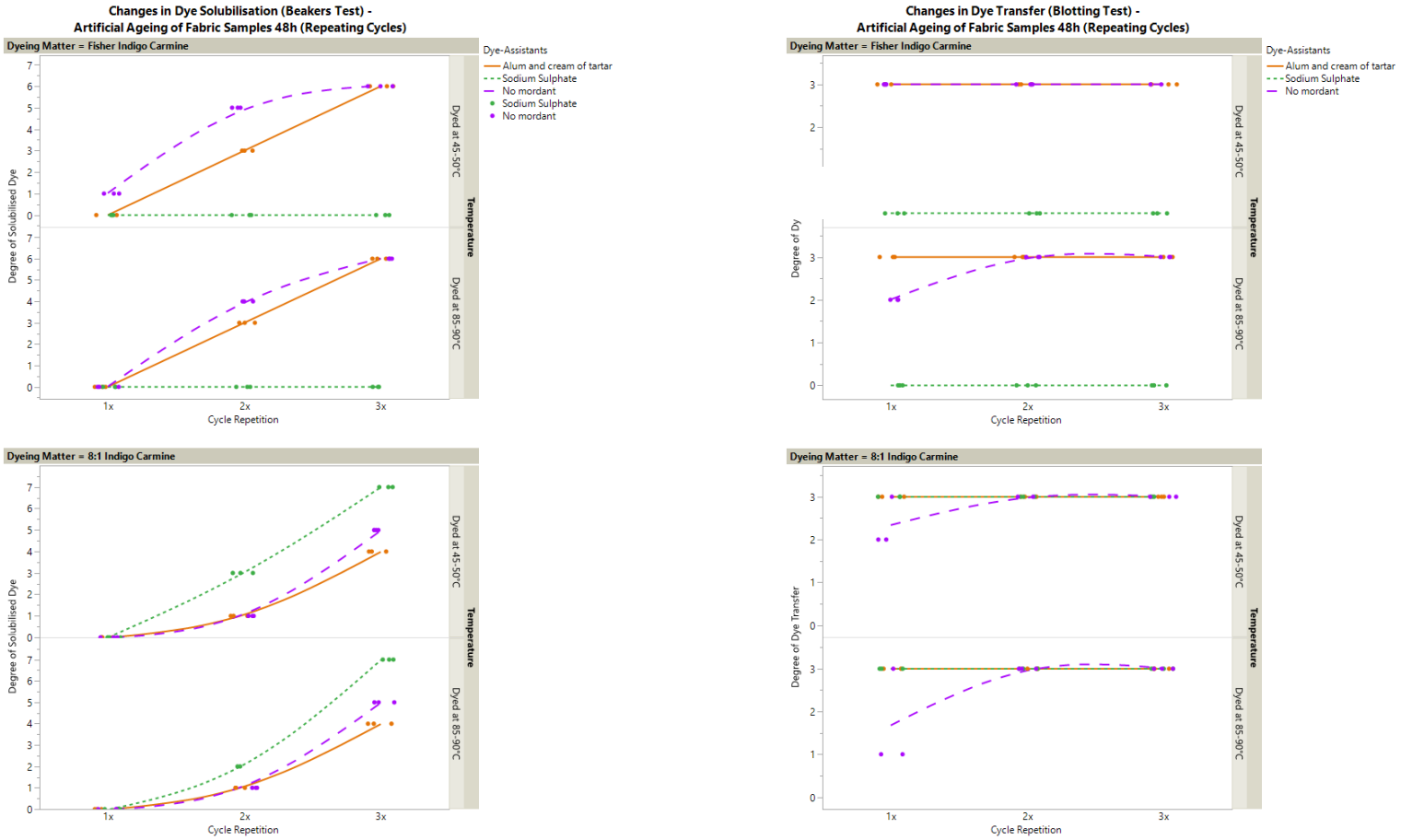
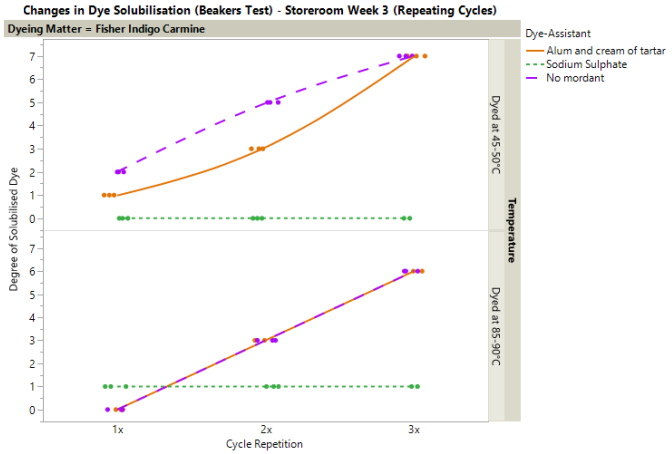
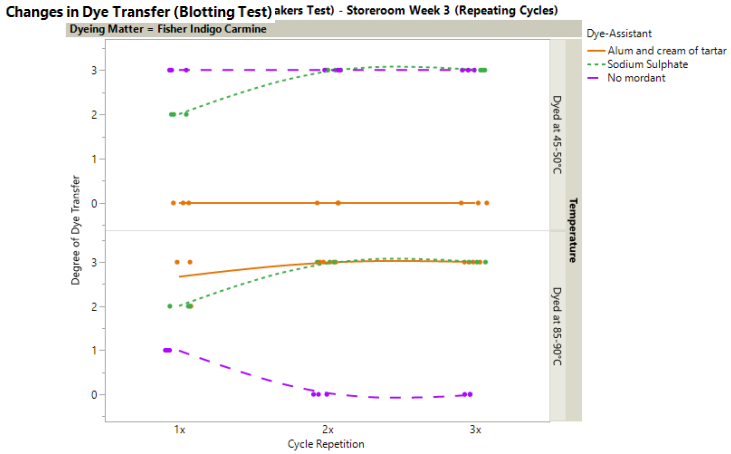


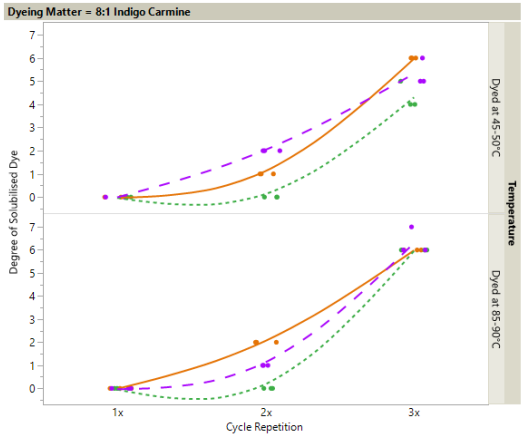
Figure 29 and 30. Repeated cycles of wetting and drying on artificially-aged fabric samples (48 hours)

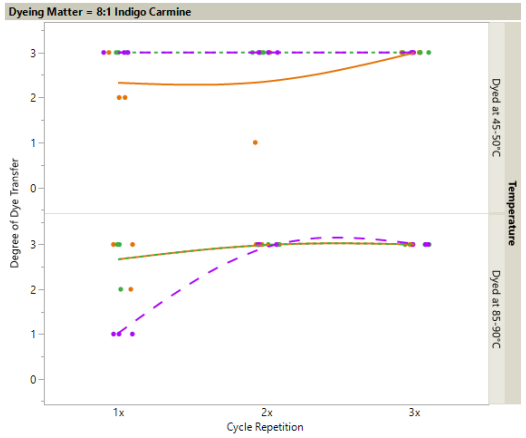


Figures 31 and 32. Repeated cycles of wetting and drying on artificially-aged fabric samples (48 hours)









Appendix 6: Spectrophotometer Graphs for Experiment C

Figure 1. Sampler 1783 – Sampling Point 1 (Wool ground slightly stained).

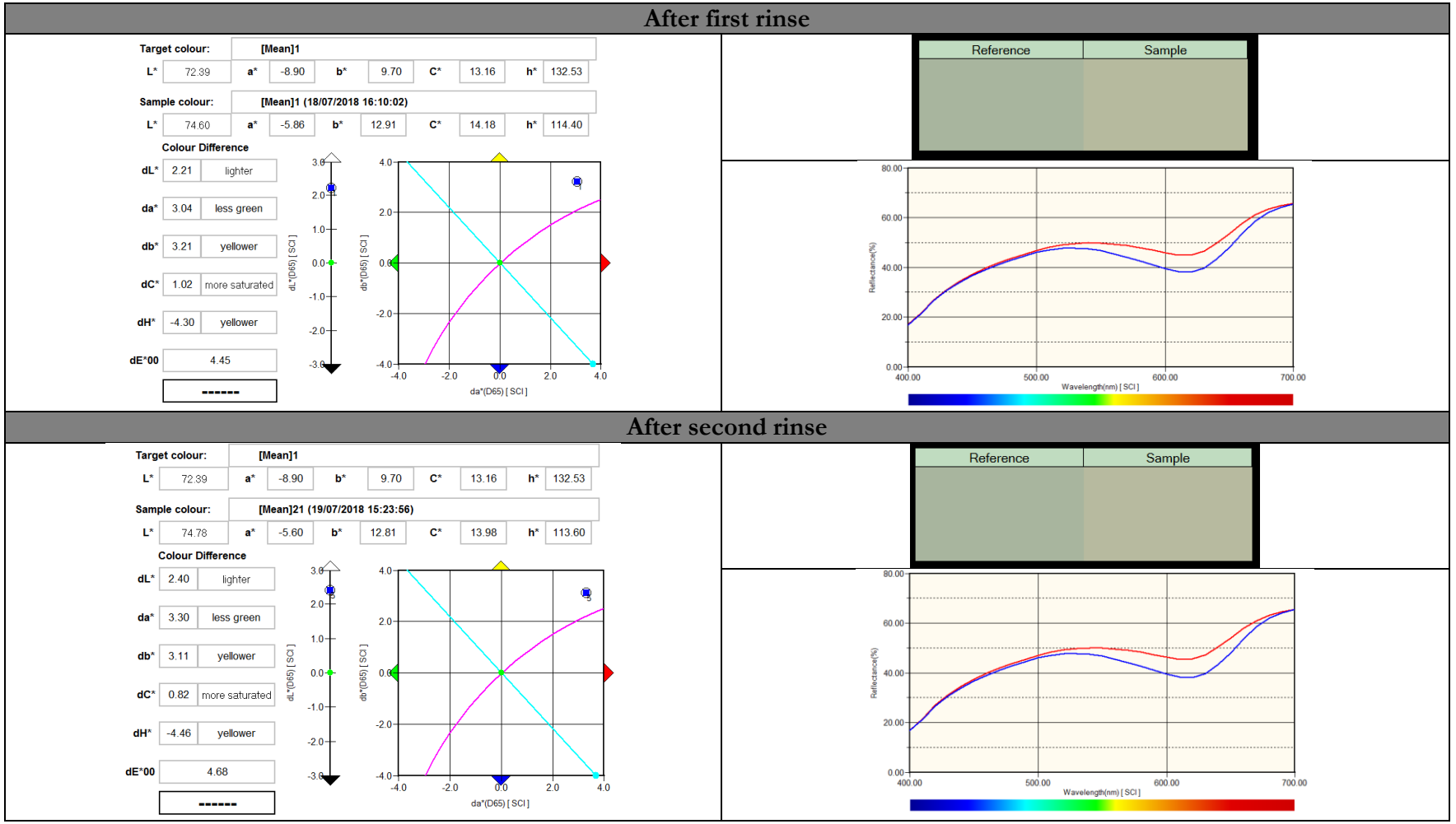


Figure 2. Sampler 1783 – Sampling Point 2 (Light green tree).

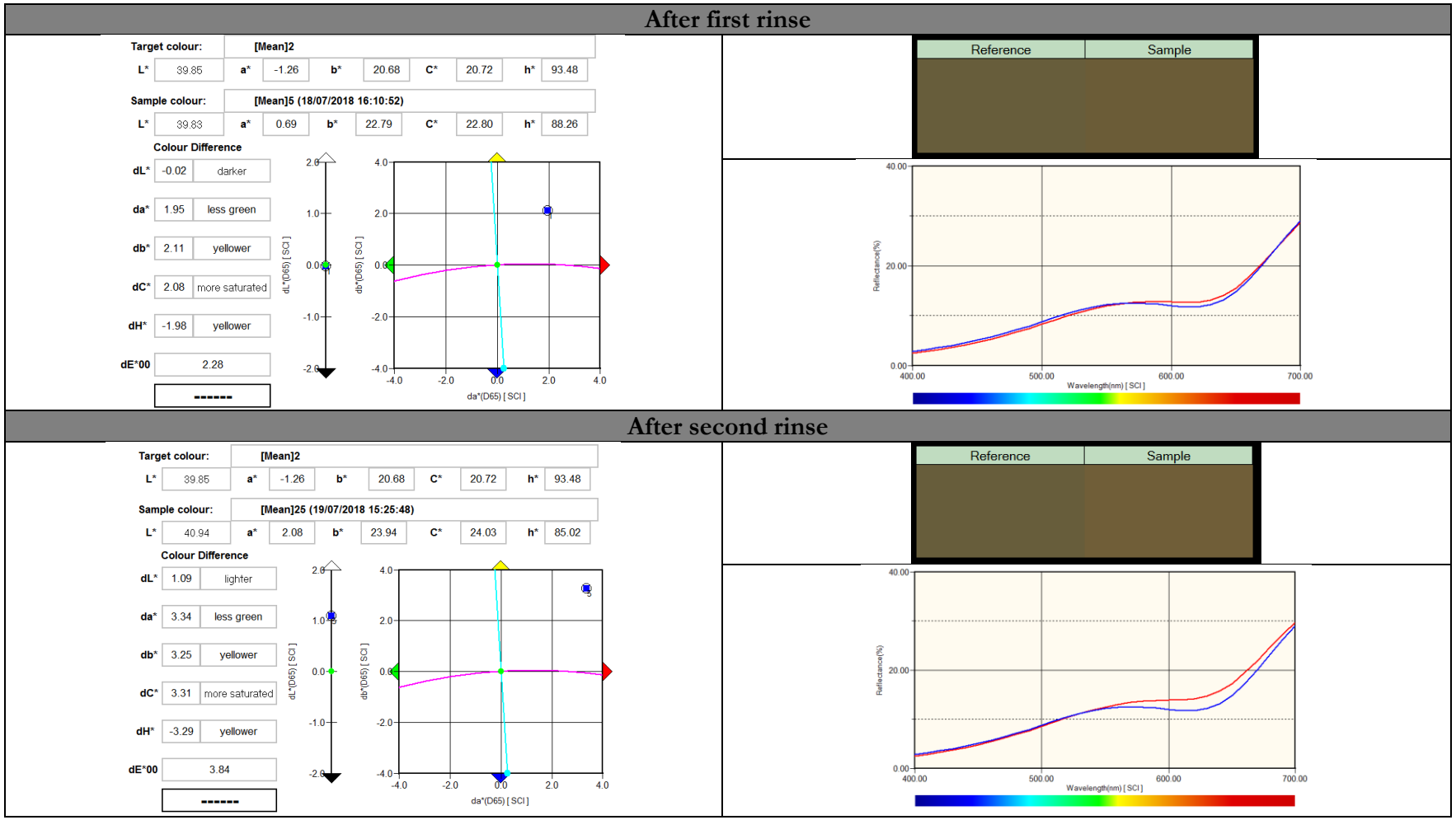


Figure 3. Sampler 1783 – Sampling Point 3 (Bright blue and green base of a tree).

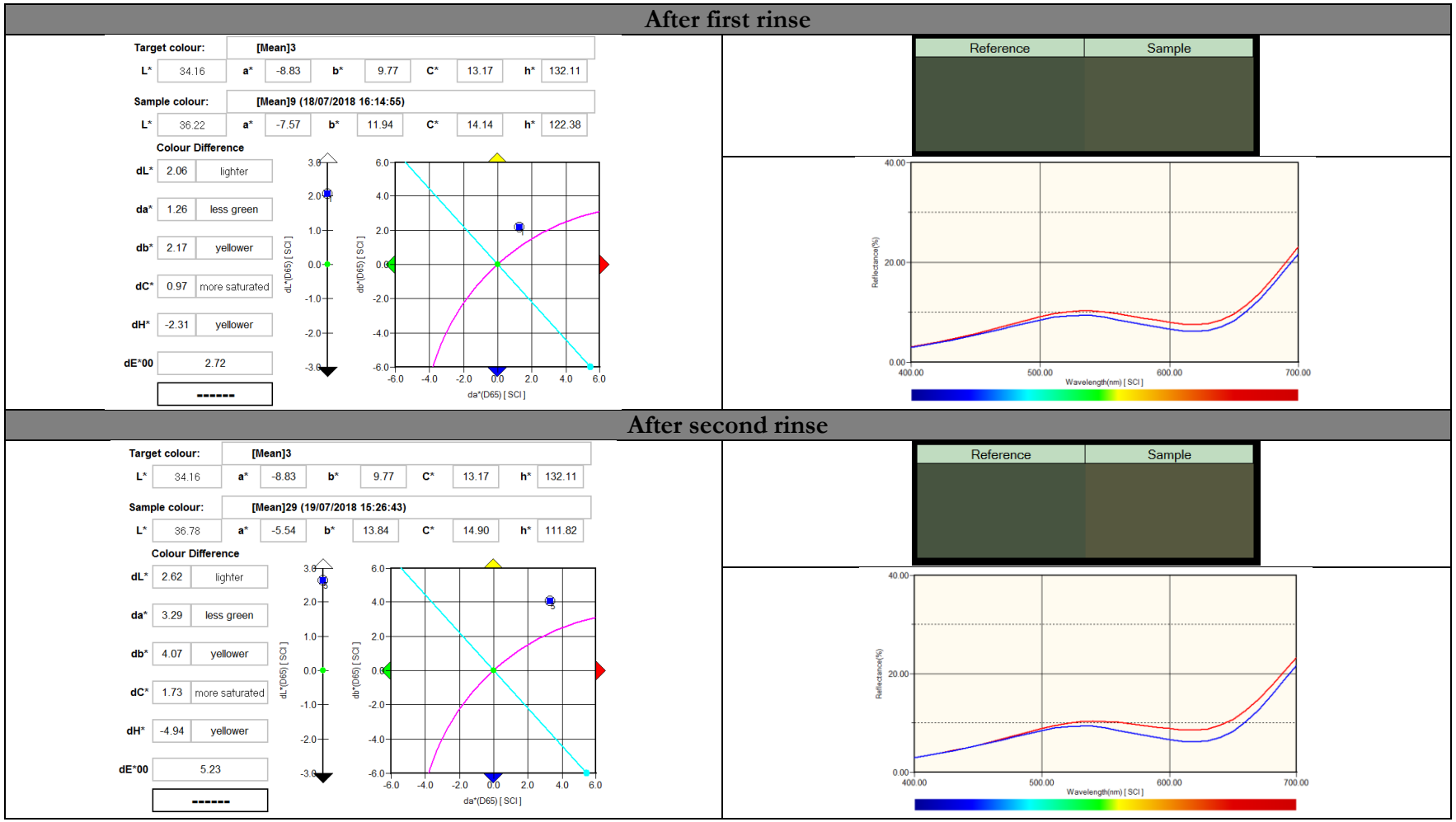


Figure 4. Sampler 1783 – Sampling Point 4 (Wool ground largely stained).

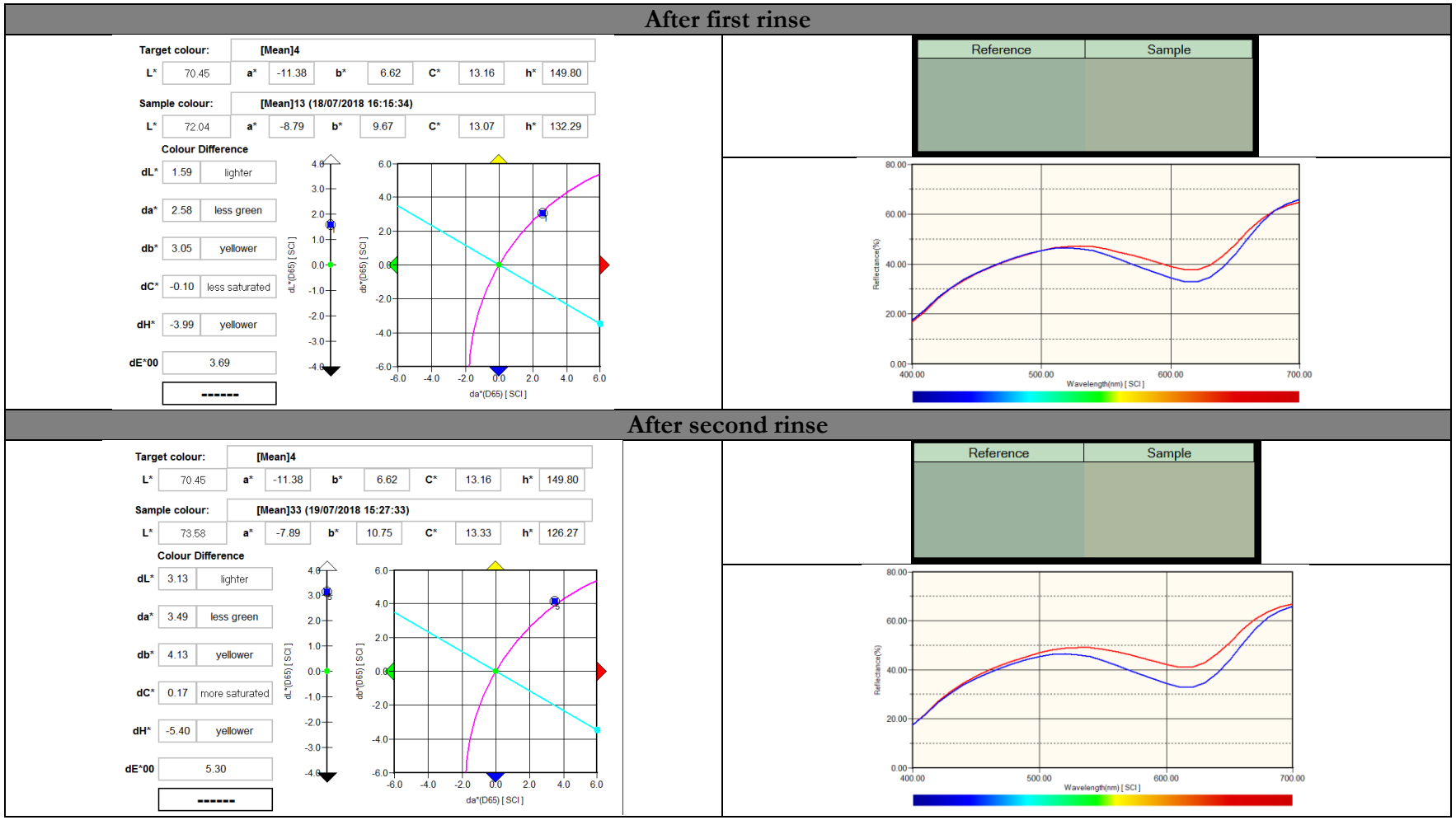


Figure 5. Sampler 1783 – Sampling Point 5 (Bright green bird with orange dots).

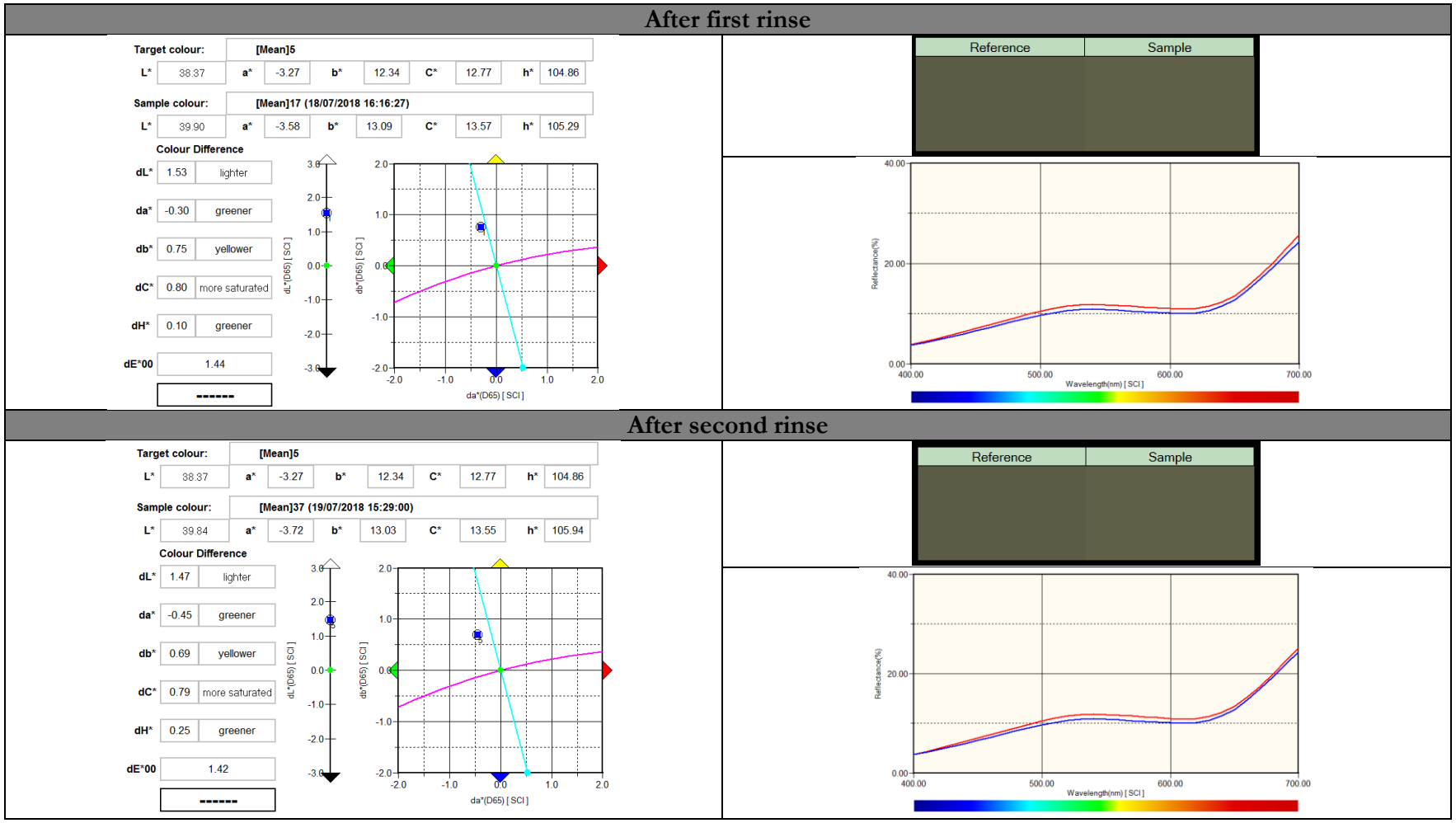


Figure 6. Sampler 1808 – Sampling Point 1 (Section of number 4).

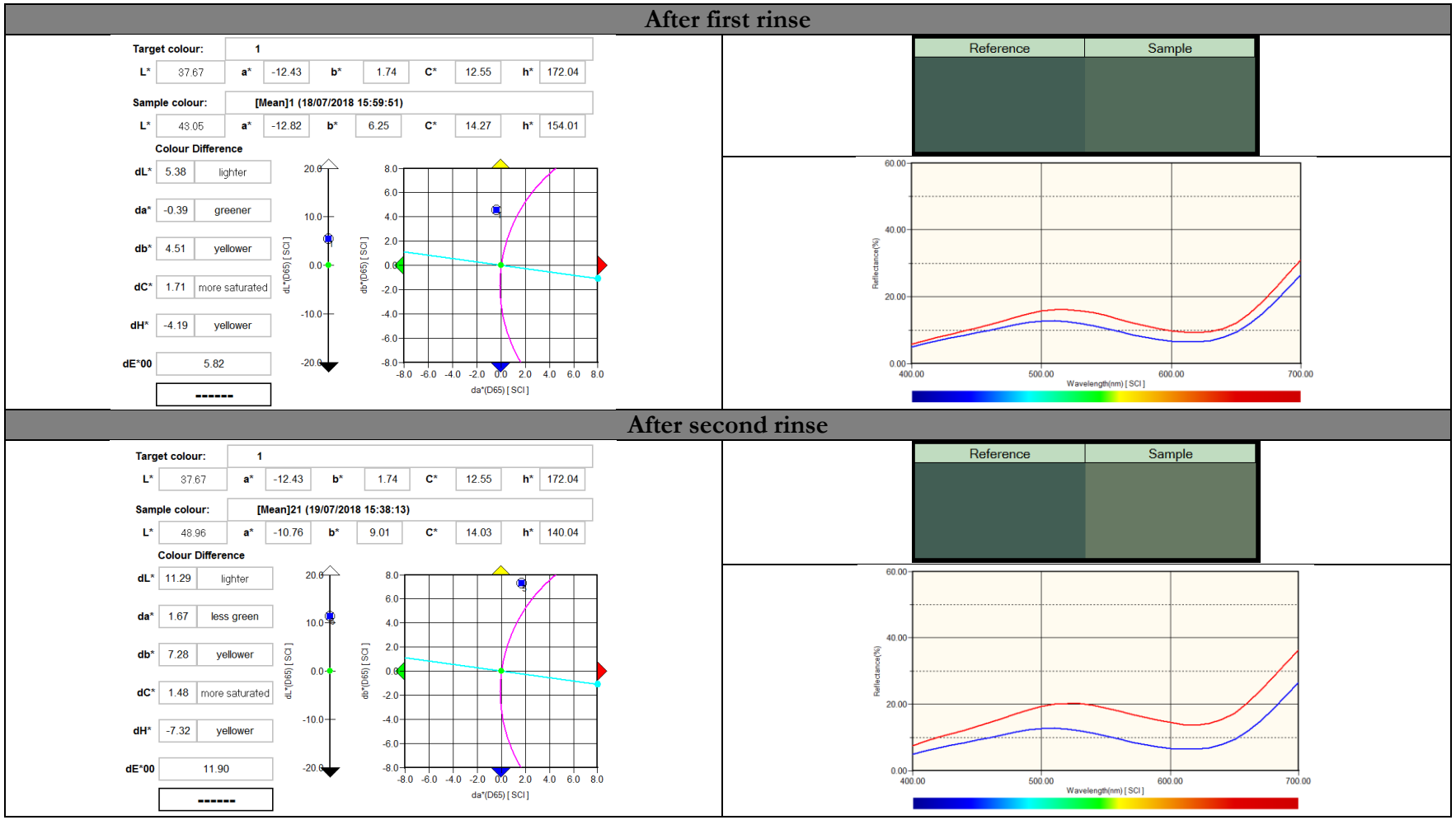


Figure 7. Sampler 1808 – Sampling Point 2 (Stem of bottom flower divider).

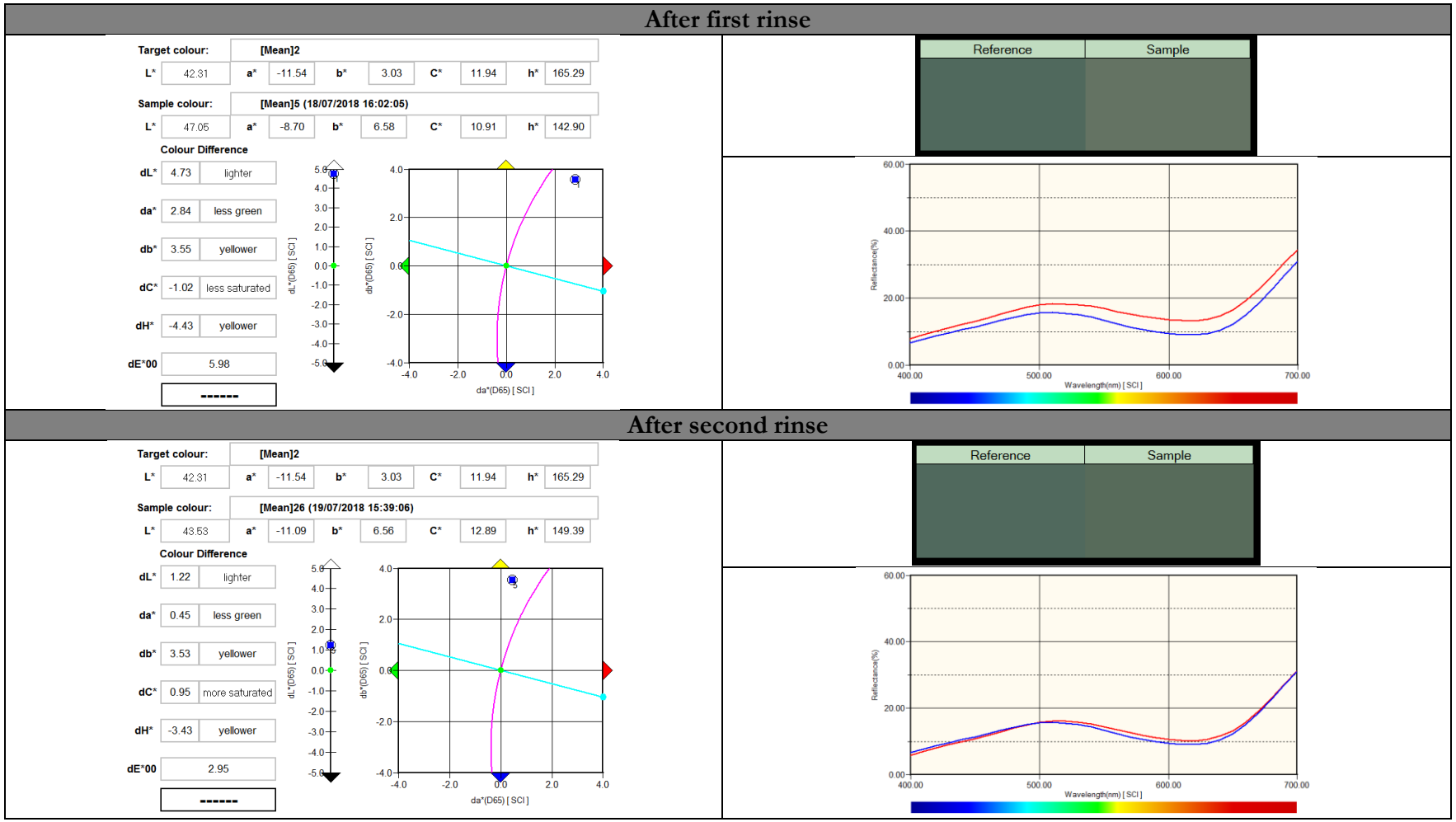


Figure 8. Sampler 1808 – Sampling Point 3 (Last 8 from 1808).

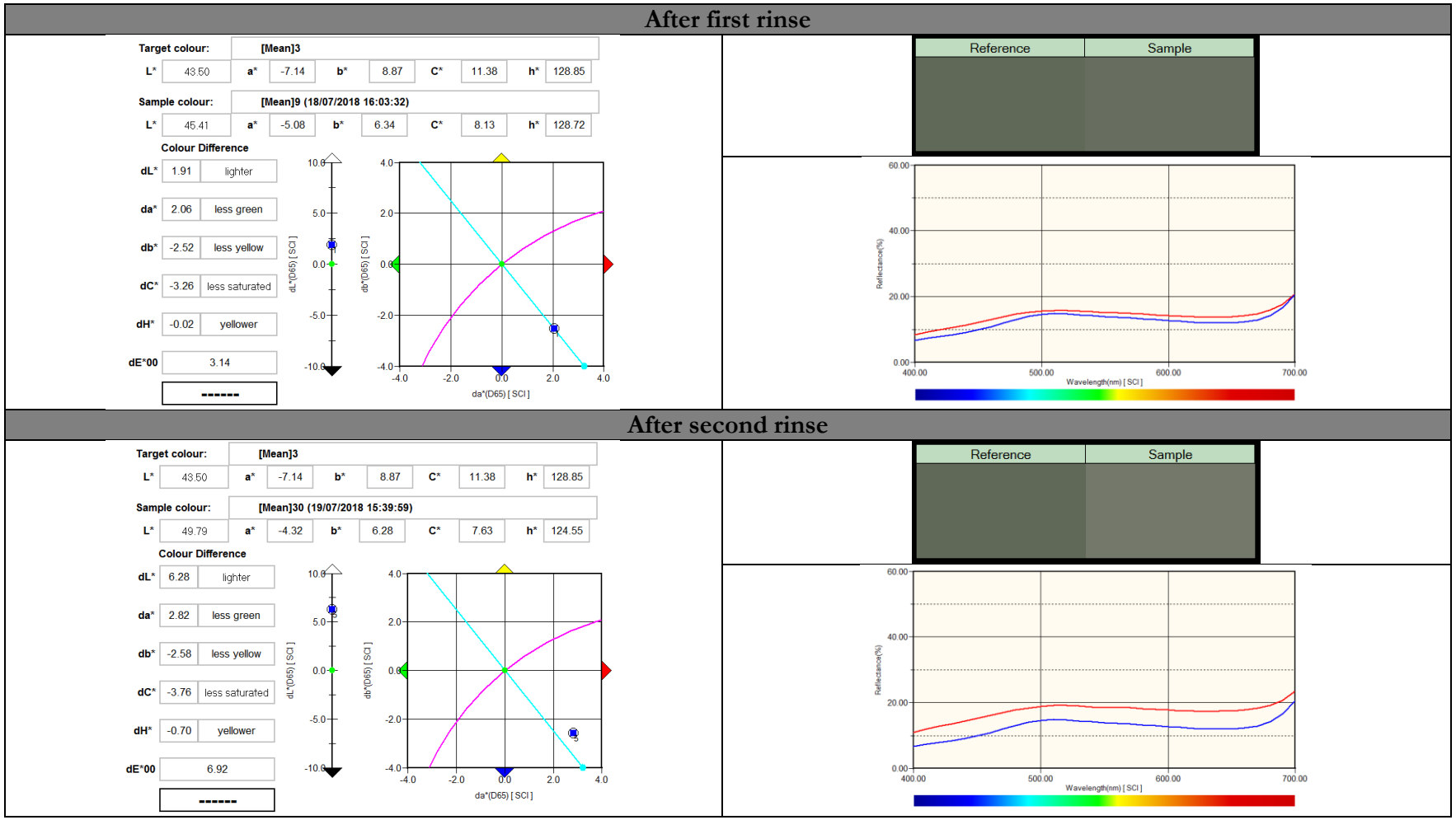


Figure 9. Sampler 1808 – Sampling Point 4 (Section of letter H).

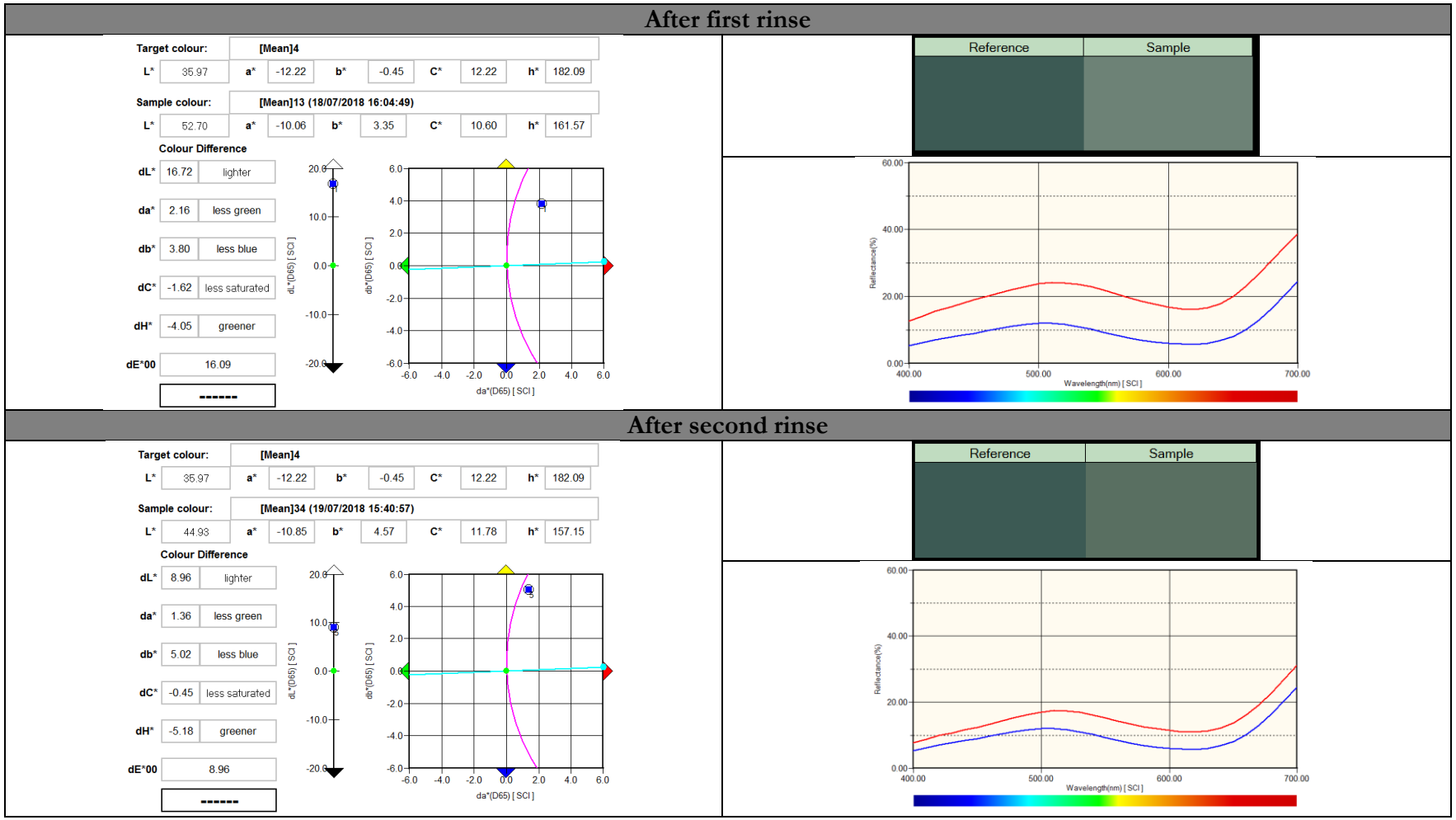
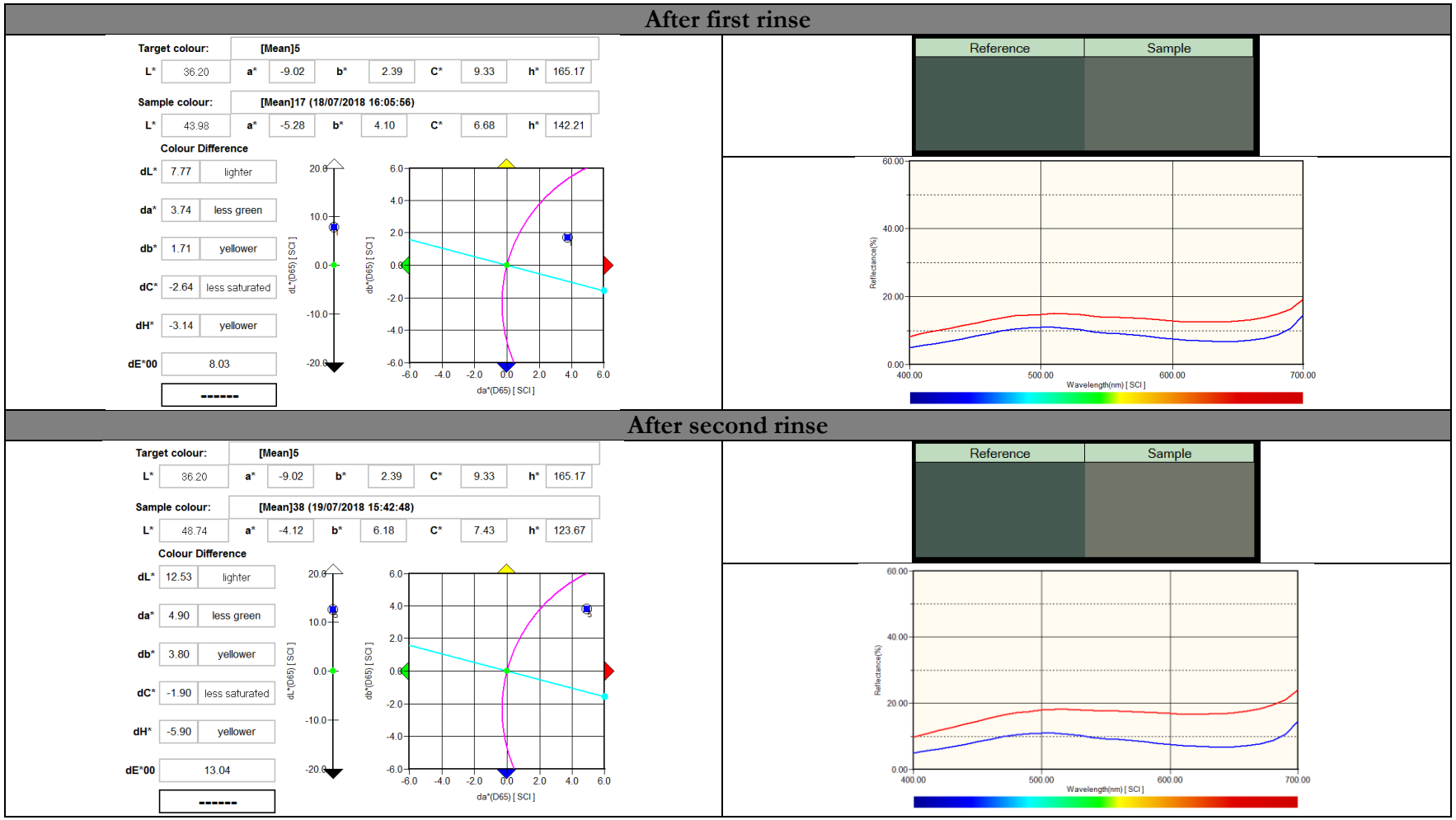


Figure 10. Sampler 1808 – Sampling Point 5 (Dot after letter Z, unstained linen).



Appendix 7: List of Objects Likely Dyed with Indigo Carmine

The objects listed below, along with the samplers used for experiment C, were considered likely to have been dyed with indigo carmine. All objects are part of the Karen Finch Reference Collection, available at the CTCTAH.

Table 1. Objects Likely Dyed with Indigo Carmine		
Name	**Tray**	**Picture**
Turkish towel with metallic threads	Dyes and dyeing	
Cloth with metallic threads	Embroidery (middle tray)	
Sampler by Sarah Ann Dorsey (1846)	Embroidery (top tray)	

Sampler by Ann Slolherd (1791) ➔ Wet cleaned by Maria Kinti (2014)	Embroidery (bottom tray)	
18th century silk fragment (brocade, light blue ground with flowers)	Complex weaves	

Appendix 8: Materials and Supplies

Aluminium potassium sulfate
Fibrecrafts (now George Weil)
Web: http://www.georgeweil.com/Default.aspx
Acquired in November 2010

Acid-Free Blotting Paper 120mm x 860mm 300gsm
Code: 535-1048
Preservation Equipment LTD (PEL)
United Kingdom
Web: https://www.preservationequipment.com/Catalogue/Conservation-Materials/Paper-Board/Blotting-Papers/PEL-Blotting-Paper

Corrugated Plastic Sheet: 6 mm thick / 1200gsm
Polypropylene-polyethylene copolymer
16 Bayton Road, Bayton Road Industrial Estate
Coventry, United Kingdom
Tel: 0800 321 3085
Web: https://www.theplasticshop.co.uk/corrugated-polypropylene-sheet-6mm-thick.html

Pure Cotton Wool Pleated
Code: 591920
Superdrug
United Kingdom
Web: https://www.superdrug.com/Superdrug/Superdrug-Cotton-Wool-Pleated-100g/p/591920

Double-sided Polyster Tape 3M (13mm)
Code: 401-4152
Preservation Equipment LTD (PEL)
United Kingdom
Web: https://www.preservationequipment.com/Catalogue/Conservation-Materials/Labels-Tapes/Double-Sided-Polyester-Tape

Indigo Carmine, ACROS Organics™ (dye content: 80% minimum)
Synonym: Acid Blue 74, C.I. 73015, 5, 5'-Indigodisulfonic acid, disodium salt
Chemical Identifier, Pure Grade
Code: 412300250 Lot: A0317915
CAS Registry Number: 860-22-0
MFCD00005723
Thermo Fisher Scientific
300 Industry Drive, Pittsburgh, PA 15275
Tel: 1-800-766-7000

Web: https://www.fishersci.co.uk/gb/en/home.html
Opened in 2012

Macherey-Nagel pH Indicator Strips 0-14 range
Code: 539-2500
Preservation Equipment Ltd
United Kingdom
Web: https://www.preservationequipment.com/Catalogue/Instruments/pH-Monitors/pH-Indicator-Strips

Natural indigo grains
Order: 36002, genuine pieces from India
Kremer Pigmente
Hauptstr 41-47 – 88317
Archstetten, Germany
Tel: 0049 7565 91120
Web: http://www.kremer-pigmente.com

Polyester roll ® 75 micron (1524mm x 50m)
Code: 415-755. Described as Melinex® sheets.
Preservation Equipment LTD (PEL)
United Kingdom
Web: https://www.preservationequipment.com/Catalogue/Archival-Storage/Polyester-pockets-sleeves-products/Polyester-Rolls

Professional Dressmaker Pins, 25g
Code: 190009
Korbond, Care & Repair
Web: http://sew.korbond.co.uk/product-range/korbond-care-and-repair/pins-buttons-fasteners/professional-dressmaker-pins

Potassium hydrogen tartrate
Fibrecrafts (now George Weil)
Web: http://www.georgeweil.com/Default.aspx
Acquired in November 2010

Ramer® sponge
Boots UK Ltd.
PO Box 5300, Nottingham, NG90 1AA
Web: http://www.boots-uk.com/

Sodium sulfate anhydrous
Code: S/6600/60 Lot: 1664584
Fisher Scientific UK
Bishop Meadow Road, Loughbourough
Leics, LE11 5RG, UK.
Tel: +44(0)1509 231166
Web: https://www.fishersci.co.uk/gb/en/home.html
Acquired in 2016

Sulfuric acid
ACS reagent, 95-98% (now discontinued)
Art: 258105 Lot: SZBD007OV
CAS Registry Number: 7664-93-9
MFCD00064589
Sigma-Aldrich
Web:
https://www.sigmaaldrich.com/catalog/product/sigma/s1526?lang=en&region=GB
Opened in 2013

Surfactant Dehypon® LS54
Art: 50295669 Lot: 0011753156
BASF
GUP/CI - LI554
67117 Limburgerhof, Germany
Tel: +49 621 60-79134
Web: http://www.basf.com/group/corporate/en/

Wool fabric: Wool Delaine bleached
W11E, Batch 015834/103
Whaleys (Bradford) Ltd.
Harris Court, Great Horton, Bradford,
West Yorkshire, BD7 4EQ, England
Web: http://www.whaleys-bradford.ltd.uk/

Wool thread: unscoured wool weft
Westlands
This bag of tapestry warps was brought from the Textile Conservation Centre

Principal Specifications CM-2300d (Konika Minolta Spectrophotometer)

Model	**CM-2300d**
Illumination / Viewing system	d:8° (diffuse illumination, 8-degree viewing), equipped with simultaneous measurement of SCI (di:8° specular component included) / SCE (de:8° specular component excluded) Conforms to CIE No.15,ISO 7724/1,ASTM E1164,DIN 5033 Teil7 and JIS Z8722 Condition C standard.
Sphere Size	Ø 52 mm
Light-receiving element	Silicon photodiode array (dual 40 elements)
Spectral separation device	Diffraction grating
Wavelength range	360 nm to 740 nm
Wavelength pitch	10 nm
Half bandwidth	Approx. 10 nm
Reflectance range	0 to 175%, resolution: 0.01%
Light source	2 pulsed Xenon lamps
Measurement time	Approx. 1.5 seconds
Minimum interval between measurements	3 seconds for SCI/SCE
Battery perfomance	Alkaline manganese:approx. 1000 measurements
Measurement/illumination area	MAV : Ø 8 mm / Ø 11 mm
Repeatability	Spectral Reflectance:Standard deviation within 0.2% (360 to 380 nm within 0.4%) Colorimetric Value : Standard deviation within ΔE*ab 0.08 (Measurement conditions: white calibration plate measured 30 times at 10-second intervals after white calibration was performed)
Inter instrument agreement	withinΔE*ab 0.4 (MAV/SCI) Average for 12BCRA Series II color tiles compared to values measured with master body at 23°C.
Measurement mode	Single measurement/automatic averaging of multiple measurements(auto mode: 3, 5, 8 times/manual mode)
Interface	RS-232C standard

Model	CM-2300d
Observer condition	CIE: 2° and 10° colorimetric standard observer
Illuminant condition	CIE: A, C, D50, D65, F2, F6, F7, F8, F10, F11, F12 (simultaneous evaluation is possible using two light sources)
Display data	Spectral value/graph, colorimetric value, color difference value; PASS/FAIL result, relative gloss value
Color space / colorimetric data	L*a*b*, L*C*h, CMC (1:1), CMC (2:1), CIEDE94, CIEDE00, Yxy, Munsell, XYZ, MI, WI (ASTM E313-73), YI (ASTM D1925)
Data memory	1700 sets of data (SCI/SCE as 1 data)
Tolerance judgment	Tolerance for color difference (1 set of tolerances can be set)
Power source	4 AA-size battery or AC adapter AC-A305
Dimensions (W × H × D)	69 × 96 × 193 mm
Weight	Approx. 670 g (without batteries)
Operating temperature / humidity range (*1)	5 – 40°C, relative humidity 80% or less (at 35°C) with no condensation
Storage temperature/humidity range	0 – 45°C, relative humidity 80% or (at 35°C) with no condensation
Standard accessories	White calibration plate, Target mask Ø 8 mm, RS-232C cable, AC adapter, AA-size battery (×4)
Optional accessories	Hard case, Dust cover set, Dust cover, SpectraMagic™NX (software), Zero calibration box.
Display languages	English, Chinese

Specifications are subject to change without prior notice.[264]

[264] "Portable Spectrophotometer CM-2300d" in *Specifications – Konika Minolta.* Konika Minolta Inc. https://www.konicaminolta.eu/en/measuring-instruments/products/colour-measurement/spectrophotometers-portable/cm-2300d/specifications.html (accessed July 30th, 2018).

Appendix 9: Health and Safety

Reference number:	R50	**Location: (Site/ Building/ Room)**	CTCTAH: Rooms 310 (Chem Lab), 312 (Dye Lab) and 315 (Wet Lab).
Assessment Date:	May 15th, 2018	**Review Date:**	May 25th, 2018
Assessors Name:	Laura G. Garcia Vedrenne	**Job Title:**	2nd Year Student

Task / Activity: Dissertation – Testing Washfastness of Indigo Carmine

Adapt and consistently reproduce historical recipes in the laboratory for dyeing wool threads and fabric with indigo carmine. The activity includes preparation of 8:1 indigo carmine (replica) and Fisher indigo carmine (commercial product), preparation of dye-assistants, dyeing procedures, wet cleaning and drying of samples. Use of heated tools, sharp tools, and controlled quantities of concentrated acid. The examination of samples includes optical microscopy and colourimetry (with a Konica Minolta spectrophotometer). Samples will be artificially aged with the Q-Sun equipment.
The concise experimental method to be used is described below:

Step 1. PREPARATION OF WOOL THREADS AND FABRIC
1. Loosely tie skeins of wool thread. Cut the size of fabric fragments that are required.
2. Pre-wash the wool skeins and fabric fragments in tap water with Dehypon® LS54. Do this for one hour at 40 °C to remove lanolin and oils.
3. Rinse thoroughly.

Step 2. DYE-ASSISTANTS
(A and D) WITH ALUM (aluminium potassium sulfate dodecahydrate) (20%)* AND CREAM OF TARTAR (potassium hydrogen tartrate)** (6.6%)*
1. Dissolve alum and cream of tartar in tap water. If necessary, heat solution to 40 °C to dissolve the salt.
2. Add skeins or fabric fragments of scoured wool to the solution. Heat mordant bath to 90 °C for one hour. Leave in cool mordant bath for at 3 hours.
3. Rinse thoroughly. Store wet inside plastic bag and use within a week.

(B and E) WITH SODIUM SULFATE (15%)*
1. Dissolve anhydrous sodium sulfate in tap water. If necessary, heat solution to 40 °C to dissolve the salt.
2. Add skeins or fabric fragments of scoured wool to the solution. Heat bath to 90 °C for one hour. Leave in cool bath for at 3 hours.
3. Rinse thoroughly. Store wet inside plastic bag and use within a week.

(C and F) NO MORDANTING
1. Set aside skeins or fabric fragments of scoured wool to leave without mordant.

*All percentages refer to o.w.f. (of weight fibre)
** Potassium hydrogen tartrate (mono) was used instead of potassium hydrogen bitartrate as it is readily available at the CTCTAH. The quantities of the

compound were duplicated for this purpose.
Step 3. PREPARING STOCK SOLUTIONS
NOTE: Only one ratio of indigo carmine was used throughout the dissertation, but all extracts (4:1 and 6:1) were tested before choosing (8:1).

(0) PREPARATION OF INDIGO CARMINE (FISHER)***
1. Dissolve pure powdered indigo carmine in tap water for dyeing. Pour the quantity of tap water required in the corresponding beakers. Then, add the required quantity of indigo carmine (Fisher) to each beaker.
→ Quantities were not modified to reach 100% dye strength.

(8) PREPARATION OF INDIGO CARMINE (REPLICA) - IC (8:1)****
1. Ground indigo grains in the dry state to turn them into powder. Use a mask.
2. Put the corresponding quantity of sulfuric acid in a glass beaker. This has to be done in the fume cupboard.
3. Use a hot plate to heat the sulfuric acid at 50-60 °C. Slowly add and mix the powdered indigo, until the required quantity has been added.
4. Stir regularly with a glass rod for 45 minutes. Then let the solution cool, allowing for any vapours.
5. Pour the mixture into the required quantity of deionised water.
6. The dye can be used after two hours and within the next 15 days. Pour the quantity of tap water required in the corresponding beakers. Then, add the required quantity of indigo carmine (8:1) to each beaker.

*** All quantities were calculated by molarity. The calculations are reported in the corresponding appendices of each experiment.
**** Considering that sulfuric acid weights 1.84 g/l

Step 4. DYEING
- ➔ Group W: Dye at 45-50 °C for 2 hours. Maintain liquor ratio if necessary. Measure pH of the solution in each beaker.
- ➔ Group Y: Dye at 85-90 °C for 2 hours. Maintain liquor ratio if necessary. Measure pH of the solution in each beaker.

Thoroughly rinse the fibres to remove excess dye and acid with running water. Monitor pH until it becomes less acidic (around 7) and let the wool skeins and fabric dry. Embroider the dyed threads onto the fabric samples accordingly, creating three replicates of each set for wet-cleaning and drying. Prepare racks for lightfastness experiment and place dyed fabric samples with double-sided tape, creating three replicates for each of the 4 lighting scenarios.

After initial examination, wet clean the embroidered fabric samples with a solution of deionised water and Dehypon® LS54. Dry samples in two different ways: by blotting and by cool air. Monitor and log washfastness throughout the different stages. Keep solutions on the fridge or fumecupboard.

The spectrophotometer should not be pointed at faces during use. The Q-Sun might be hot when placing/removing trays.

What are the hazards? (See list of sample hazards)	**What are the risks?**	**Who might be harmed?** (eg Staff, students, visitors)	**What control measures are required to eliminate or reduce the risks?**	**Risk Evaluation**			**Risk Rating**
				Consequence (1 – 3)	**Likelihood (1 – 3)**	**Overall risk (C x L)**	**Low, Medium or High**
Handling and using chemicals	Damage to health Spills	Staff and students	See CoSHH form number: R50-C1 Use the appropriate PPE when handling dye stuffs and additives. This includes gloves, labcoat, and goggles. Long hair to be tied back. Ensure appropriate dispensers and containers are used; beakers should be Pyrex-grade. Use small quantities when possible. Chemical spills to be cleaned following any COSHH guidance using spill kit in the chemistry lab (Room 310) or wet room (Room 315), or using paper towels as appropriate.	3	1	3	Medium
Handling of concentrated sulfuric acid and exothermic reactions	Damage to health Spills or breakage of items	Staff and students	See CoSHH form number: R50-C1 All of the above. Pyrex-grade beakers that are big enough to allow for any foaming, spluttering, and expansion of the solution, as well as resistant enough to allow heating, should be used throughout the process. Someone must be nearby (in Level 3) throughout the preparation of indigo carmine and while handling concentrated sulfuric acid. Acid should be added to water. This is essential and by no means should this be done in the inverse order.	3	1	3	Medium

Slips, trips, and falls	Physical and chemical harm to health Spillage or breakage of items Damage to historical objects	Staff, students and visitors	Good workroom practice. Mop up any water spills immediately. Ensure that routes are clear and that extension leads are not obstructing pathways.	2	1	2	Low
Broken glassware	Cuts	Staff, students and visitors	Good workroom practice. Report damaged glassware. Dispose of all broken glassware in the appropriate box located in the chemistry lab (Room 310) or wet room (315).	1	1	1	Low
Electrical equipment	Shock, burns	Staff, students, cleaners and visitors	Visually revise equipment. Ensure that all electrical equipment (bain marie, scale, and more) have been PAT tested. Turn off and unplug everything at the end of the day.	1	1	1	Low
Use of hotplates	Physical harm to health: burns	Staff, students, cleaners and visitors	Avoid touching hot surfaces. Use magnetic stirrers and heat resistant gloves to avoid contact with hot liquids or surfaces. Leave a warning label beside the equipment indicating the time when it was last used, while cooling down. Pyrex-grade beakers that are resistant to heat should be used.	2	1	2	Low

Completed by (print name and position, and sign): Laura G. García Vedrenne (student)	**Date:** May 15th, 2018
Approved by (print name and position, and sign): Dr Anita Quye, Senior Lecturer, Conservation Science	**Date:** May 15th, 2018

CoSHH Assessment

Assessment Title: Dyeing wool threads and fabric with indigo carmine

Assessment Reference Number: R-50 / C1 | **Date:** May 15th, 2018

School / Service / Location: Centre for Textile Conservation and Technical Art History, Level 3 Robertson Building – Rooms 310 (Chem Lab) and 315 (Wet Lab).

Safety Coordinator:

Details of Hazardous Substances (Please attach safety datasheets where available)

Name of Substance (Include all substances used or produced)	Quantity kg / g / ml	Physical Form	GHS Hazard Classification (Tick all that apply)								
Sulphuric acid	About 100 ml – concentrated	Liquid					X	X			
Indigo carmine (Fisher)	Less than 20 g – will be diluted	Powder					X				
Indigo carmine (Extract)	Less than 40 ml – will be diluted	Liquid					X				
Indigo grains	Less than 30 g – will be mixed with acid	Powder									
Alum (aluminum potassium sulfate dodecahydrate)	Less than 5 g – will be diluted	Powder									
Cream of tartar (potassium hydrogen tartrate or bitartrate)	Less than 2 g – will be diluted	Powder									
Sodium Sulphate	Less than 3 g – will be diluted	Powder									
Dehypon LS54	Less than 3 ml – will be diluted	Liquid					X				X

Special Hazards (*Separate risk assessment may be required)

Carcinogenic Substance	**Details:** Exposure to strong inorganic mists containing sulphuric acid may cause cancer by inhalation.	**Skin Sensitiser**	**Details:** Sulphuric acid causes severe skin burns and eye damage. IC is an eye and skin irritant. Dehypon LS54 may also cause irritation.	**Respiratory Sensitiser**	**Details:** Do not breathe dusts. Sulphuric acid may cause respiratory irritation. IC may cause tract irritation.
Biological Material*	**Details:**	**Radioactive Substances***	**Details:**	**Explosive Atmosphere***	**Details:**

Further Details / Other Special Hazards: Indigo Carmine and Dehypon LS54 are toxic to aquatic life with long lasting effects. Harmful if swallowed. Sulphuric acid causes burns by all exposure routes and is a highly corrosive material. It is also hazardous for the environment.

Exposure to Hazardous Substances

Substance	Possible Exposure Route (Please tick)					Workplace Exposure Limits	
	Inhalation	Ingestion	Skin	Injection	Other (State)	8h TWA	15min STEL
Indigo carmine (Synthetic)	X	X	X			(Contains no substances with occupational exposure limit values) LD50 Oral - rat - 2,000 mg/kg	
Indigo grains	X	X	X			4 mg/m^3	
Sulphuric acid	X	X	X			0.05 mg/m^3	0.15 mg/m^3

Description of Activity (Continue on a separate sheet if required)

BRIEF: Indigo powder is added (by parts) to sulphuric acid and heated on a hot plate (below 50-60°). The additives and dye solutions are measured out and then gradually heated in a dye bath with bain-marie up to 40-90°C. The diluted solutions required for dyeing will be prepared as required from powder/liquids. (For full description, see Risk Assessment R-50)

Persons at risk: Students, teachers and visitors.

University of Glasgow CoSHH Assessment

Summary of Control Measures				
Assessment of risks and any existing control measures	Handling and use of chemicals will involve only the use of small amounts. Fume cupboard must be used while preparing indigo carmine (extract). Use of PPE (chemical resistant gloves, labcoat, dust mask, tightly fitting goggles) and tied hair. Solutions will be properly labelled. Attention is paid to add acid to water when necessary, instead of vice versa, to avoid violent reactions.			
Risk Rating (Before Control)	**High**	**Medium ✓**	**Low**	
Procedural Controls (e.g. lone working, hygiene)	No food or drink to be consumed in the workrooms or labs. Avoid dust formation. Prevent skin exposure. Sulphuric acid should be kept away from water. If diluting is necessary, always add acid to water.			
Engineering Controls (e.g. fume cupboard)	Sulphuric acid should be used inside the fume cupboard to provide a well ventilated area. Ensure that eyewash stations and safety showers are close to the workstation location.			
PPE Requirements (Please give details) **Face fit testing required	**Dust Mask****	Yes, for preparation of indigo carmine stock solutions	**Gloves**	Yes - nitrile
	Respirator**		**Footwear**	Yes – closed toe shoes
	Eye Protection	Yes – goggles with side shields	**Protective Clothing**	Yes – blue labcoat
	Face Shield	Yes – for large quantities of sulphuric acid	**Other (Specify)**	
Instruction and Training	Reading was done beforehand.			
Supervision Required?	Yes, from teaching staff. A member of staff should always be present in Level 3.			
Other safety precautions: (Including specialist first aid requirements)	First aid. Seek medical advice. Inhalation - Supply fresh air. If indigo carmine or sulphuric acid is breathed in, move person intro fresh air. If not breathing, give artificial respiration. Skin contact - Wash instantly with water and soap and rinse thoroughly. In the case of sulphuric acid, take off contaminated clothing and rinse skin with water-shower. Wash clothing before reuse. Eye contact - Rinse opened eye for at least 15 minutes under running water. Speedy action is critical. No contact lenses should be used. If swallowed - Do not induce vomiting, give water to rinse out mouth if conscious and drink afterwards plenty of water. In the case of indigo carmine, 2-4 cupfuls of milk can also be given to victim, as long as they are not unconscious.			
New Risk Rating	**High**	**Medium**	**Low ✓**	
Supporting Information Checklist (Include details for each where relevant)				
Waste Disposal	Dilute quantities disposed down the sink. Indigo carmine (Fisher) waste and undiluted quantities disposed with non-chlorinated waste. Minimise the generation of waste related to indigo carmine residues.			
Emergency Procedures (including spill / leak control)	Shovel/sweep up into container for removal. Mop up spills. If extinguishing is required, use water spray, alcohol-resistant foam, dry sand, dry chemical or carbon dioxide EXCEPT for sulphuric acid, which should not be treated with water.			
Atmospheric Monitoring	None required			
Health Surveillance	None required			
Supporting Risk Assessments (Please attach where relevant)	**Biological**	**DSEAR**	**Radiation**	
Assessment Details				
Assessed By: Laura G. Garcia Vedrenne			**Date:** May 15th, 2018.	
Approved By: Anita Quye			**Date:** May 15th, 2018.	
Date of next review:				
Continuation sheet number:				

University of Glasgow CoSHH Assessment

CoSHH Assessment Acknowledgement

By signing this document I acknowledge that I have read and understood the attached CoSHH assessment and have familiarised myself with the safety control measures and protective equipment necessary to carry out the task safely. I hereby agree to follow the safe system of work required and implement the required safety procedures fully.

Full Name	Signature	Date Completed
Laura G. Garcia Vedrenne	Laura G. García	May 15th, 2018

Appendix 10: Declaration of Originality Form

University of Glasgow | School of Culture & Creative Arts

Declaration of Originality Form

This form **must** be completed and signed and submitted with all assignments.

Please complete the information below (using BLOCK CAPITALS).

Student Number: 2245984G

Course Name: DISSERTATION - MPHIL IN TEXTILE CONSERVATION

Assignment Number/Name: DISSERTATION

An extract from the University's Statement on Plagiarism is provided overleaf. Please read carefully THEN read and sign the declaration below.

I confirm that this assignment is my own work and that I have:

Read and understood the guidance on plagiarism in the Student Handbook, including the University of Glasgow Statement on Plagiarism	☑
Clearly referenced, in both the text and the bibliography or references, **all sources** used in the work	☑
Fully referenced (including page numbers) and used inverted commas for **all text quoted** from books, journals, web etc. (Please check with the Department which referencing style is to be used)	☑
Provided the sources for all tables, figures, data etc. that are not my own work	☑
Not made use of the work of any other student(s) past or present without acknowledgement. This includes any of my own work, that has been previously, or concurrently, submitted for assessment, either at this or any other educational institution, including school (see University Calendar 31.2)	☑
Not sought or used the services of any professional agencies to produce this work	☑
In addition, I understand that any false claim in respect of this work will result in disciplinary action in accordance with University regulations	☑

DECLARATION:

I am aware of and understand the University's policy on plagiarism and I certify that this assignment is my own work, except where indicated by referencing, and that I have followed the good academic practices noted above

Signed