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John Mercer FRS, FCS, MPhS, JP: The Father of Textile Chemistry

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Abstract

John Mercer (1791-1866) was a pioneering textile and colour chemist with a legacy of achievements. His invention of mercerising that bears his name, treating cellulosics with sodium hydroxide to bring about advantageous changes in fibre and fabric properties, will stand for all time as one of the most important textile chemical treatments ever developed. However, Mercer's contributions to the textiles and coloration industries went far beyond mercerisation. A self-taught chemical experimentalist *par excellence*, his keen observations and interest in calico printing led to many novel developments, such as his work on Chrome Yellow and other 'mineral colours'. Mercer developed new methods for fixing Prussian Blue on calico and wool, developed new mordants for dyeing, improved the extraction of carminic acid from cochineal, and improved the oiling process in Turkey Red dyeing. He saved lives with his research into early antimicrobials, preventing the spread of cholera in Lancashire textile villages. Mercer was an unsung hero of early photography, and developed light-sensitive imaging materials and made some of the earliest recorded monochromatic colour photographs. His forward-looking views on Technical Education, that workers in the industry should be fully instructed in the nature of the various substances used in their arts, later came to fruition in the establishment of the textile departments in Manchester, Leeds and Glasgow. To this day Mercer remains the only textile chemist who has ever been elected as a Fellow of the Royal Society since 1852. He is thus quite rightly considered as the Father of Textile Chemistry.

Keywords: Mercerisation; Cotton dyeing; Calico printing; Textile history; Chemistry history; Early photography.

> Some men are born great, some achieve greatness,
> And some have greatness thrust upon them.
>
> Twelfth Night, William Shakespeare, 1601-1602.

John Mercer (1791-1866)

Introduction

John Mercer was born in Dean, Great Harwood, Lancashire on 21 February 1791 into a yarn spinning cottage industry, a domestic occupation mainly conducted by the women and children of the house to supplement the income of the male agricultural labourers. In the 1790s, agricultural labourers constituted the majority of the population, who were disenfranchised and often lived in destitution and semi-starvation. At this time, Britain was in the throes of change in the textile industry; the invention of the flying shuttle by John Kay in 1733 had led to wider hand loom woven fabrics that required greater spun yarn supplies than could be obtained by the cottage hand spinning methods. The invention of the spinning jenny by James Hargreaves in 1764, the water frame of Richard Arkwright in 1767, and Samuel Crompton's mule spinning process in 1779 had revolutionised and greatly increased yarn production.

Mercer later became a pioneer in the beginning of the chemical and industrial revolution that would convert Britain from an agricultural economy into an industrial economy based upon the factory system which it had invented. By the time of his death in 1866, Britain would be the manufacturing workshop of the world and close to its zenith as the major global industrial power. As we shall see, John Mercer lived through a fascinating period of development in the textile industry, dominated by advances in machine making and the mechanisation of textile processing allied to advances in chemical science and the industrialisation of chemical manufacture.

2016 was the sesquicentenary of the death of John Mercer and this review of his life, work and pioneering contribution to textile dyeing, printing and finishing are intended to celebrate his endeavours and to record the legacy of his coloration and finishing achievements as the father of textile chemistry.

Early Life

John Mercer's ancestors were mostly agriculturists having immigrated to Lancashire from Holland some 700 years earlier [1]. He was born into a world of textile revolution without any of the advantages that many other pioneers of textile coloration inherited. For a start, he did not possess the advantages of William Henry Perkin of a sound education and chemical training, or of living in a large house with servants, and with a father wealthy enough from his building contracting business to be able to bankroll any of his ideas. On the contrary, John's father Robert Mercer had a spinning factory and later became a handloom weaver/manufacturer, a livelihood that brought in subsistence wages, no more, and as the family grew their financial problems multiplied [1,2]. His uncle Richard Mercer was also the owner of a small hand loom factory and another of his father's brothers named Henry had a factory in Lower Town, Great Harwood [1].

The rapid advances that were then being made in the mechanisation of the weaving process were the root cause of the slow demise of handloom weaving, leading to much privation and hardship in rural Lancashire. John Mercer lived his early life in rural Lancashire where farming and textile manufacture eked out a bare subsistence. Mercer’s nephew Edward Andrew Parnell states that, “John always retained an enthusiastic attachment to these (then) picturesque scenes of his childhood; no earthly spot, in his estimation, was more beautiful than Harwood” [2]. This clearly is an over-romanticised view of John's life which in all probability masks his family hardship. John Mercer never went to school because in those days education had to be paid for privately, and so he was sent to work by his mother at the age of nine to wind bobbins [1,2]. John's father Robert died on 7 August 1802 at the age of 46, his death coming only shortly after that of his uncle Roger Clayton; his younger brother Richard died soon after aged ten on 15 February 1803 [1,2]. This triple tragedy within the space of some seven months must have devastated the Mercer family whose main source of income disappeared. It also must have been very traumatic for John Mercer who was only eleven when his father, his uncle and younger brother Richard, to whom he must have been very close, all died leaving his mother to bring up John alone.

When John Mercer was ten he received his first instruction from a pattern designer in calico printing working as a draper in Oakenshaw. John was taught the letters of the alphabet, spelling and arithmetic by a Mr Joseph Blinkinsop; at this time in England a family had to pay for their children to be educated at school, but John's family were poor and Mercer never went to school, and was forever grateful to Blinkinsop for his early education [1,2]. A consequence of the death of his father was that John Mercer's life now became very rootless and peripatetic as he moved from one home to another. Around this time he took up hand loom weaving and became noted throughout Harwood for his facility with mathematical puzzles [1,2]. He continued his mathematical studies in the evenings under the tuition of John Lightfoot, an Exciseman of Great Harwood [2,3]. Interestingly, many years later in 1863, Lightfoot's son, John Emanuel, with whom Mercer studied, perfected the process of producing aniline black (C.I. Pigment Black 1) to such a degree that he was considered the veritable inventor [4].

In 1806, when John Mercer was fifteen, his mother Betty was remarried to Thomas Mercer (who was not a relative of his father); John lived in Lower Town and was a handloom weaver, but soon became a warper, before giving it up to resume handloom weaving [1,2].

Early Experiments in Dyeing

One day in 1807, John Mercer visited his mother who was draped in a beautiful orange-coloured dress and he was astounded to learn that she had dyed it herself [1,2,5]. It was an annatto orange and John in his own words was "all on fire to learn dyeing." After visiting various people to learn dyeing without success, John Mercer went to Hargreaves Wraith, the druggist in Blackburn some five miles away to buy materials for dyeing [1,2]. Knowing not what to buy, he asked the shopman who mentioned that he sold peachwood, Brazilwood, logwood, quercitron, alum, copperas and others to the fancy dyers in Blackburn; John bought three pennyworths of each and returned home full of dyeing and dyeing materials [1]. It was in this way that John Mercer commenced his career in textile coloration, teaching himself textile dyeing entirely empirically by careful experimentation and observation [1,2]. By great industry, perseverance, and close observation he at length acquired a good deal of useful knowledge and ascertained methods of dyeing in most of the colours then required. Just below where John lived was a sizehouse, a large building with boiling warps in it [1]; he got pots, a middle bit of cloth about six inches at every woven piece end, that belonged to the weaver, so that he could get plenty of trial cloths. He had hot water, pots and dyewoods and commenced to experiment with combinations of dyewoods and mordants. He soon had scores of shades hung up on strings. His name began to be known throughout Harwood, but he had no place to start a textile dyeing business [1].

A singer at John's church, Richard Sowerbutts, told John that he had a very convenient building for dyeing and that if John had no objection he would be John's partner [1,2]. Richard lived in the end house which John afterwards purchased. John later built another in the garden where the dyehouse had been. Harwood was full of handloom weavers and so John and Richard could obtain cloth remnants and short pieces of fabric for dyeing [1,2]. Difficulties with a blue vat dyeing were overcome when Richard Sowerbutts picked up a lime stone that had dropped from a farm cart, and on putting it in the vat they discovered they could dye blues for bed gowns *etc*. [1]. The inhabitants of Great Harwood also wore fustian coats and breeches. When these got old and soiled they were brought to be dyed by John Mercer.

In September 1809, Mercer gave up his successful dyeing business after he was invited to enter the colour shop of Oakenshaw Print Works as a colour-mixer and became an apprentice [1-3,5]. John Mercer was now 17½ years of age and had great expectations of his new position. Alas, it proved not to be because the old foreman of the colour shop, John Broadley, was jealous of John's position and put many obstacles in his way [1,2]. John was reduced to fetching cold water from the pump at the back of the stove hole for colour mixing and for washing out china black pots which were difficult to clean with cold water. At other times, John had to dissolve cold bay gums, which involved stirring two to three hundredweight (100-150 kg) of gum in large cow tubs all by himself [1].

The introduction of Napoleon's "Berlin decree" on the continent in 1806, which required the burning of printed calicos and other goods of English manufacture, had by 1810 caused many companies to make a great reduction in the output of printed fabric. John Mercer opted to leave and went to live in Bowley where he again became a handloom weaver and surprised his friends by his ingenious devices for weaving stripes, checks and designs, especially fabrics woven with a blue or red weft [1,2]. John's mother and her second husband Thomas Mercer had come to live with him in Bowley, but both caught a fever and died within days of each other in April 1810.

Introduction to the Chemical World

While living at Hindle Fold in 1813, John had become a Methodist, but preferred the services of the Wesleyans whom he joined and became an active and influential member of the chapel. He went to live with the Wolstenholme family at Cliffe and turned his attention once more to dyeing. The Wolstenholme family had two daughters, and John courted Mary, the younger daughter; they were married on 17 April 1814. Just before his marriage, Mercer had gone to Blackburn to procure his marriage licence and made several purchases of books from a second-hand book stall [1,2,5]. Amongst these purchases was John Mercer's first systematic introduction to chemistry, a book entitled *The Chemical Pocket-book or Memoranda Chemica* [6]. It was this book that John Mercer said "introduced me into a new world. I devoured it" [1], and he read in the book a short account of antimony trisulfide (Sb_2S_3), which stimulated his interest, and he went to Hargreaves Wraith, the druggist at Blackburn, to obtain some and experimented with it with the object of applying it in calico printing [2]; this led to his first major invention for calico printing in 1817 [5]. Prior to this time, no good orange colour was suitable for calico printing other than a mixture of quercitron yellow and madder red, which were difficult to apply. After many experiments, John obtained a solution of antimony (Sb(III)) in sodium sulfide (Na_2S), which gave the bright orange antimony trisulfide when the printed fabric was passed through weak sulfuric acid [2]; this immediately began to attract the notice of the calico printers in the neighbourhood [5]. John Mercer was passing through Oakenshaw when he was met by John Fort, one of the proprietors of Oakenshaw Print Works; he asked Fort if he wanted an experimenter and Fort immediately offered him the post of experimental chemist at their colour shop for five years at a salary, at first, of thirty shillings a week, which John Mercer immediately accepted [1,2]. He was now free to put his inventive genius to the test in order to expand the business of calico printing at Oakenshaw Print works. In this he was successful, inventing new colours and new printing styles. Over the next seven years, his continuing endeavours led to many successful developments and improvements, which resulted in him being admitted into partnership in the firm in 1825 and continued in this capacity until 1848 [5].

John Mercer's Chemical Contributions to Calico Printing

John Mercer applied himself with great energy and skill to the business of calico printing at Oakenshaw Print Works. He discovered that antimony trisulfide could be used to produce much brighter orange coloration than that which had been hitherto possible by means of annatto. Mercer further extended the colour gamut by exposing cloth printed with antimony trisulfide to a weak solution of copper(II) or lead(II) compounds to give various shades of brown and olive [2]; he also produced a white discharge on the antimony orange by printing mercuric chloride ($HgCl_2$) on the colour. These printing styles were much liked, and as a result a large demand existed for them for several years. John Mercer was a chemical experimentalist *par excellence* and his keen observations and interest in calico printing led to many novel developments in colours, long before the research of W H Perkin led to the introduction of synthetic dyestuffs from coal tar derivatives.

In 1823, Fort showed John Mercer a fabric specimen of madder purple ground with a bright yellow discharge. John immediately suspected that the yellow was lead chromate ($PbCrO_4$), also known as Chrome Yellow, and his chemical tests confirmed this to be so [3]; Chrome Yellow (C. I. Pigment Yellow 34) was typically formed by treating a water soluble lead(II) salt with potassium dichromate (K_2CrO_4), precipitating the lead chromate (Equation 1):

$$2Pb(NO_3)_2 + K_2Cr_2O_7 + H_2O \rightarrow 2PbCrO_4 + 2KNO_3 + 2HNO_3 \quad (1)$$

He obtained one hundredweight (51 kg) of impure potassium dichromate from Alexander Kurtz, the first to manufacture the chemical on the large scale. After experimenting, Mercer printed the calico with lead acetate ($Pb(CH_3COO)_2$) or lead nitrate ($Pb(NO_3)_2$), transforming this to lead(II) sulfate by addition of sodium sulfate (Equation 2); on passing the fabric through a solution of potassium dichromate and addition of alkali he obtained an orange colour, resultant from the formation of Chrome Orange (C. I. Pigment Orange 21) [3], a mixture of lead chromate ($PbCrO_4$, Equation 1) and basic lead chromate (Chrome Red, $PbCrO_4.PbO$, Equation 3):

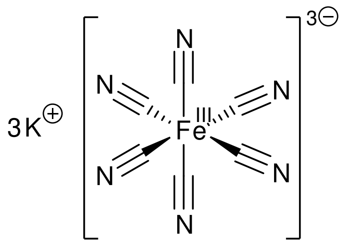
$$Pb(NO_3)_2 + Na_2SO_4 \rightarrow PbSO_4 + Na_2NO_3 \quad (2)$$

$$2PbCrO_4 + 2NaOH \rightarrow \mathbf{PbCrO_4.PbO} + Na_2CrO_4 + H_2O \quad (3)$$

Printing styles containing Chrome Yellow and Chrome Orange on various coloured grounds were created, as well as cloth grounds in the same colours with designs in various colours for foreign markets. Such 'mineral colours' are formed *in situ* in cotton when water soluble metal salts are applied and subsequently converted to insoluble metal oxides, which occupy free volume in the fibre [7]. Alexander Kurtz sent two men from London to Oakenshaw to obtain information on this new application, which Mr Fort freely gave them. It was then readily adopted by the calico printers to whom the method was communicated.

It was also in 1823 that Mercer was attracted to the dark brown glaze on coarse earthenware pots made in his neighbourhood. Finding that this was produced using a manganese-based mineral, he set to work to produce a similar colour on calico. This led to the introduction of manganese bronze (a mixture of manganese oxides, the hue of which depends upon the degree of oxidation) [5]. This dyestuff became popular and went in and out of fashion almost every ten years. He discharged the bronze ground using tartaric acid or a tin salt, which led to various patterns of red, orange, yellow, blue, green and black using natural dyestuffs.

In the same year, Mercer heated indigo in caustic alkaline liquor in contact with metallic tin generating a solution of white indigo which could be used in a variety of printing applications. Mercer also used a mixture of potassium chromate with sulfuric acid to generate chromic acid. Cloth dyed with indigo was padded with potassium chromate solution and allowed to dry in the shade followed by printing with a discharge containing sulfuric and oxalic acids, which discharged the blue indigo to white. Another of his ingenious inventions in indigo printing involved discharging indigo-blue by means of alkali and red prussiate of potash (potassium ferricyanide; **1**) [5]. Mercer also developed a new method for fixing Prussian Blue (**iron(III) hexacyanoferrate(II); 2**) to which various alkaline solutions of arsenic and antimony were applied to obtain various shades of green.



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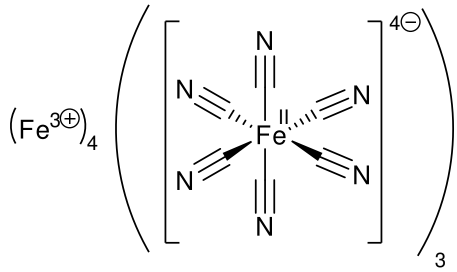

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Catechu, an extract obtained from several species of acacia trees (especially *Acacia catechu*) that is rich in vegetable tannins, was introduced into calico printing in Lancashire in 1829. Around 1830, Mercer developed an excellent oxidative method of fixing the colouring principle of catechu, by addition of manganese acetate ($Mn(CH_3COO)_2$), followed by steaming the cloth, which gave a very rich and strong colour termed Russell Brown, after Lord John Russell, a popular statesman of the day.

Potassium thiocyanate (KSCN) mixed with sulfuric acid was used by Mercer for discharging manganese bronze without injuring blue or interfering with the subsequent dyeing with madder or logwood. In 1835 he found that a mixture of potassium ferricyanide (**1**) and potassium hydroxide could yield a moderate oxidation system capable of oxidising and bleaching indigo, cochineal and safflower. It also altered the colour of Brazilwood and logwood to yellow, but did not affect madder or Persian-berry yellow. Thus, it was used to discharge indigo when madder was also present on the cloth, as the madder was unaffected by the discharging treatment. Mercer also found that some aluminium lakes could be dissolved by ammonium oxalate ($[NH_4^+]_2[COO]_2^{2-}$); these were used to prepare blended fabrics of cotton and wool to accept dyes with equal effectiveness.

One of John Mercer's major improvements was the replacement of the dunging operation – the use of cow dung dissolved in hot water for the removal of superfluous uncombined mordant from the first stage of the dyeing process as well as the remaining thickening agent. After fabric ageing, Mercer devised infinitely superior substitutes based on sodium phosphate (Na_3PO_4), and the more effective sodium arsenate (Na_3AsO_4). An American inventor, J D Prince, had the original idea to use a soluble phosphate as a substitute for cow dung and visited Mercer to confer with him at Oakenshaw in 1839, which led to Mercer's first patent jointly with Prince (British Patent 5,684).

Oakenshaw Print Works expanded its printing operations in 1839 by undertaking the printing of delaine (high-grade fine woollen or worsted fabric), in which the printing of Prussian Blue (**2**) onto wool fibres was a serious problem. Mercer came to the conclusion that this was due to the presence of some deoxidising power arising from some deoxidising material in the wool fibres. He discovered that by passing the fabric through a weak solution of chlorine, generated from bleaching liquor and hydrochloric acid, that wool was rendered capable of combining with Prussian Blue, tin oxides and colouring matters with equal affinity for cotton giving “full, rich, saturated colours”. This was adopted in preference to chromic acid, which give the same effect as chlorine, but left a slight stain that on printed wool delaine was generally objectionable. Had John Mercer patented this process he would undoubtedly have obtained a large sum from granting licences to use the method, however, he communicated this process to a few friends in the trade and as a result it gradually was practised by calico printers in England, Scotland and France. In Leeds, the woollen dyers adopted the chromic acid method as the slight tint derived from the chromate was not a problem. This discovery of Mercer's is described as the most important made in dyeing and printing woollen goods [2], and one hundred and fifty years after John Mercer’s death, his method of chlorine pre-treatment for printing wool goods is still in commercial operation.

Around 1824/25, Mercer improved the extraction of cochineal; prior to this, the digestion of cochineal in hot water left around one third of the valuable colouring matter (carminic acid, typically 17-24% of dried insects’ weight) undissolved in the dregs, which was an important financial matter. Mercer discovered that the addition of a neutral alkaline oxalate to the water enabled the whole of the colouring matter to be dissolved. This method was communicated by Fort to a few calico printing friends who then used it regularly, although it was not generally known to others in the trade for many years. Mercer also used a solution of a neutral alkaline oxalate for dissolving the colouring matter of lac. About 20 years after Mercer’s discovery, a French chemist came to England to induce calico printers to take up his new method for exhausting cochineal, but on visiting Oakenshaw Print Works he discovered that Mercer's method was similar in principle, simpler, and as effective.

John Mercer's discoveries in the field of calico printing were probably the basis of the commercial success of the company, which had a large warehouse in Manchester. In 1825, some seven years after John Mercer had entered Oakenshaw Print Works, he was offered and accepted a partnership in the firm, and remained with the company until its dissolution in 1848, which came about as a result of the downward trend in prices for printed calico. Fort Brothers had always provided high quality prints and first-class goods, and in the face of close competition it was decided to close the company; when the full value of the stock was realised it showed that the profits of the previous year had been very good, resulting in John Mercer becoming rich and acquiring what Parnell termed “a competence” [2].

John Mercer had also directed his attention to the preparatory oiling process, an essential element in Turkey Red dyeing, in order to speed up the process. Prior to the patent of John Mercer and John Greenwood in 1846, the cloth was impregnated with an alkaline emulsion of a vegetable oil some five to eight times. This included long exposure times in air to oxidise the oil between each oiling application. John Mercer shortened this process by treating the oil with oxidising agents such as hypochlorite of lime, potassium dichromate, potassium chlorate or potassium nitrate/sulfuric acid.

Oxidation or chlorination of the oil then enabled the omission of the long ageing time in the hanging room. Another patent was later granted to Mercer and Greenwood in 1852 for improving the oiling process using olive oil in Turkey Red dyeing.

Work on mildew and preventing cholera

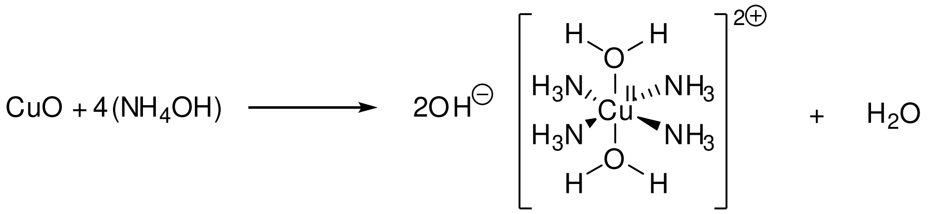
In 1843, Mercer found that mildew had grown in some of Oakenshaw Print Works printed calico sent to South America, which had caused the discharge of the colours during the voyage. After some experimentation, he found that starch paste that contained the most gluten caused mould to appear within four days, mould appearing in the other samples in the reverse order of their proportion of gluten. Mercer solved the problem by using the best starch and adding a little potassium dichromate to prevent mould growth in printed calicos that were exported by ship on long voyages. Mercer made other experiments that showed that pure tartaric acid in distilled water, after being boiled and allowed to stand in a vessel not absolutely air-tight, eventually developed mould on the surface. In experiments on starch, the mould was sometimes green, or yellow, or red, which suggested to Mercer that there was a variety in the germs derived from the air.

In 1847, there was an outbreak of cholera in Sykeside, a small village some two and a half miles from Great Harwood. Fort Brothers employed some 700-800 people and the nearest doctor lived some 3-4 miles from Great Harwood. Mercer had read all the medical journals about cholera and prepared a large quantity of magnetic oxide of iron (magnetite; Fe_3O_4) as well as a large supply of chloride of lime (calcium hypochlorite; $Ca(ClO)_2$). Mercer had previously prepared magnetic oxide of iron and it had been used to decontaminate drinking water with great success, and whenever an epidemic had arrived in the neighbourhood Mercer had sprinkled chloride of lime on the floor of Fort Brothers' print shop for sterilisation. The cholera epidemic at Sykeside was quelled by John Mercer who ensured that the corpses, clothing and every house in Sykeside was dusted with chloride of lime. As a result, apart from four deaths, Mercer's prompt action prevented any more cases of cholera arising in the village. Today, calcium hypochlorite is commonly used to sanitize public swimming pools and disinfect drinking water.

Cotton solubilisation and Mercerisation

Cellulose primary structure is simple: a long chain of glucose units attached together by $\beta(1\rightarrow4)$ linkages. The supramolecular structure of cellulosic fibers can be described by a two-phase model with regions of high orientation (crystalline) and low orientation (amorphous) [8-10]. It is the ability of these chains to hydrogen-bond together into fibres (microfibrils) that gives cellulose its unique properties of mechanical strength and chemical stability. Molecules of native cellulose (cellulose I) fibres are highly oriented, arranged parallel to one another, but their degree of orientation parallel to the fibre axis is reduced since they tend to form a spiral around the fibre. Cellulose microfibrils contain two crystalline forms, cellulose Iα and Iβ, in which the chains are packed slightly differently. The chain conformation in both forms is similar, a flat ribbon with a 180° twist between successive glucosyl residues. This chain conformation is stabilised by two hydrogen bonds parallel to the glycosidic linkage, one from C3 hydroxyl group to the ring oxygen of the preceding glucose unit and the other from the C2 –OH to the C6 –OH of the next glucose unit (Figure 1) [11].

Hydrogen bonding in cellulose means that it is generally insoluble in most solvents. However, John Mercer appears to have been the first person to have observed the solubility of cotton in an ammonium hydroxide solution of cupric oxide, which forms the chemical complex tetraamminediaquacopper dihydroxide (**3**) (Equation 4).



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(4)

The solubility of cellulose in tetraamminediaquacopper dihydroxide solution has been attributed to the Swiss chemist Mathias Edward Schweizer in 1857 [12], and this solution is referred to as Schweizer's reagent, however, John Mercer is believed to have discovered the effect of tetraamminediaquacopper dihydroxide solution on cellulose some years before. In more recent times, the mechanism of solubilisation has been demonstrated to occur when $[Cu(NH_3)_2]^{2+}$ moieties coordinatively bind to the C2 and C3 hydroxyl groups in cellulose Iβ, and the hydrogen bond between the C6 primary OH group in the position and the ring oxygen of the next anhydroglucose unit is interrupted, but the other hydrogen bond is enhanced (Figure 1) [13-15]. The dissolution power is restricted to cellulose Iβ with degrees of polymerization < 5000 [16].

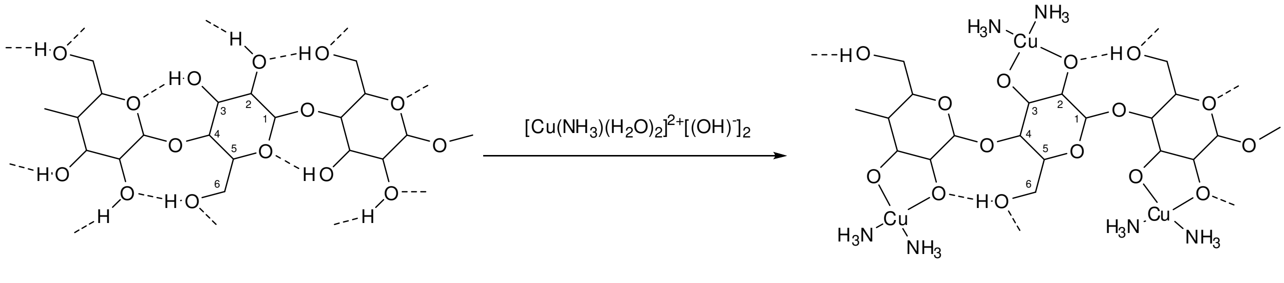

Figure 1. Solubilisation of cellulose Iβ by tetraamminediaquacopper dihydroxide solution.

In 1843, John Mercer became interested in the constitution of solutions of substances capable of forming chemical combinations with water and the existence of definite hydrates in solution. He was also interested in the differences exhibited by solutions of different strengths in viscosity and mobility. He discussed this with his friends in their monthly meetings in Whalley and also suggested transmitting such solutions through a capillary tube in the expectation of finding a variation in mobility associated with different degrees of chemical hydration. Mercer decided to try to attempt a partial separation of different hydrates by slow fractional filtration which led him to investigate the effect of filtering a solution of caustic soda through cotton. He made a filter composed of six folds of bleached strong fine cotton cambric which had been compacted three times through a calender. He then poured a solution of caustic soda of 60º Twaddell (6.7 M NaOH) through the cotton filter. Filtration was very slow and the liquor which passed through was of 53º Twaddell (5.9 M NaOH). However, the changes in the cotton filter fabric were profound; Mercer observed that the fabric had become semi-transparent, had contracted both in length and breadth and had thickened (or "fulled" as Mercer termed it). After further experiments, Mercer subjected some cotton fents to the action of caustic soda and showed his "fulled" cotton to his partners and some friends as a curiosity in 1844.

The amount of scientific investigation of mercerising has been enormous. A 1966 review by Warwicker of the literature on the effect of caustic soda and other swelling agents on the fine structure of cotton cited 1484 references [17]. Alkali has a significant effect on morphological, molecular, and supramolecular properties of cellulose. In its interaction with native cellulose, aqueous sodium hydroxide above a certain concentration is able to penetrate the cellulose Iβ crystalline lattice to produce a series of well-defined crystalline complexes holding a number of sodium ions and water molecules within the lattice [18].Okano & Sarko [19] presented that a total of five unique alkali-celluloses (Na-celluloses) could be generated reproducibly, depending on the alkali concentration used and temperature of treatment, which are named Na-celluloses I, IIA, IIB, III, and IV (Figure 2). In mercerisation, cellulose Iβ adopts a modified crystal structure, irreversibly forming cellulose II, which is the stable fibre form after drying [20]; two hypotheses have been proposed for the transformation mechanism of cellulose I to cellulose II, namely, chain-polarity transformation (parallel-to-antiparallel) (Figure 3) [9,10,21,22], and chain-conformation-transformation (bent to bent-twisted) [23]. It has been demonstrated recently [24] that the most stable crystal form of cellulose Iβ has intramolecular hydrogen bonds between C2 and C6 hydroxyls and C3 hydroxyl and the glucose ring oxygen and intermolecular hydrogen bonds between C2 and C6 hydroxyls of adjacent chains (Figure 3). On conversion by the action of sodium hydroxide, the most stable crystal form of cellulose II only has intramolecular hydrogen bonds between the C3 hydroxyl and the glucose ring oxygen, and intermolecular hydrogen bonds between C2 and C6 hydroxyls of adjacent chains (Figure 4).

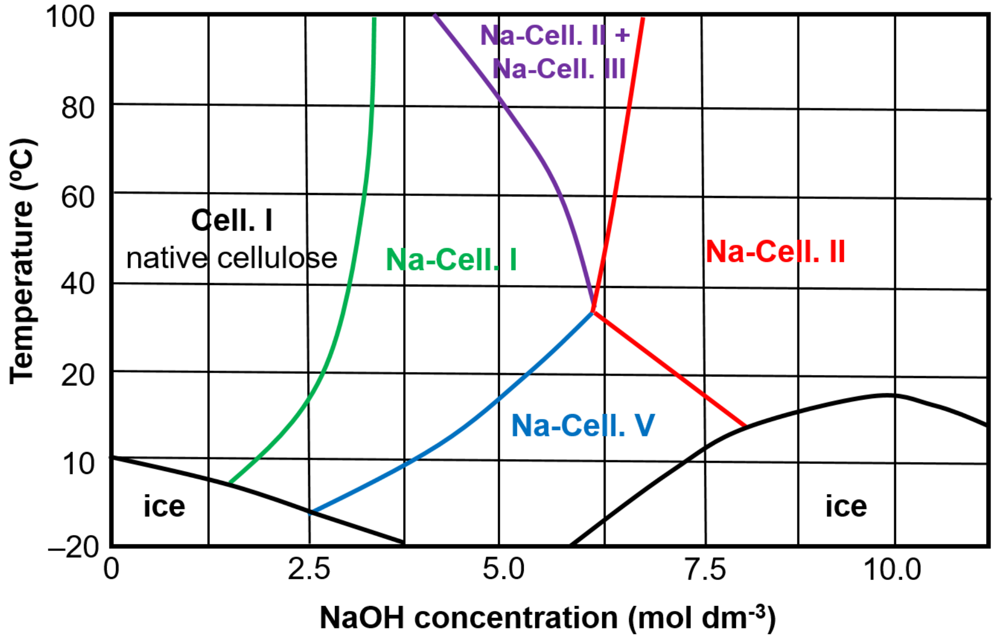

Figure 2. Phase diagram of the ternary system cellulose/NaOH/water (Adapted from Liebert [25]).

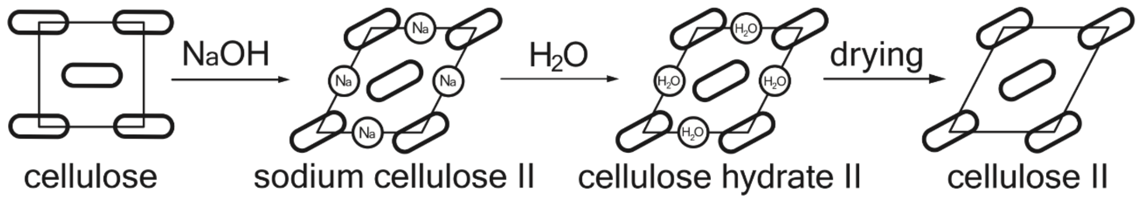

Figure 3. Cellulose crystal structure change on alkaline treatment (mercerisation).

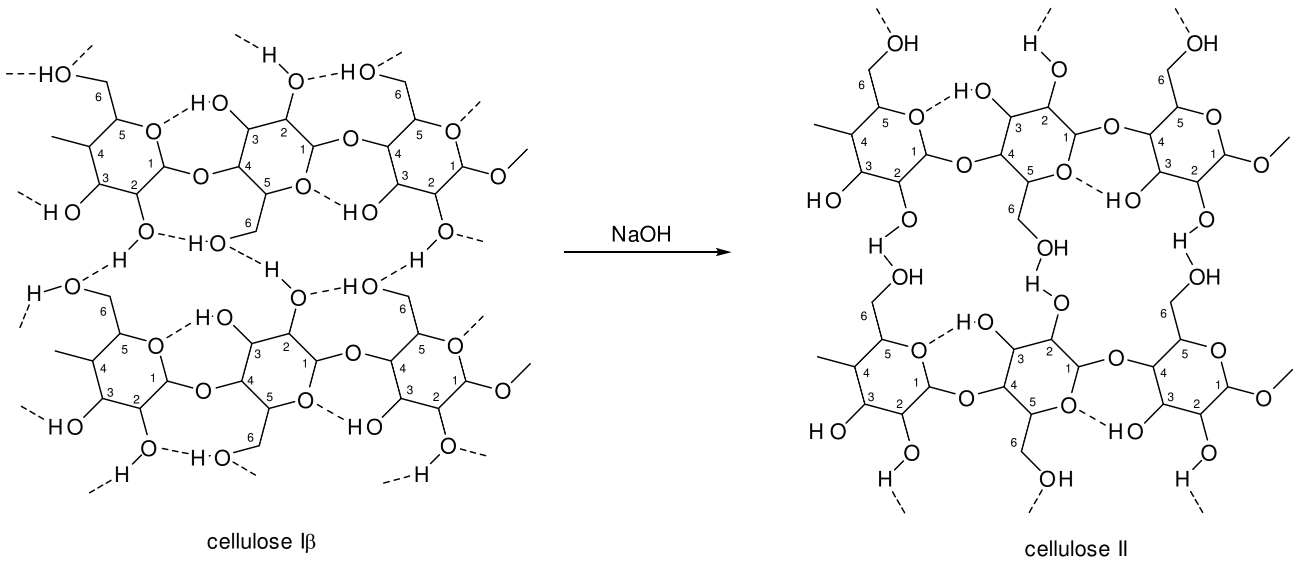

Figure 4. Cellulose Iβ crystal (showing hydrogen bond network) and conversion to cellulose II crystal (showing hydrogen bond network).

Mercerisation of cotton is a fibre-swelling/structural relaxation treatment that may be carried out on yarns, but more usually on fabrics, without tension (as in Mercer's original method) or with tension (as in Lowe's method discussed later) [26,27]. Hank or warp mercerisation of yarns often creates dyeability differences because of yarn tension variations that occur during mercerisation. During mercerisation in a 22–27% NaOH solution, both mature and immature cotton fibres swell so that the secondary wall thickness is increased. The fibre surface appearance and the internal structure of the fibre are modified. This improves the uniformity of fabric appearance after dyeing, and there is an apparent increase in colour depth after mercerisation that has been claimed to give cost savings of up to 30% on pale colours (*e.g.* 1–2% omf (on mass of fibre)) and even 50–70% on heavy depths when using some reactive dyes [20,28]. Dead cotton fibres (*i.e.* those with little or no secondary wall) are, however, not improved after mercerisation. Woven fabric mercerisation is normally carried out under tension on chain or chainless fabric mercerising ranges [27], whereas tubular fabric mercerising ranges are widely used for weft knitted cotton fabrics [29]. Mercerisation leads to a number of changes in fibre and fabric properties [20,26-29]:

- A more circular fibre cross-section
- Increased lustre
- Increased tensile strength, a major factor for technical textile fabrics
- Increased apparent colour depth after dyeing
- Improved dyeability of immature cotton (greater uniformity of appearance)
- Increased fibre moisture regain
- Increased water sorption
- Improved dimensional stability.

The sorptive capacity of mercerised cotton is greater when the fabric is mercerised without tension and an increase in drying temperature can also decrease the sorptive capacity, especially at temperatures above 80 °C [30]. It is important to point out that the process invented by Mercer is now often called "slack mercerisation", "mercerisation without tension", or sometimes "causticisation". Although Mercer's original treatment with sodium hydroxide produced great improvements in dyeability and in some physical properties, it had the disadvantage of causing fabric shrinkage and increased thickness; this reduced the popularity of the procedure. Today, what is most commonly regarded as "mercerisation" is actually the method discovered by Horace Lowe in 1890 that involves maintaining tension during alkali treatment and washing off, which prevents the shrinkage obtained by Mercer's original method. Lowe mentions in his British Patent 4,452 of 1890 that the process generates a silk-like lustre, and this brilliance was so pronounced that he jokingly remarked "I have converted cotton into silk." The development of the stenter in the 1870s after John Mercer's death had provided a method of holding cotton fabric to width while the caustic soda was washed out.

Lowe's observation that the application of tension during mercerising produced a high degree of lustre, enhanced Mercer's original work and has generated a cotton fabric treatment that is still in use today. After the publication of Lowe's patent, a cotton lustring syndicate of twelve firms was initiated in England around 1896, some from Bradford, others from Huddersfield, mercerising both yarn and hanks and later in 1898 cotton fabrics, imparting the appearance and lustre of silk to cotton.

Mercer, as a calico printer, always regarded the increased affinity for dyes as the most important technical aspect of his experiments on the caustic soda treatment of cotton. Mercer's process improved the colour and strength of printed cotton calico, but its commercial application did not become extensive. A French company offered £40,000 (£5.3 million in 2019) for the patent, which Mercer was willing to accept, but his partner in the patent Robert Hargreaves was not so disposed and so the negotiation failed.

The pressures of business prevented Mercer from pursuing his work on alkali treatment of cellulose further, and it was not until he retired from Oakenshaw Printworks in 1848 that he could re-investigate the action of chemicals upon cotton. Mercer made an arrangement with Robert Hargreaves of Broad Oak Print Works, Accrington to allow him to further his investigations and carry out treatments on machinery. In return Hargreaves received a share of the resultant patent. After many experiments John Mercer was awarded British Patent 13,296 on 24 October 1850 for the preparation of cotton. Mercer's patent is comprehensive as can be seen from the final paragraph:

> "And I claim as of my invention the subjection of cotton, linen and other vegetable fibrous material, either in the fibre or any stage of its manufacture, either alone or mixed with silk, woollen, or other animal fibrous material, to the action of caustic soda or caustic potash, dilute sulphuric acid, or solution of chloride of zinc of a temperature and strength sufficient to produce the new effects, and gave to them the new properties above described, either by padding, printing or steeping, immersion or any other mode of application."

Puckered effects or crêpe styles may be produced by direct printing of thickened (by printing gum) caustic soda in stripes on the fabric which, when dry, act as a resist to the action of the alkali, but Mercer considered this to be of secondary importance. Fabrics exhibiting the crêpe style were, however, exhibited at the Great International Exhibition at the Crystal Palace, London in 1851 (Figure 5), and Lyon Playfair showed crêpe fabrics to the British Association for the Advancement of Science in the same year.

Figure 5. Queen Victoria presides at the state opening of the great exhibition of All Nations, May 1st 1851. Royalty-free stock illustration ID: 244396882

Mercer exhibited a wide and interesting collection of mercerised articles at the Great Exhibition to illustrate his invention, which attracted great attention from both a scientific and technical point of view [2]. Mercer was one of the jurors of the same class in which he exhibited and so he was precluded by the Exhibition rules for receiving the ordinary mark of distinction awarded to the best exhibitors. However, the jury found Mercer's process for modifying cotton fibres to be of sufficient importance to merit special commendation, and thus recommended it as worth of the distinction of a council Medal. At the end of the Great International Exhibition, Queen Victoria declined all offers of presents from the exhibitors, except for two; one of these was John Mercer from whom Queen Victoria received a present of two of his mercerised cotton handkerchiefs. Queen Victoria in turn donated the gift of a carriage to John Mercer for his outstanding work.

The increased durability of mercerised cotton fabric and the pronounced contraction that occurs did not find favour with calico printers at that time; a good fabric appearance at the lowest cost was the primary consideration [2]. The extra costs associated with mercerising would not be wanted by calico printers of the period, indeed, caustic soda in 1850 was not then widely available

[26]. It was Sir William Mather who later pioneered the use of caustic soda in the pre-treatment of cotton in the 1880s. However, one application of mercerised cotton that became very successful was in the manufacture of calico printers' 'blankets' for machine printing, for which John Mercer and Robert Hargreaves obtained a patent. According to Parnell [2]:

> "The blanket consisted of two plies of unbleached mercerised cotton cloth cemented by caoutchouc [India rubber], capable of being easily connected at the ends, so as to make a continuous even band. Being much thinner than the old woollen and Macintosh blankets they afford a neater and better impression. They are also cheaper and more durable than the old blankets. Their superiority, which was soon recognised, led to their general adoption."

Parnell comments that in 1886, some 20 years after Mercer's death, mercerised cotton blankets were still in general use in calico printing [2].

John Mercer also made many experiments on the action of caustic soda and sulfuric acid on paper. He observed that immersion of the paper in the chemical solution for a few moments followed by washing caused the paper to become translucent. Similar effects were noted on cotton cloth. Using one pint of 70° Tw caustic soda liquor (7.8 M) with 20 ounces of snow or pounded ice gave excellent results as did the use of 115-125° Tw (10.8-11.8 M) sulfuric acid at 10 ºC. Mercer impregnated paper with gelatine size and dried it followed by dipping it into sulfuric acid, washing and drying. This produced a "very fine white paper, which folds quite easily." Mercer probably regarded this as an interesting curiosity, yet a few years later it was manufactured extensively by paper manufacturers as parchment paper.

Mercer's pioneering experiments in colour photography

In 1834 William Henry Fox Talbot, the inventor of photography on paper, commenced his experiments with silver salts as light-sensitive imaging materials. However, John Mercer earlier in 1828 had noted the formation of Prussian Blue on cotton by a light-induced reaction. Parnell quotes John Mercer's own description from his experimental notebooks:

> "I spotted a piece of white cloth with a solution of pernitrate of iron [iron(III) pernitrate, $Fe(NO_4)_3$], and exposed it to the sun. On testing it afterwards with a solution of red prussiate of potash it gave a blue – but no blue before exposure. This is worthy of note. I have not seen it noticed by any chemical writer." [2]

John Mercer later made some significant inventions of toning procedures for cyanotypes, but unfortunately these were only published in an insubstantial form, and subsequently reinvented by others; Mercer is arguably an unsung hero of early photography. When John Mercer retired from Fort Brothers he could devote his time to his chemical interests. In 1847 he established a novel method for obtaining negative cyanotypes. Mercer writes:

"I found that if paper or cotton cloth is smeared with a solution of pernitrate of iron or persulfate of iron [iron(III) persulfate, $Fe_2(S_2O_8)_3$] with certain quantities of oxalic acid and tartaric acids, dried in the dark, then exposed to the light (solar), and immediately dipped in solution of red prussiate containing a little free sulfuric acid (preferably free from yellow prussiate), where the light has caused deoxidation, the blue is fixed and where the peroxide remains unchanged there is no colour. The cloth or paper must be washed immediately in water containing a little sulfuric acid, and afterwards in pure water. The picture is a reverse blueprint."

In the 1850s John Mercer produced some of the earliest recorded monochromatic colour photographs. He had experimented with iron salts in 1828 and mentioned his intention to produce photographic pictures on paper and on fine calico by means of persalts of iron and red prussiate in a letter to Lyon Playfair in December 1847. By October 1854 he directed his attention to obtaining good pictures in blue, on paper and cloth, and to obtain other colours by a variety of interesting chemical reactions using salts of iron, copper, silver, tin and gold. In 1855, Mercer converted the Prussian Blue of cyanotype images into Purple of Cassius; this is a long-celebrated ceramicists' pigment, used to impart glass with a red coloration (often known as Cranberry glass). The pigment is formed by the reaction of gold(III) salts with tin(II) chloride, which precipitates colloidal gold metal dispersed in tin(IV) hydroxide [31]. Mercer converted iron(III) hexacyanoferrate into silver hexacyanoferrate by treatment with silver nitrate (equation 5). Silver hexacyanoferrate was then reduced to silver metal using sodium stannite, followed by treatment in a bath of sodium tetrachloroaurate(III) in which the **Purple of Cassius** was precipitated (equation 6).

$$[Fe^{III}]_4[Fe^{II}(CN)_6]_3 + 12AgNO_3 \rightarrow 3(Ag^{I}_4[Fe^{II}(CN)_6]) + 4Fe^{III}(NO_3)_3 \quad (5)$$

$$Ag^{I}_4[Fe^{II}(CN)_6] + 5Na_2[Sn^{II}(OH)_4] + 2NaAu^{III}Cl_4 \rightarrow$$
$$4Ag^0 + \mathbf{2Au^0} + \mathbf{5Sn^{IV}(OH)_4} + Na_4[Fe^{II}(CN)_6] + 8NaCl \quad (6)$$

His experimental studies examined various metals that provided different colours depending upon their degree of oxidation and their combinations with different natural dyestuffs. Nieto-Galan [32] cites the historical use of metallic bases of lead, zinc, tin, mercury, silver, gold or manganese that were exposed to sunlight and then combined with dyestuffs (such as madder, cochineal, logwood, murexide, quercitron bark, prussiates, chromates, *etc.*), and also the use of sulfocyanide of copper (copper(I) thiocyanate; $Cu^{I}SCN$) with silver nitrate. He points out that these were clear examples of the connection between photography and dyeing and calico printing at that time and that John Mercer's involvement with this was considerable.

At the annual meeting of the British Association for the Advancement of Science held in Leeds in 1858, John Mercer presented his photographic experiments and some samples on paper and on cotton cambric at the meeting. The subject excited considerable interest and his friends pressed him to continue his experiments [2]. A professional photographer who viewed Mercer's samples at Leeds in 1858 stated: “I have never in any kind of paper photography seen anything so beautiful as the Prussian Blue seems in softness and gradation.” Mercer sent some of his photographs on cambric (a lightweight, closely woven white cotton fabric) to the Photographic Society of Vienna and received a letter from the secretary of that Society expressing the great admiration which his photographs had generated. He also asked, if John was agreeable, that his process might be published in the Society’s journal. Mercer pursued his photographic experiments occasionally, but regretfully no further account of them was published. In the same meeting of the British Association in 1858, John Mercer showed how paper impregnated with ferric oxalate (iron(III) oxalate; $Fe_2(C_2O_4)_3$) might be used as an actinometer, a chemical system which determines the number of photons in a beam integrally or per unit time. Mercer placed a slip of prepared peroxalate paper between the leaves of a book, pulling it out half an inch at a time every five seconds; after ‘raising’ in the red prussiate bath it could then be compared with a graduated standard.

Mercer's Views on Technical Education

In the early nineteenth century, the textile dyeing and calico printing industries were continually under development because of new colours and the application of process controls through the new metrics of chemistry and physics. Many of the substances used in dyeing and calico printing were relatively simple materials that could be controlled and systematically varied to obtain different effects; indeed, many chemicals used were synthesised on the spot. Chemical knowledge derived from practical experience was especially important at this time for calico printing, and calico printers constituted the largest single group of men from the process industries that were involved with the London-based Chemical Society, of which John Mercer was a founder member in 1842. In 1853 John Mercer gave evidence to the Society of Arts Committee on Industrial Instruction, summarising the situation in calico printing as follows:

> “Many of the higher print houses and manufacturing chemists have from time to time supplied themselves with young men to superintend the chemical and colouring departments of their works, from the chemical schools of Scotland, a few from London, but most from abroad.”

He had observed about 21 such men employed within local firms, which seems to support the view at the time that Germany and France had developed better educational establishments in the chemical sciences than Great Britain, although practically educated chemists in calico printing could develop entrepreneurial roles through partnership (*e.g.* John Mercer), by establishment of new firms, or by both methods. This expansion of chemistry into calico printing contrasts starkly with John

Mercer's comment that when he became connected with calico printing in 1818, the only printing firms in England who employed a man possessing a knowledge of chemistry were the Thompsons of Clitheroe and the Hargreaves of Accrington. John Mercer's views on technical education are interesting:

> "I do not consider that the present chemical schools are well adapted for the sons of print-masters, managers and colourmen. During the two or three years they can spare for such training they ought to receive instruction not only in general principles, but in subjects related to their intended labour in the future. They should be fully instructed in the nature of the various substances used in their arts…It appears to me that the time is come when something ought to be done to give the rising generation, generally, more instruction in rudimentary scientific subjects than is afforded in our ordinary country schools…Of proper technical schools there ought not to be many; say one at Manchester, one at Leeds, another at Sheffield, and another at Glasgow; with a central parent school in London. These would be quite sufficient; each of the country schools should have a speciality, and in that take precedence of the others."

His forward-looking views later came to fruition in the establishment of the textile departments in the Manchester College of Technology, and in the University of Leeds with the Department of Textile Industries and the Department of Colour Chemistry and Dyeing. In addition, the Textile Department at Strathclyde University was also established in Glasgow. Later in the 20th Century textile chemistry and colour chemistry degree schemes were established both in Leeds and Manchester.

John Mercer and Scientific Societies

Sir Lyon Playfair who had been engaged as a chemist in the calico printing industry and was a friend of John Mercer persuaded him to become a founding member (in chemical manufacture) of The Chemical Society in 1842. A few years later the noted chemists James Thompson, Walter Crum and Lyon Playfair were dining at the home of Professor Thomas Graham, who was the first President of the Chemical Society from 1841–1843, and again from 1845–1847 (and after whom Thomas Graham House, the headquarters of the Royal Society of Chemistry in Cambridge, UK is named). It was resolved by them that John Mercer should be nominated for election to the Royal Society. Lyon Playfair (President of the Chemical Society from 1857–1859) wrote to John Mercer to inform him of this proposal and at first John Mercer hesitated. However, in a final letter to Mercer, Playfair wrote "I think you ought to accept this offer of your friends moving in this matter for you. It is a great tribute to a man who has acquired a knowledge of science without the aid of academies, and under every disadvantage and circumstance." After some pressure John Mercer gave his assent and he was elected a Fellow of the Royal Society of London in 1852.

On 17 April 1849 he was elected an Honorary Member of the Literary and Philosophical

Society of Manchester which he had attended over many years. Later, in January 1860 he was elected an Honorary Member of the Glasgow Philosophical Society. John Mercer later served on the council of the Chemical Society in 1860. As well as being a chemical juror for the Great Exhibition of 1851, Mercer served the same role for the Great Exhibition in London of 1862. John Mercer accepted a role as Justice of the Peace in 1861. Having been disadvantaged himself when young and possessed of Christian and charitable virtues Parnell remarks that "the claims of the justice to the community were not infrequently outweighed by the feeling of pity and compassion for the "offender" [2]. John Mercer retired in 1866 with a handsome fortune.

John Mercer's Legacy

In 1864, John Mercer was examining the progress in the construction of a reservoir in his neighbourhood when he fell a few feet into the water and it was some time before he could get rid of his wet clothing; this brought on a severe cold that later developed into a painful disease, which continued over the next two years. Ultimately it proved fatal and he died aged 76 on 30th November 1866. He was buried in the family vault in the churchyard of St Bartholomew's & St John's Church, Great Harwood.

John Mercer's life is a testament to a man who, had he been born with means and educated within academe, would have become one of the most distinguished chemists of the time. His upbringing in poverty and his necessity to earn a living precluded him from publishing articles in scientific journals. He was a self-taught chemical philosopher whose achievements within the calico printing industry were substantial and the product of clarity of thought, keen scientific observation, and experimentation par excellence. His invention of mercerising which bears his name will stand for all time as one of the most important chemical treatments ever developed in the long history of the textile industry. To this day he remains the only textile chemist who has ever been elected as a Fellow of the Royal Society since 1852. He is thus quite rightly considered as the Father of Textile Chemistry and the Society of Dyers and Colourists has perpetuated his name in its Mercer lectures which commenced in 1944, one hundred years after Mercer's discovery of the reaction of caustic soda on cotton fibres, yarns and fabrics.

A note from the corresponding author

I was very sad to hear the news of Dr. Ian Holme's passing. When I first started my career as a lecturer at The University of Leeds, in what was then the School of Textile Industries, Ian had just retired and he gave me all his lecture notes to help me start my career. He was a very kind and generous man and was always interested in what was going on in the School and my research. To the end he was working on reviews for *Coloration Technology*, including this one on John Mercer. I wanted to ensure that his review made it to the journal; I have edited the manuscript, added some additional chemistry, and some more recent research, but this review is very much Ian's work in Ian's style – I hope that he would be pleased with the final version.

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