Some Unremembered Chemists

A series of articles that explores the lives and work of selected chemists who have made a significant contribution to the advancement of the discipline, the profession and well-being of mankind, yet who are little remembered.
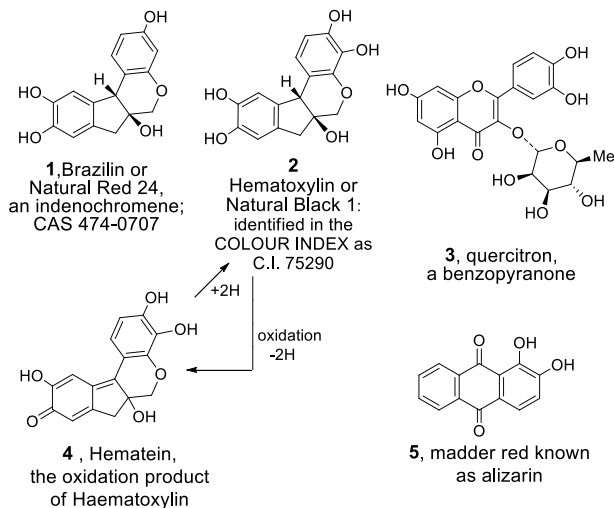
John Mercer FRS, FCS, MPhS

Part II. The industrialist, the chemist and the man

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In the first part of this article, the rise of John Mercer as a self-taught dyer in the town of Great Harwood, Lancashire, England, was described from his birth[1] in 1791 until he was re-employed at the nearby Clayton-le-Moors "Oakenshaw Print Works" in 1818 as an experimental chemist in the colour-shop[1-5]. Mercer had experimented from as early as 1807 with, amongst others, the compounds depicted in Scheme 1. He advanced the use of dyes and the art of dyeing quite significantly. At this time all dyestuffs were supplied in crude state, with nothing available from synthetic preparation.[6] It was, therefore, important to purify the dyes to avoid overspill (the dye spreading beyond the desired part) in the dyeing process, and chemists were employed at the various dye works for this and to improve the process.

1, Brazilin or Natural Red 24, an indenochromene; CAS 474-0707

2 Hematoxylin or Natural Black 1: identified in the COLOUR INDEX as C.I. 75290

3, quercitron, a benzopyranone

+2H

oxidation -2H

4 , Hematein, the oxidation product of Haematoxylin

5, madder red known as alizarin

Scheme 1

From the time of his employment (previously, he had been an apprentice, but that was terminated in 1810 as a result of Napoleon's Fontainebleau Decree), Mercer's skill and energy provided many inventions of new styles and new colours in the dye industry and, importantly, they led to new branches of *industrial chemistry*, as it was then known.[3,4] It was his "antimony range" of dyes that led to his (re)employment, and this he developed further to give browns of differing hues on calico[2] with copper(II) and lead(II) compounds.[6] His work with chromium compounds is reputed[3,4] to have created the industrial manufacture of bichrome (potassium dichromate, $K_2Cr_2O_7$). At the time of his initial experiments with it, the cost was

ten shillings and sixpence an ounce but by 1885, after his studies and with industrial manufacture becoming more common, its cost was less than sixpence per pound. He rediscovered and introduced into England a method of applying lead chromate ($PbCrO_4$) to cotton cloth in 1823. This yellow dye was then of great importance and formed within the fabric by treating it with lead acetate and then potassium chromate. That same year he introduced manganese bronze (a mixture of manganese oxides whose hue depends upon the degree of oxidation) formed from manganese salts, a dyestuff that went in and out of fashion in a cyclic manner almost every ten years. He also greatly improved the methods of printing indigo by using potassium ferricyanide [$K_3Fe(CN)_6$] and potash.

Of almost equal importance was his method of preparing mixed cotton and woollen fabrics that would subsequently accept dye with equal effectiveness. He found that some aluminium *lakes* [a lake is a pigment formed by precipitating a dye with an inert binder (the mordant), usually a metallic salt] from organic dyes were dissolved by ammonium oxalate [$(NH_4)_2C_2O_4$], and this led to the use of aluminous colour-precipitates in steam colour work. He also devised a new and cheaper method of preparing sodium stannate (Na_2SnO_3), a compound that was valuable to the calico dyer that provided him with much monetary gain.

Of the numerous improvements made by Mercer, the use of alkaline arsenites, e.g., Na_3AsO_4, in the *dunging* operation was one of the more important.[3] Superfluous uncombined mordant that remained on the cloth from the first stages of the dyeing process, and any remaining thickening agent with which the mordant was printed in, had to be removed after *ageing* and prior to attaching the dye. Unless adequately removed, the mordant dissolved in the dye-bath and caused discolouration of the whites, a deterioration of the dyeing liquor, and the dye spread beyond the defined pattern. Traditionally, the removal was accomplished by passing the cloth through hot water in which cows' dung had been dissolved – hence the name. Mercer's discoveries led to far superior substitutes, the principal ones of which were sodium silicate and arsenate.

Once established, John Mercer was sought after by chemical manufacturers and dyers, and he is reputed to have given his services freely. His self-taught skills and knowledge had, from the earliest times, led him to make accurate records of his work to the extent that solution

strengths and chemical quantities were recorded in (the then new) equivalents. He is regarded as one of the earliest workers in volumetric analysis. In 1827, he was able to value bleaching powder and bichrome using standard solutions. He speculated on the nature of white indigo **7**, the reduced soluble form of the indigo, **6**. When calico is submerged in a bath of white indigo and then removed, the white indigo quickly reacts with atmospheric oxygen and reverts to the insoluble, intensely colored indigo in the fabric. His views on what happened here were contrary to the accepted ideas but, subsequently, the redox process as we know it was proved correct.[3]

6, indigo   **7**, indigo white (leuco-indigo)
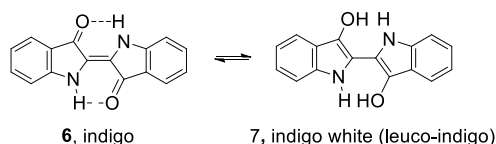
From the time of his first experiments early in the nineteenth century, Mercer had been concerned with avoiding waste. In about 1825, he introduced a new way of recovering the colouring matter of cochineal (the aluminium salt of carminic acid, **8**). The traditional method of the time, involved digesting in hot water, but Mercer found that some 25% of the dye was left in the dregs. At ten shillings per pound of weight this was an unnecessary waste. By adding a neutral alkaline oxalate to the water he found that 100% of the dye was extracted. Some 25 years later a French chemist visited the Oakenshaw works[3] to describe his method of cochineal extraction, but he had to concede that, although similar, the Mercer method required fewer steps and was superior.

8, carminic acid
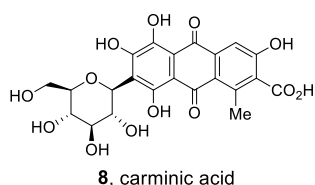
In 1841, Lyon Playfair (the noted chemist who had been James Thompson's private assistant and then a PhD graduate of Liebig in Giessen) was employed as a chemist at Thompson's Primrose print-works in Clitheroe (a town some 12 km from Great Harwood). He recognized Mercer's abilities and the two men became friendly. They began to meet weekly in a pub in Whalley, a village midway between the towns, to discuss science and matters of the day affecting the print works. These meetings attracted as many as ten like-minded individuals and it was at one of these gatherings that Mercer advanced his theory of catalysis, which he illustrated with many examples.[3] Subsequently, he read this theory to the 1842 Manchester meeting of the British Association for the Advancement of Science. Playfair extended these concepts and they were finally settled by Kekulé. Playfair's influence had Mercer extend his knowledge and by the time that he formally retired he was regularly using the *Bereichte* and other journals of the era.

Further observations made by Mercer in 1843, and discussed at these Whalley meetings, led Playfair subsequently to discover the nitroprussides, e.g., $Na_2Fe(CN)_5NO$. Playfair was so enamoured with the work of John Mercer

that he persuaded him to become a foundation member (in chemical manufacture) of *The Chemical Society* in 1842 (FCS). Later, a group of noted chemists of the day, James Thompson, Walter Crum and Lyon Playfair, on dining at the home of Professor Thomas Graham, concluded that Mercer should be nominated for election to the Royal Society. In a final letter to Mercer, Playfair stated that it "would be a great tribute to a man who has acquired knowledge of science without the aid of academies, and under every disadvantage" and it was this persuasion that had Mercer accede.[3] He was elected a Fellow of *The Royal Society* (FRS) in 1852.

It was Mercer's discoveries of 1844 that gained him the fame and kudos he deserved, and a considerable fortune. He provided a formulation for red ink, which gave him the sum of £10,100, and then his experiments in treating cotton with sodium hydroxide, sulfuric acid and zinc chloride led to the *mercerization* process, which he patented in 1850. There appear to be few records of the red ink formulation, although his experiments were carried out in partnership with Robert Hargreaves at his Broad Oak factory, near Accrington. In contrast, the mercerization process is well known. What Mercer found was that any one of sodium hydroxide, sulfuric acid or zinc chloride caused individual cotton fibres to become thicker and shorter, giving the cloth much greater strength. It also became semi-transparent and better able to absorb dye. In his original process, the overall size of the fabric shrank, with the result that the process became popular only after H. A. Lowe improved it in 1890; the cotton was held during treatment to prevent it shrinking. The fibres then gained a lustrous appearance. This represents the modern form of the process with mercerized cotton (Fig. 1) now the norm.


Fig. 1. Spools of mercerized cotton thread (from e*n.wikipedia. org/wiki/File:SpoolsOfThread* and *en.wikipedia.org/wiki/ File:Mercerised cotton thread of 800px-Spool_of_white.jpg*).

Although discovered by Mercer in 1844, the fine details of the mercerization process are still not fully understood. Cellulose consists of a polymeric chain of D-glucose molecules depicted by structure **9** (Scheme 2). In the polymer, the alternate rings are rotated $180°$ with respect to one another and the chain is strengthened by H-bonding, as shown in **10**. The discourse by Speakman[7] provides the essentials of what is known about the process of mercerization. Thus, the change in lustre of cotton fibres on treatment with concentrated NaOH is due to a change in the shape of the fibres. On the cotton plant the fibres are attached to the cotton seeds in a closed cotton pod. The fibres are straight with a circular cross-section and have a central cavity filled with a dilute aqueous solution of various salts and other small molecules, akin to thick-
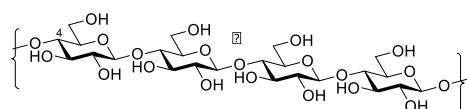
9, Cellulose: ⬡-linked poly-D-glucose
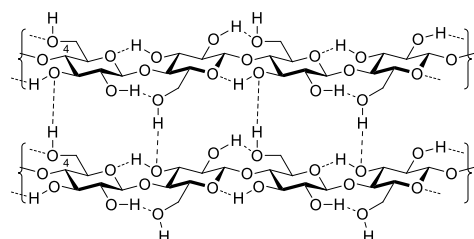
10, crystallized region of cellulose, showing H-bonding in the aligned parallel chains of the less thermodynamically favoured sheet of non-mercerized cotton
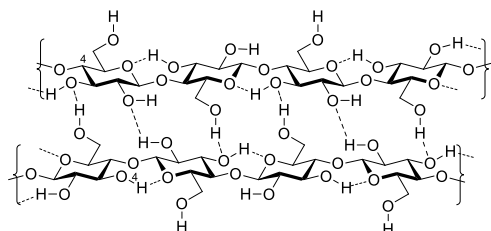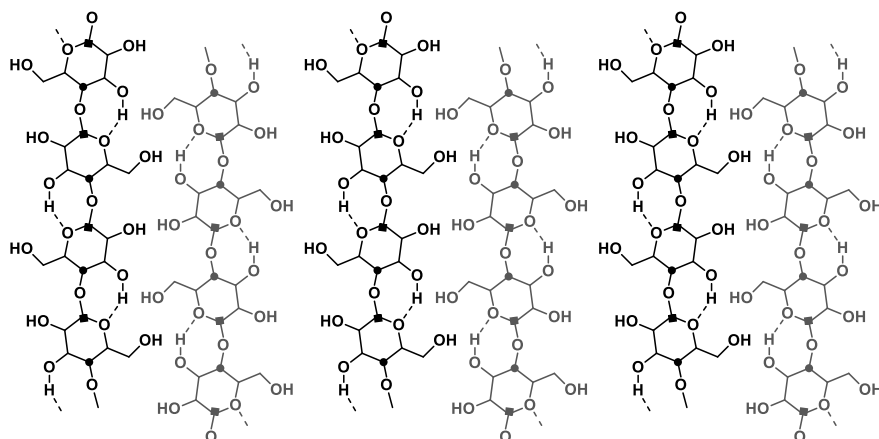
11, crystallized region of cellulose showing H-bonding in the parallel chains and their opposte orientation in the thermodynamically favoured sheet of mercerized cotton,

Scheme 2.

C1 ■
C4 ●
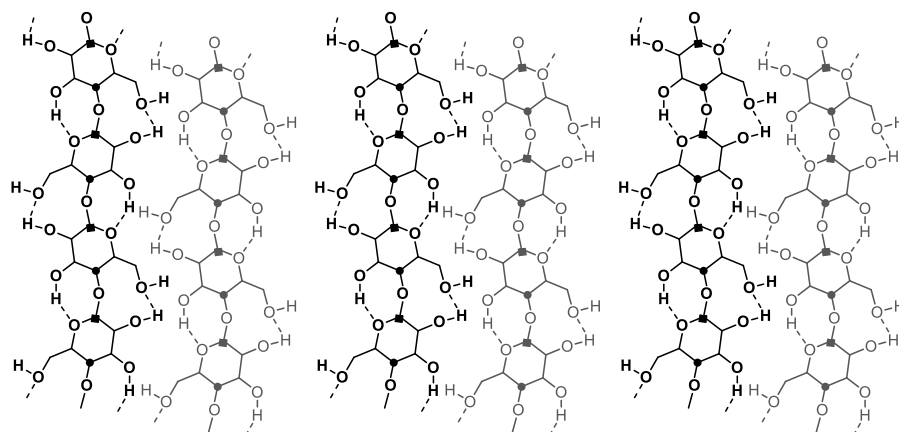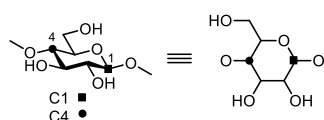
Scheme 3. Two **parallel** sheets of cellulose - *unmercerized*.

Scheme 4. Two **antiparallel** sheets of cellulose - *mercerized*.

walled tubes. When the fibre reaches its final length, the pod opens, the fibres dry in the sun, flatten and twist and acquire a tortured shape. Electron microscopy and X-ray diffraction experiments have shown that the cell walls of the cotton fibres contain microfibrils, each composed of about 1000 fully extended cellulose molecules. Each of these molecules consists of some 6000 glucose residues. Along the microfibril, ordered regions that are crystalline alternate with shorter non-crystalline ones. Untreated cotton is some 60% crystalline and has all the cellulose chains running parallel to one another and is stabilized by H-bonding, as shown by **10** in Scheme 2. The chains are arranged in sheets as depicted in Scheme 3 for three cellulose molecules in two separate sheets (not to scale). The bonds shown in bold depict one sheet and the plain bonds the other. There is no H-bonding between sheets and the cotton is in its less thermodynamically stable form.

During mercerization, NaOH enters the central core of the fibril and breaks the H-bonding network and the fibres swell:

$$R\text{-}OH + NaOH \rightarrow R\text{-}ONa + H_2O$$
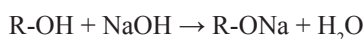
The chains can move one with respect to the other. However, when the NaOH is washed out of the cloth the sodium salts revert to their normal hydroxyl nature and the H-bonding network is re-established giving new microfibrils. The sheets are disrupted during the NaOH treatment and the regenerated microfibrils are formed in such a way as to generate the thermodynamically more stable form. The cellulose chains now run in opposite, antiparallel, directions depicted by **11** in Scheme 2 and the new sheet format of Scheme 4. Since the sheets do not align one with the other, the independent sheets carrying **9** do not lie in the same direction, and it appears that the antiparallel arrangement comes from new H-bonding between cellulose molecules of different sheets when the NaOH is removed. No single chain rotates through 180°.

An alternative explanation involves the stacking of the fibrils during the crystallization process. Here neighbouring parts of the molecule run in opposite directions in the zigzag plates and are antiparallel allowing for the reorganization.[8]   Furthermore, stirring the polymer molecule during crystallization causes a portion of the long molecules to become extended, while the

remainder crystallize to give plates at intervals along the rods. These rods are disc-shaped and give rise to a partly crystalline structure with wheel-like plates along its axis – such a structure is termed a synthetic polymer shish-kebab (a β-*cylindrite structure*). Mercerized cellulose has been shown to have such shish-kebab components by electron microscopy.[8] The chains in the kebab parts of the cellulose shish-kebab molecule are folded in just the same way as from an unstirred solution and are, therefore, likely to be antiparallel; the chains in the shish (extended) part of the molecule are assumed also to be antiparallel. Although many fine details still remain to be established as illustrated by a recent review,[9] Mercer's discovery of treating cotton cloth with sodium hydroxide to facilitate the dyeing process and imparting lustre means that it is entirely fitting that the commercial process immortalizes his name.

Mercer's immersion in colour led him to produce some of the earliest recorded colour photographs. In a letter to Lyon Playfair written in May 1857, he states that he had been experimenting for 2-3 years making photographic experiments, not as an artist but as a chemist. However, the earliest record of him observing the effects of sunlight on material dates back to the 1820s. His studies and 'amusements' led to him discovering a new way of measuring the power of solar rays and to the blue-print concepts. From 1854 he began producing colours on paper and cloth using the impact of light on various chemicals and obtained pictures "in a variety of pleasing tints".[3] His studies led to him exhibiting a number of the photographs at the 1858 British Association meeting in Leeds. A professional photographer of the day said that he had never seen anything on paper as beautiful as the Prussian blue in softness and gradation that Mercer had obtained.[3] His specimens attracted much attention in Vienna and the photographic society there sought the process from him.

At the 1858 meeting of the British Association, Mercer described the reducing action of light on complex salts of iron to give a blue colour, the depth of which depended upon the light intensity, a discovery of his that dated to 1828. This '*blue-printing*' proved of immeasurable value to the drawing offices. He intended to use blue-printing to measure the intensity of sunlight, an idea that was adopted by several metrological stations.

At the same meeting of the British Association, John Mercer advanced the concept of simple mathematical relations between the atomic weights of the elements. Unfortunately, this was generally ignored. Mendeleev's Period Table of 1869 and the subsequent periodic system followed,[10] yet the extract from Parnell's book[3] (Fig. 2) shows that Mercer had a grasp of the octet and the periods (based on O = 8)

So with the lithium and magnesium groups:

O − Li = 1	Mg − L = 5
S − L = 9 − 1 = 8	Ca − L = 13 − 5 = 8
Se − Na = 17 − 9 = 8	Sr − Na = 21 − 13 = 8
Te − K = 25 − 17 = 8	Ba − K = 29 − 21 = 8

Fig. 2. Extract from pages 324 and 325 of *The Life and Labours of John Mercer, F.R.S* – ref. 3.

The principal partners of the Oakenshaw Print Works retired in 1848 and John Mercer elected to do the same, devoting himself more to experimental study. However, after his wife's death in 1859 his enthusiasm waned. He died on 30 November 1866 following complication from falling into the water of a reservoir (under construction) some two years earlier. It appears that he was an unselfish person with a furtive mind given to flights of scientific fancy with his friends. He was an experimentalist *par excellence* and had remarkable insight into chemistry. It has been said that had he devoted himself entirely to research, he would have been among the most distinguished chemists of the day.[5] Although he patented some of his inventions, he freely gave away many others to great advantage and considerable profit of the recipients. He became an honorary member of the Manchester Philosophical Society in 1849 and of the Glasgow Philosophical Society (MPhS) in 1860. He accepted a role equivalent to) Justice of the Peace in 1861, but Parnell says that "the claims of justice to the community were not infrequently outweighed by his feeling of pity and compassion for the "offender". It is clear that John Mercer was an upstanding and outstanding member of the community.

References and Notes

1.   Lancashire Lantern: **Lancashire Pioneers**: www.lancashirepioneers.com (accessed Dec 2012).

2.   Calico is a plain-woven textile made from unbleached, and often not fully processed, cotton.

3.   *The Life and Labours of John Mercer, F.R.S*, E.A. Parnell, London: Longmans Green, 1886, xiv, pp.342.

4.   The Palissy of Calico-Printing, a review of Parnell's book by T.E. Thorpe, *Nature* **1866**, *35*, 145-147.

5.   *The Oxford Dictionary of National Biography: John Mercer*; see: www.oxforddnb.com/view/article/18573?docPos=3 (accessed Dec 2012).

6.   Séquin-Frey, M. *The Chemistry of Plant and Animal Dyes*, *J. Chem. Ed.* **1981**, *58*(4), 301-305.

7.   Speakman, P. *Shirts and shish-kebabs; John Mercer and mercerization*, *Biochem. Educ.* **1991**, *19* (4), 200-203; see also Langan, P.; Nishiyma,Y.; Chanzy, H. *J. Am. Chem. Soc.* **1999**, *121*, 9940-9946.

8.   Chanzy, H. D.; Roche, E. J. *J. Polymer Sci. Polymer Phys.* **1975**, *13* , 1859-1862.

9.   Habibi, Y.; Lucian A. Lucia, L.A.; Rojas O.J. *Chem Rev.* **2010**, *110*, 3479–3500.

10. Mendelejew, D. (1869). *Zeit. Chem.*, **1869**, 405–406.