Historical Article

The Early History of Polyaniline: Discovery and Origins

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Abstract. Prior to the discovery of its conductive properties in the 1960s, polyaniline was studied and applied as a variety of colored materials and dyes. The history of the discovery and origins of polyaniline are presented beginning with the initial oxidation of aniline by F. Ferdinand Runge in 1834 and concluding with the first electrochemical oxidation of aniline by Henry Letheby in 1862. In the process, the reports of aniline oxidation products between 1834 and 1862 are evaluated and discussed in light of modern knowledge, highlighting the various historical contributions to the current field of conjugated polymers. Finally, an initial argument for polyaniline as the first synthetic organic polymer is presented.

Keywords. Polyaniline, aniline black, emeraldine, conjugated polymers, oxidative polymerization.

INTRODUCTION

Modern society is largely a plastic-based culture in which organic plastics have become more ubiquitous than other common materials such as metals, glass, or ceramics. As a result, some have postulated that there is sufficient justification to refer to the period beginning with the 20th century as the Age of Plastics.[1] The bulk of commercial plastics are made up of various saturated organic polymers that are primarily electronic insulators. In contrast, conjugated polymers (Figure 1) are a less common class of organic plastic materials that are native semiconducting materials. In addition, these materials are capable of enhanced electronic conductivity (in some cases quasimetallic) in either their oxidized (p-doped) or reduced (n-doped) state.[2,3] Conjugated polymers are thus organic materials that combine the conductivity of traditional inorganic materials with many of the desirable properties of organic plastics, including mechanical flexibility and low production costs.[2,3] This unique combination of properties has led to considerable fundamental and technological interest in these materials over the last few decades, resulting in the current field of organic electronics. In the process, a variety of modern technological applications have been developed, including sensors, electrochromic devices, organic photovoltaics (solar cells), field effect transistors, and organic light-emitting diodes (OLEDs).[2,3]
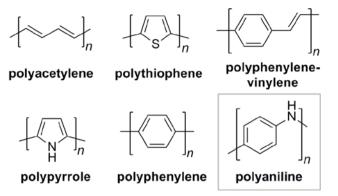
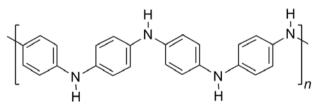**Figure 1.** Common parent conjugated organic polymers.

Discussion of the history of these materials typically begin in the mid-to-late 1970s with the collaborative work on conducting polyacetylene by Hideki Shirakawa, Alan G. MacDiarmid, and Alan J. Heeger,[4-7] for which they were awarded the 2000 Nobel Prize in Chemistry. The common view that their work marks the historical origins of these materials is further supported by the language of the award which states that it is "*for the discovery and development of electrically conductive polymers*".[8] More recently, however, a number of reports have begun to reveal a more accurate and complete account of the history of these materials, highlighting in particular the documented efforts that predate the commonly cited polyactylene work of the 1970s.[9-16]

The first report of the conductive nature of these materials was by Don Weiss in 1963,[17-19] but the general study of these polymeric materials far predates even this pioneering work. Of the core parent polymers given in Figure 1, the oldest of these materials is generally considered to be polyaniline, although exactly when this material was first studied is often a point of debate. Various authors have credited different figures with the origin and discovery of this material, originally known as aniline black.[20-22] These figures have included F. Ferdinand Runge[20-23] (1794-1867), Carl Fritzsche[9,20] (1808-1871), John Lightfoot[24,25] (1831-1872), and Henry Letheby[11,26] (1816-1876). The current report will attempt to evaluate the work of these figures in light of current knowledge and thus present the first detailed account of the discovery, origins, and development of polyaniline up through the 1860s.
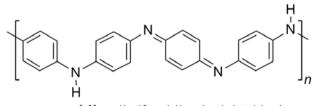
CURRENT KNOWLEDGE OF POLYANILINE
PRODUCTION AND CHARACTERISTICS

In order to be able to evaluate the work of the researchers above, it is first necessary to briefly review
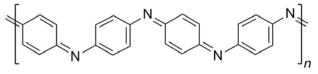
our modern understanding of the chemistry and characteristics of polyaniline. Polyaniline is readily produced by oxidative polymerization, via either chemical or electrochemical oxidation of aniline.[21,22,26,27] Most often, such oxidations are carried out in acidic aqueous environments with a pH below 3-4, which is most favorable for the production of the polymeric product.[21,22] A significant excess of oxidant is required due to the fact that polymer product undergoes oxidation at a lower potential than the initial aniline, thus consuming oxidant that cannot contribute to polymerization. As a consequence, the polymer product is also always isolated in its oxidized (p-doped) form. Neutral, non-doped samples are possible, but must be obtained via reduction following the oxidative polymerization process. Polyaniline can thus occur in a number of well-defined oxidation states, of which isolated polymer samples are viewed to exist as averages of these forms.[22,27] These states and their corresponding names were initially proposed by Arthur G. Green (1864-1941) and Arthur E. Woodhead in 1910,[28-31] and range from the fully reduced *leucoemeraldine* through the partially oxidized *protoemeraldine*, *emeraldine* and *nigraniline*, to the fully oxidized *pernigraniline*. The three primary forms are given in Figure 2. It should be pointed out that the terms *emeraldine* and *nigraniline* predate the

Figure 2. Primary oxidation states of polyaniline.

Figure 3. Protonic equilibria of polyaniline's emeraldine form.

Figure 4. Friedlieb Ferdinand Runge (1794-1867). [Edgar Fahs Smith Memorial Collection. Kislak Center for Special Collections, Rare Books and Manuscripts. University of Pennsylvania].

work of Green and Woodhead, with nigraniline originally referring to true aniline black and emeraldine representing a green, reduced form of the material.[23,32]

Unlike the other parent conjugated polymers shown in Figure 1, the electrical conductivity of polyaniline is affected by both traditional doping via oxidation, as well as the extent of polymer protonation.[21,22] This protonation effect is often referred to as protonic acid doping[21,22,27] and the acid doping level can be tuned simply by controlling the pH of the dopant acid solution. As such, each of the forms given in Figure 2 can exist as either its base or protonated salt. The most common forms of polyaniline, however, are either the emeraldine base or emeraldine salt (Figure 3).

As detailed in Figures 2 and 3, the color of the polymeric material is dependent on both its state of oxidation and protonation. Thus, the most common emeraldine salt is green to green-black, while the emeraldine base is violet-blue to blue-black. In both cases, the observed color is dependent on concentration. The state of the polymer also affects its relative solubility. Thus, while the emeraldine base is soluble in organic solvents such as *N*-methyl-pyrrolidone, polyaniline protonated by common mineral acids is only soluble in aqueous acids.[22,27]

RUNGE, KYANOL, AND ITS OXIDATION

The oldest of the figures to which the polymerization of aniline is first attributed is Friedlieb Ferdinand Runge (Figure 4), who was born in Billwärder, Germany (near Hamburg) on February 8, 1794.[33-36] The son of a pastor,[33-35] Ferdinand (he went by his middle name) was the third of seven children.[35] His mother died in 1806 and his father later remarried, with an additional child from the second marriage.[35] His family was quite poor and could not afford to send the children for further education beyond the local primary school.[34,35] Thus, he was apprenticed at age 15 to his uncle, studying pharmacy at the Ratsapotheke in Lübeck.[34-36] He then moved to Berlin in 1816 in order to study medicine, but transferred to Göttingen after two years, where he attended chemistry lectures by Friedrich Stromeyer (1776-1835).[34,35] After only one semester, however, he transferred again to Jena. At Jena, Runge studied analytical chemistry under Johann Wolfgang Döbereiner (1780-1849)[34,35] and finished his *Dr. med.* with a dissertation on belladonna in 1819.[33-36] Wanting to become a professor, Runge then returned to Berlin that same year to habilitate as *Privatdozent*.[33-35] This required him to first acquire a *Dr. phil.* degree, which he completed in 1822 with a dissertation on indigo.[33-35]

He remained in Berlin where he lectured on phytochemistry and technical chemistry until October of

1823, after which he traveled Europe with the primary goal of visiting Paris.[34,35] Upon his return, he joined the University of Breslau as *Privatdozent* in 1826. He was promoted to extraordinary professor of technical chemistry in 1828,[34,35] but this was not a permeant position and he found his conditions unfavorable for development of his practical ideas. He finally ended his academic career in 1831.[34,35] He moved to Berlin where he was offered a position in the chemical works of the Königliche Seehandlungs Societät (Royal Sea Trade Society) at Oranienburg (small town near Berlin) in 1832[33-35] or 1833.[36] It was here that he began the most fruitful period of his career. Among his accomplishments, he discovered a number of species from coal-tar, including pyrrole, quinoline, phenol, and aniline. He then became the technical director of the chemical plant in 1840.[33] Runge constantly clashed with his superiors, however, and he was ultimately dismissed in 1851,[36] with his last day of employment December 31, 1852.[34,35] He was granted a small pension, however, providing that he resided locally where his advice could be sought if needed.[35,36] He thus remained in Oranienburg where he died on March 25, 1867 at age 74.[33-36]

Shortly after the start of his new position at Oranienburg, Runge began the investigation of distillates of coal-tar, which he separated into acidic and basic fractions.[37] From the basic fraction, he isolated a volatile oil with a scarcely noticeable, but peculiar, odor. When treated with acid, the oil formed colorless salts, and both the oil and its salts became aquamarine when treated with chlorine of lime. Because of this color response, he named this oil *kyanol*, from a combination of the Greek *kuanós* ("blue") and the Latin *oleum* ("oil").[37] This oil was later shown to be identical to the product *krystallin* isolated from the dry distillation of indigo, which had been previously reported by Otto Unverdorben (1806-1873) in 1826. These materials are now both known as aniline.[33]

Runge then found that treatment of aniline with other oxidizing agents resulted in the formation of various dark insoluble dyes. These efforts began with the application of a hydrochloric acid solution of gold oxide to a porcelain plate, followed by a drop of aqueous aniline. Heating the combination to 100 °C then resulted in purple-colored spot, which became blue-gray when dried.[38] He then went on to show that if one first coated a hot porcelain plate with a solution of copper oxide in hydrochloric acid, and allowed it to dry, an added drop of aniline nitrate solution heated to 100 °C then resulted in a dark green-black spot.[38] Using copper oxide in nitric acid and aniline hydrochloride gave the same result. In order to confirm that it was the metal oxidant that was

causing the color change, he then showed that heating just aniline nitrate or aniline hydrochloride gave no decomposition or reaction. However, the addition of any copper salt then caused the formation of the black material.[38] Lastly, he showed that the addition of aniline hydrochloride to a hot porcelain plate coated with potassium bichromate also produced a dark black spot.

In the process, Runge noted that if sufficient amounts of the aniline nitrate or aniline hydrochloride salts could be produced, the colored products resulting from their treatment with metal species could provide a practical use.[38] To illustrate this, he first treated cotton with lead chromate, after which he printed the fabric with aniline hydrochloride to give green patterns within twelve hours. If more concentrated solutions of the aniline hydrochloride were used, black patterns developed rather than green. Both developed patterns remained unchanged by rinsing in water.[20,38]

Runge had a strong interest in dyeing and the coloring of fabrics, as illustrated by his publication of a three-volume series entitled *Farbenchemie*. The first of these was published in 1834,[39] the same year as his initial aniline publications, and these volumes summarized the technical methods and state of the coloring field at the time.[33] Due to this interest and the results of his studies from various coal tar species such as aniline, Runge approached his superiors in 1836 to propose that the chemical works at Oranienburg could produce such synthetic dyes from coal tar, but such efforts were never approved.[33,36] Runge moved his focus onto other studies and it was only much later that the merits of his discoveries with synthetic dyes were recognized. Following Runge's initial reports, further related studies on aniline did not appear until 1840 with the efforts of Carl Fritzsche.

FRITZSCHE AND ANILINE FROM INDIGO

Carl Julius Fritzsche was born on October 29, 1808 in Neustadt, Germany (then within the Kingdom of Saxony).[40,41] His father was a physician and the town where Fritzsche grew up had no grammar school, so he was educated through private lessons until he was 14. He then moved to Dresden, where he was employed in the pharmacy of his uncle for five years.[40] After that, he moved to Berlin where he became an assistant to Eilhard Mitscherlich (1794-1863) in 1830.[40,41] As Fritzsche took a doctorate in botany at the University of Berlin in 1833, Mitscherlich is credited with all of Fritzsche's chemical training.[40-42] His initial papers focused on botanical subjects, but with chemical character, and his

following papers began to take on greater chemical content.[40] He then emigrated to Russia in 1834,[40-42] where he became the manager of Struve's mineral-water works in St. Petersburg.[41] He became an adjunct member of the St. Petersburg Academy of Sciences in 1838, becoming an associate member in 1844, and a full member in 1852.[40,42] His chemical work, most of which appeared initially in publications of the St. Petersburg Academy of Sciences,[40] touched on uric acid derivatives, various oxides of nitrogen, and most critical of the discussion here, indigo and its derivatives. All of the efforts discussed below were carried out in a small laboratory next to his house, but he later shared the new, spacious chemical laboratory of the St. Petersburg Academy with Nikolay Zinin (1812-1880) beginning in 1866.[40,42] Fritzsche enjoyed good health until he suffered a stroke in 1869.[40-42] Although he recovered from it, he suffered from paralysis on one side, and his speech and memory suffered.[40,42] Nevertheless, he continued working until his death on June 20, 1871.[40,41]

In 1840, Fritzsche published a paper detailing the isolation of a new species from the decomposition of indigo.[43] Treating indigo with a hot, highly concentrated solution of base gave a salt mass of reddish-brown color, from which was then distilled a brown oil. Further purification isolated a colorless oil, which he called *anilin* after the Spanish name of indigo, *añil*.[41] This material was a base which formed light and highly crystalline salts and was isolated as 18-20% of the original indigo.[43] During the publication of this paper, the editor of the *Journal für praktische Chemie*, Otto Erdmann (1804-1869), recognized the similarity of *anilin* with Unverdorben's *krystallin*, and highlighted this in a note following Fritzsche's paper.[44] Two years later, Nikolay Zinin reduced nitrobenzene to give a species that he called *benzidam*.[45] In a short note directly following Zinin's paper, Fritzsche identified *benzidam* as his own *anilin*, stating that there can be no doubt about its identity.[46] The following year, August Hoffmann (1818-1892) then presented evidence that Unverdorben's *krystallin*, Runge's *kyanol*, Fritzsche's *anilin*, and Zinin's *benzidam* were all the same compound,[47] which ultimately became known as phenylamine or aniline.

Fritzsche found that aniline reacted with exposure to air, taking on first a yellow color and then turning into a brown mass. Continuing his 1840 study of the oil, he found that under 'certain circumstances' treatment with HNO_3 caused the production of a blue or green material, which he thought might be indigo, but he was only able to generate it in small quantities.[43] He then found that dissolving aniline salts in chromic acid (H_2CrO_4, typically as a H_2SO_4 solution) produced a dark green precipitate, which ultimately became black-blue in color.[43] Combustion analysis of the precipitate revealed a significant amount of chromium. Lastly, he treated aniline salts with potassium permanganate, which resulted in a brown precipitate containing manganese oxide.

Fritzsche admitted that he had not been able to study these color-forming reactions in much detail and planned to return to these in later publications.[43] Thus, while he did not follow up on the direct results reported in 1840, he did return to the treatment of aniline with oxidants in 1843, this time applying potassium chlorate.[48] Mixing an alcohol solution of aniline salt with potassium chlorate in HCl resulted in a blue precipitate, which turned green upon washing with alcohol, and became dark green upon drying. Analysis of the composition of the solid revealed an empirical formula $C_{24}H_{20}N_4Cl_2O$, which is in near perfect agreement with the structure of the emeraldine salt given in Figure 3 (X = Cl^{-}).[48] Although this seems to be Fritzsche's last report on the oxidation of aniline, the green aniline materials introduced by Runge and Fritzsche were later applied to commercial dyes by Frederick Crace-Calvert (1819-1873), Samuel Clift, and Charles Lowe.

CALVERT, CLIFT, LOWE AND EMERALDINE

Frederick Crace-Calvert was born near London on November, 14, 1819.[49] In 1835, he moved to France where he studied chemistry at the University of Rouen under Gerardin. After two years, he then moved to Paris to continue his studies at the Sorbonne and the College de France. He then became the manager of the chemical works of Robiquet and Pelletici at the age of 21, but soon left to become an assistant to Michel Eugène Chevreul (1786-1889) in 1841.[49,50] He returned to England in late 1846, where he was appointed as a honorary professor of chemistry at the Royal Institution, and later as lecturer on chemistry at the School of Medicine in Manchester. He became interested with the properties of carbolic acid and built works for its manufacture in 1865. Due to his various contributions, he became a Fellow of the Royal Society and of the Chemical Society, as well as other societies both at home and abroad. He was seized with a fatal illness in 1873, and died in Manchester on October 24, 1873.[49]

Sometime prior to the summer of 1860, Crace-Calvert, Samuel Clift, and their assistant Charles Lowe developed green and blue dyes from the oxidation of aniline for the coloring of cotton, for which they filed a joint patent on June 11, 1860.[24,51,52] These methods involved the application of an aniline salt (either the hyrdochloride or

tartate) and potassium chlorate to give a green color after 12 hours. This green color was given the name *emeraldine*,[24,50-55] which ultimately became the name adopted for the most common form of polyaniline (Figure 3). If the initially produced green dyed fabric was boiled in an alkaline or soap solution, the green color could be converted to a blue color, which was given the name *azurine*.[24,51-54] Both the blue color and the method of its production from emeraldine is consistent with the formation of the emeraldine base as outlined in Figure 3. Crace-Calvert presented these results as part of an address before the Society of Arts, which was then published in the February 7th issue of the *Journal of the Society of Arts* in 1862.[52] Later that same year samples printed by these techniques were exhibited in the chemical section at the London International Exhibition of 1862.[55] The following year Crace-Calvert also included this in his book *Lectures on Coal-Tar Colours, and on Recent Improvements and Progress in Dyeing and Calico Printing*.[53]

Crace-Calvert, Clift, and Lowe induced the printers Wood and Wright to apply their methods to generate green and blue colors in the end of 1860.[53] Wood and Wright considered the resulting colors good enough to be commercialized and introduced improvements resulting in a dark shade that could be considered black.[25,53] The improvements were achieved by either adding iron salts or other oxidizing agents to the potassium chlorate, followed by treating the color produced on the fabric with either a weak solution of potassium bichromate or bleaching powder. It was also found that copper nitrate could be mixed with aniline hydrochlorate, without the addition of potassium chlorate, and the mixture could be printed on the fabric to gradually give a dark green or black. These two methods gave either a green or blue color, but one that was so dark that it could be viewed as black.[53] About the same time, black dyes produced from the oxidation of aniline were introduced by John Lightfoot and Heinrich Caro (1834-1910).

LIGHTFOOT, CARO, AND ANILINE BLACK

John Lightfoot, Jr. was the son of Thomas Lightfoot (1811-1866), but was named after his grandfather John Lightfoot, Sr. (1774-1820).[25,50] His grandfather, father, and uncle were all colorists and connected with the Broad Oak Print Works of Accrington, about 20 miles north of Manchester.[24,25,50] As part of his practical education, Lightfoot traveled to France and Alsace in 1854.[50] He then continued the family tradition by joining Broad Oak in ca. 1855.[25] At Broad Oak, Lightfoot played a leading role in the us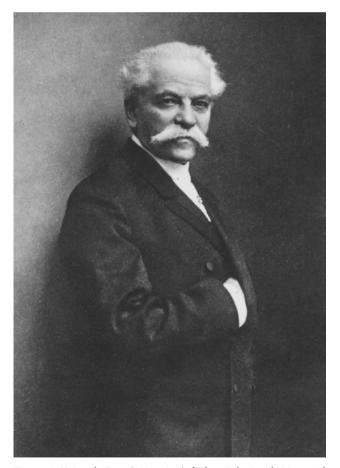e of madder, archil (or orchil), and indigo colors. He also began experimenting with the semisynthetic colorant known as murexide, the behavior of aniline colors, methods of fixing new dyes to wool and cotton, and imitations of madder and aniline colors.[25]

According to Lightfoot, it was November 1859 when he first observed that aniline hydrochloride in the presence of potassium chlorate imparted a fast and brilliant black to cotton during printing.[25,51] Initial efforts in the application of this aniline hydrochloride and potassium chlorate mixture produced little to no color after 24 hours, but he found that when the same formulation was printed with copper rollers, a green color was produced within 12 hours. Believing that the copper was a critical factor, he then added a copper salt to the mix to ultimately give an intense black.[24,51] The conclusion that the copper was a necessary factor is not consistent with the previous reports of either Runge[38] or Fritzsche,[48] both of which produced either green and black materials by treating aniline hydrochloride with chlorate salts alone. In reviewing the formulation given by Lightfoot,[51] however, it is clear that he used too little potassium chlorate to sufficiently oxidize the aniline salt and thus an additional oxidant such as copper was required for him to generate the color in sufficient intensity. Of course, prior to the addition of the copper salts, Lightfoot's process of printing cotton with the green or black aniline dyes was nearly identical to that originally reported by Runge.[38] In fact, from a chemical standpoint, the methods only differed in the chlorate salt utilized. Although Lightfoot recognized that the high price of aniline in 1859 was a disadvantage, he continued with experiments in July 1860 and had produced a few samples by 1861.[24,25]

In 1862, he reported his discovery as a letter to the Editor in the December 6th issue of *Chemical News and Journal of Industrial Science*, along with some sample swatches.[56] At the end of Lightfoot's letter, the editor added a note that the color was not a pure black, and as with the previous cases of either Runge[38] or Wood and Wright,[53] was most likely so dark a blue or green as to appear black. However, Lightfoot's black was considered superior to that of Wood and Wright.[25] Patents for this process were filed in early 1863,[51] with the US patent granted in May of the same year.[57] In this patent, Lightfoot describes the dyeing of fabric with mixtures of aniline hydrochloride and potassium chlorate, followed by the addition of copper chloride.[24,55,57] The patent, however, also covered the use of other copper salts or even salts of other metals.[57] The rights were then sold to Jakob J. Muller-Pack of Basle.[25]

A significant limitation in Lightfoot's printing process was that it caused severe corrosion to the rollers of the printing machines, which also led to streaking on

the cloth.[24,25,55] This limitation was solved by Charles Lauth, who registered a patent in 1964 that specified the use of insoluble copper sulfide. The insoluble salt was inactive at the time of printing and later converted to soluble copper sulfate by action of the chlorate salt during development of the aniline black, which dramatically reduced the damage to the rollers of the printing machines.[24,55] Lauth's process was sold to Muller-Pack, who combined it with Lightfoot's process in an effort to dominate the European and US markets.[25]

During this same time period, a second black aniline dye was produced by Heinrich Caro (Figure 5) in 1860.[24,25] Born on February 13, 1834 in Posen, Caro attended the Realm Gymnasium in Köln from 1842-1852.[58] From 1852-1855 he attended the Königliche Gewerbeinstitut (Royal Trade Institute), which trained students for industry, while also attending lectures at Berlin's Friedrich-Wilhelms-Universität (now the Humboldt University of Berlin).[58,59] In April 1855, Caro took

Figure 5. Heinrich Caro (1834-1910). [Edgar Fahs Smith Memorial Collection. Kislak Center for Special Collections, Rare Books and Manuscripts. University of Pennsylvania].

a modest appointment in the Troost factory in Mülheim, where he mainly performed analytical work outside the printing shop.[58] In March 1857, Caro was then sent on a study trip to England in March of 1857, where he visited a large number of printing and dyeing factories, in particular that of John Dale and Roberts. Upon his return to Germany, he then carried out his military service in 1857-1858.[58]

In November, 1859, Caro moved to England to try his luck there. Although his initial efforts were in vain, he was finally able to obtain a job with John Dale, co-owner of the Cornbrook Chemical Works of Roberts, Dale & Co. in Manchester.[58-60] He later returned to Germany in 1866, and on November 1, 1868 he became the coordinating technical director for the Badische Aniline and Soda Fabrik (BASF).[24,58-60] There he oversaw development of new colors including artificial alizarin, eosin, methylene blue, and azo dyes, as well as the initial stages of the indigo synthesis, and contributed towards the structural elucidation of the triphenylmethane dyes.[59] He was appointed to the company's board of directors in 1884 and continued to serve on the board until 1890.[60] Caro died after a short illness on September 11, 1910 in Dresden.[58]

In 1960, while working for Roberts, Dale & Co., Caro developed a process for making aniline purple by the oxidation of aniline with copper salts. After alcoholic extraction of the desired purple dye, a black residue remained which provided an excellent fast black dye for printing on cotton. Roberts, Dale & Co. then commercialized this dye for sale to printers in 1862.[24,54,59] As with Lightfoot's original formulation, this residue played havoc with the printing machinery, but it could be successfully printed with wooden hand blocks.[24] The efforts of Roberts, Dale & Co. established the advantages of aniline black over other black colorants of the time and it has been proposed to have been the motivating factor for Lightfoot to patent his process in 1863.[24] As discussed above, the color found more widespread application in British printworks following the introduction of insoluble copper sulfide by Charles Lauth in 1864.[59] By 1871, these black dyes from aniline became known as *aniline black*.[51] Aniline black later became the first real general term for polyaniline. Following the introduction of aniline black dyes, the next major innovation came from the physician and chemist Henry Letheby.

LETHEBY AND THE ELECTROLYSIS OF ANILINE SULFATE

Henry Letheby (Figure 6) was born in Plymouth, England in 1817,[61-63] and received his early education

Figure 6. Henry Letheby (1816-1876) [by W. & D. Downey albumen carte-de-visite, 1860s © National Portrait Gallery, London].

there.[61] He continued his chemical studies in the laboratory of the Royal Cornwall Polytechnic Society in Falmouth,[61,62] where he eventually became assistant and did some lecturing.[61] He then moved to London in 1837 to attend the Aldersgate Medical School, where he became assistant to Jonathan Pereira (1804-1853), professor of chemistry at the London Hospital.[61,62] Letheby became a licentiate of the Society of Apothecaries in 1837, and then received his M.B. (Bachelor of Medicine) from London University in 1842,[62,63] after which he succeeded Pereira as the chair of chemistry and toxicology at the London Hospital in 1846.[61,62] He was elected as London's medical officer of health in 1855,[61-64] while also serving as the city's public analyst.[62-64] In addition, he served as the city's chief gas examiner [62-64] and as a consulting chemist to the Great Central Gas Company[61,64] In

1858, he received a M.A. and Ph.D. from an unknown German university.[62] He was a fellow of both the Linnean Society of London and the Chemical Society of London.[62,63] Because of failing health, Letheby resigned his city posts in February 1874.[62] After a brief illness, he died at the age of 60 on March 28, 1876, at his home in London,[61-64] and was buried in Highgate cemetery on March 30th.[62]

After the investigation of two cases of fatal poisonings by nitrobenzenes, Letheby began investigations into chemical tests for the presence of aniline, as he had found that nitrobenzene was reduced to aniline after ingestion. Thus, he reported the study of acidic solutions of aniline with various oxidizing agents to produce blue-to-purple colors in 1862.[65] Continuing his investigations, Letheby then oxidized sulfuric acid solutions of aniline via a Pt electrode at the positive pole of a small Grove's cell (an early high current battery) to generate a deep blue to bluish-green pigment that adhered to the electrode as a fine powder.[65] As with many of the previous reports of chemical oxidation, the exact color observed depended on the concentration of the aniline solution used.

He then prepared the material on a larger scale, using greater quantities of aniline and two larger Grove's cells connected together for intensity.[65] Using this setup, a thick layer of dirty bluish-green pigment quickly covered the large platinum sheet (4×6 in) acting as the positive electrode. The pigment was then removed from the electrode, washed with water and dried to give a bluish-black powder. The powder was insoluble in water, alcohol, ether, or ammonia, and was only soluble in sulfuric acid. Immersion in ammonia did cause the powder to acquire a brilliant blue color, but the resulting blue pigment still did not dissolve.

When dissolved in concentrated sulfuric acid, the solution formed was either blue, green, or violet depending on the degree of concentration. Diluting the resulting acid solution with water then resulted in the precipitation of a dirty emerald green powder, which could be made blue with treatment of concentrated ammonia or blue to purple with the addition of concentrated sulfuric acid. The blue pigment generated by any of the means above could also be partly decolorized by various reducing agents, and in this condition, it became soluble.[65]

ANALYSIS AND DISCUSSION

Although the various studies presented above included little to no structural or compositional data, all of the reaction conditions and resulting proper-

ties reported are completely consistent with the modern knowledge of the oxidative polymerization of aniline, as well as the chemistry and characteristics of the resulting conjugated polymer, polyaniline. In addition, it is clear that all four of the historical figures that have been previously credited with the origin and discovery of polyaniline did indeed play critical roles in the early history of this material. However, if we are to assign priority to any of these figures, the credit must be properly given to Runge. Not only was he the second to discover aniline itself after Unverdorben, but he was the first to report its oxidative polymerization and the first to document the successful application of these products as both green and black dyes for printing on cotton.[38] Although Runge's contributions were not usually recognized during the time periods discussed above, Heinrich Caro paid tribute to Runge during the celebration of his own 70th birthday in 1904, crediting Runge with various discoveries including the first formation of emeraldine by copper salts.[33] While Caro does not go so far as to credit Runge with the discovery of aniline black, author Emilio Noelting (1851-1922) begins his 1889 book *Scientific and Industrial History of Aniline Black* with the statement that the history of aniline black can be traced to the "very old researches of Runge".[20]

The proper recognition of Runge should not diminish the contributions of the remaining three gentlemen, however, all of which left their mark on the history of polyaniline. Although Fritzsche did little to advance the oxidative polymerization of aniline beyond what was previously reported by Runge, he was the third to discover aniline and more importantly gave it the name by which we recognize it today.[43] Needless to say, there would not be the current term *polyaniline* without the contributions of Fritzsche! Also of significant importance is the fact that Fritzsche was the first to analyze the elemental composition of the polymerized product to reveal an empirical formula in near perfect agreement with the structure of the modern emeraldine salt of polyaniline.[48] Of course, the work of both Runge and Fritzsche may have been lost as academic curiosities if it had not been for the efforts of Crace-Calvert, Lightfoot, and Caro to develop these materials into commercial products. In addition, it is their application of this material as a black dye that resulted in the longstanding name *aniline black*, the primary common designation for this material until the ultimate use of the modern *polyaniline*. It is hard to quantify how much impact their work had on maintaining interest in polyaniline until its more critical electronic properties were ultimately discovered in the 1960s.[9,10,16] Lastly, one cannot overlook the contributions of Letheby. Although he most

certainly was not the first to report the oxidation of aniline to polyaniline, as is often claimed, he was the first to demonstrate its electrochemical oxidation and the very first to report on this method for the production of conjugated materials.[65] The electrochemical generation of conjugated polymers was the most common route to conductive films of these materials prior to the 1990s, and this still is the most common method utilized for the production of polyaniline.

In closing, I would like to postulate a final question for further consideration. If the work discussed above places the first report of the polymerization of aniline to polyaniline with the work of Runge in 1834, *is polyaniline then the earliest known synthetic organic polymer?* I am not the first to propose this possibility,[26] but I still feel that this is worth bringing to light once more and to provide at least initial support for such a claim. Although the term *polymer* was first coined by Berzelius in 1832, it did not have the same meaning as its modern usage and did not originally refer specifically to macromolecules.[66,67] In addition, none of the studies above ever used the term to refer to the oxidation products of aniline and the modern concept of macromolecules was not accepted until the 1920s, after which it was decades before Staudinger, Carothers, Flory, and others could convince the scientific community that these unusual molecules were real.[9] The earliest man-made polymer is generally considered to be polystyrene, whose polymerization was first observed in 1839[68] in which freshly distilled storax resin produced an oil (styrene, but then called styrol) that converted into a rubberlike substance in the presence of air, light, and heat.[66,69] Of course, from the discussion above, Runge's conversion of aniline to green-black materials predates the observed formation of polystyrene by five years. In addition, unlike the spontaneous polymerization of styrene, aniline was polymerized via the purposeful addition of an oxidizing agent and its polymerization was carried out under a number of different conditions. A complicating factor in this argument is that what made polystyrene interesting was its obvious changes in physical properties, while the obvious changes in the polymerization of aniline was the resulting color produced, rather than any particular physical change. As such, in that time period of the early 19th century there were no related properties to connect the two materials and polyaniline was not recognized as what we would call an oligomer or polymer until 1910.[28-31] Still it is clear that polyaniline represents not only an important beginning in the path to conducting organic materials, but to organic polymers in general.

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