Historical Article

The Early History of Polyaniline II: Elucidation of Structure and Redox States†

SETH C. RASMUSSEN

Department of Chemistry and Biochemistry, North Dakota State University,
NDSU Dept. 2735, P.O. Box 6050, Fargo, ND 58108-6050, USA
Phone: +1-701-231-8747; E-mail: seth.rasmussen@ndsu.edu

Abstract. Polyaniline, one of the primary parent conducting polymers, is a quite old material with a history dating back to 1834. With the distinction of being the oldest known fully synthetic polymer and successfully commercialized as several popular cotton dyes in the 1860s, this material was originally known by the name of its black dye, aniline black. Of course, throughout this early history, the chemical identity and structure of these early polyaniline products were completely unknown, and it was not until the 1870s that initial attempts began to reveal various structural aspects. The current report will present a detailed historical account of the efforts to determine the structures of these early aniline oxidation products over the time period of ca. 1870-1915. In addition to the identity and structure of specific products, studies revealing the interconversion of one species to another via both redox and acid-based processes will also be discussed, with these collective efforts resulting in a comprehensive model of these materials that has remained essentially unchanged to this day.

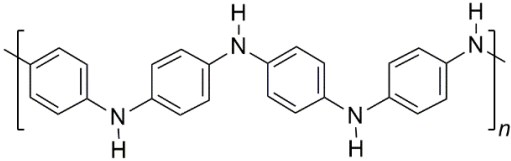**Keywords.** polyaniline, aniline black, emeraldine, nigraniline, structure elucidation

INTRODUCTION

Polyaniline is one of the most commonly studied parent conjugated polymers (Figure 1),[1-8] with its oxidized emeraldine form (Figure 2) representing one of the earliest examples of a conducting organic polymer. While such conducting polymers generated from the oxidation (p-doping) or reduction (n-doping) of conjugated polymers are generally viewed to be quite modern materials,[1,3-7] electrically conductive polymers actually date back to the early 1960s. Conjugated polymers as a whole are even older, with a history dating back to the early 19th century.[9-14]
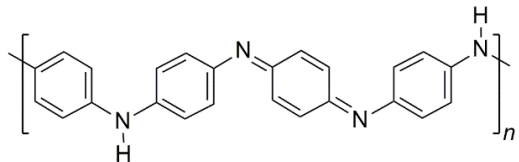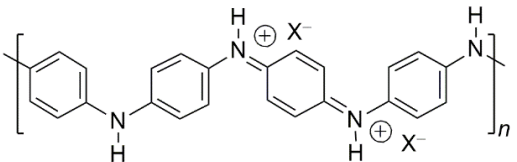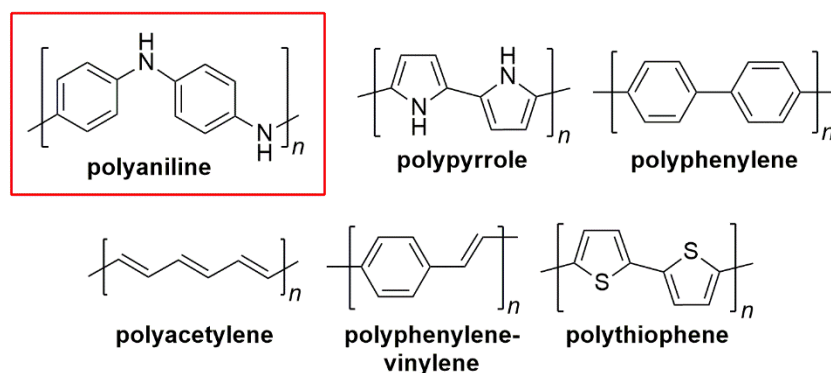

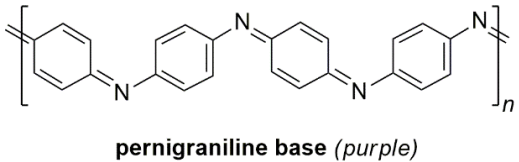**Figure 1.** Common parent conjugated organic polymers.

Within this long historical record, polyaniline holds the distinction of being the earliest known conjugated polymer and dates back to 1834 with the work of the German chemist F. Ferdinand Runge (1794-1867) who
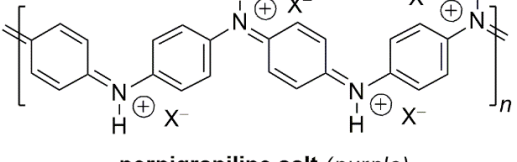
---

treated protonated aniline salts with various oxidants to generate green and black materials.[15] As such, it predates the 1839 report of Eduard Simon (1789-1856) detailing the generation of the material now identified as polystyrene,[16] making polyaniline also the oldest known fully synthetic organic polymer.[12,17] Of course, the modern name polyaniline was not introduced until the 1960s,[18-20] prior to which it was referred to by various color-based names, the most common of which was *aniline black*. This emphasis on color was largely due to the fact that the primary application of early polyaniline was as green, blue, and black dyes for cotton, with the commercialization of these dyes dating back to 1860.[10-13] At the same time, it is important to note that the chemical identity and structure of these early polyaniline products were unknown at the time and it was not until the beginning of the 20th century that deeper knowledge of the material's composition began to take shape.

Figure 2. Various common forms of polyaniline.

The structural details of polyaniline are complicated by the fact that it is the only member of the common conjugated polymers to exhibit both protonated and free-base forms (Figure 2). In addition, while conjugated polymers are all redox active materials, thus leading to conducting polymers in their non-neutral redox states, polyaniline exhibits multiple known oxidative states, each with distinct properties and characteristics. Although previous reports have presented an in-depth early history of polyaniline up to ca. 1870,[13,14] the current report will present a detailed historical account of the efforts to determine the structures of these early aniline oxidation products, beginning with attempts in the 1870s to reveal the mechanistic processes involved in their synthesis. In addition to the identity and structure of specific products, studies revealing the interconversion of one species to another via both redox and acid-based processes will be discussed, with these collective efforts of ca. 1870-1915 resulting in a comprehensive model of these materials that has remained essentially unchanged to this day. The beginnings of these efforts can be traced to a particularly noteworthy report by Heinrich Rheineck in 1872.[21]

RHEINECK AND NIGRANILINE

Although Heinrich Rheineck played an important role in the history of polyaniline, very little is actually known about him. Originally from Neckarsulm, Germany (near Stuttgart), he enrolled in the study of pharmacy at the University of Tübingen in the fall of 1860.[22] At Tübingen, he carried out research under Adolph Strecker

(1822-1871) on the action of sodium on allantoin, resulting in a single paper published in 1865.[23] He then worked in Hohenheim as an assistant chemist in agricultural chemistry for several years,[24] but had moved to Hagen, Germany in North Rhine-Westphalia (near Dusseldorf) by 1871.[24-26] Here he studied aspects of inorganic dyes such as Prussian blue.[26] His time in Hagen was short, however, and by 1872, he had moved to nearby Elberfeld (ca. 30 km to the southwest),[21,27] most likely employed by one of the smaller aniline dye companies located there. It was at Elberfeld that Rheineck then published his seminal work on aniline black.[21] This paper attracted a fair amount of interest and it was republished a number of times.[27-29]

Rheineck began the discussion of his study by stating that like other aniline dyes, aniline black is produced by the oxidation of aniline, thus resulting in the molecular condensation of repeated aniline units. Furthermore, these oxidation products are still of a basic nature, with aniline black a definite base. He then proposed that this base be called *nigraniline* (Latin *nigrum* "black" + *aniline*) in analogy to the name *rosaniline* for aniline red.[21]

In order to support these conclusions, he produced samples of aniline black following common conditions for its production on fabrics (aniline hydrochloride, potassium chlorate, and copper chloride). This aqueous mixture was allowed to evaporate in a porcelain dish and repeatedly moistened until a dry, velvety black powder was produced, after which the product was washed with hot water. As it was well known that this material appeared dark green on fabric and turned dark blue-violet after treatment with alkalis, Rheineck proposed that the blue-violet material was a free base, with the initial green material the corresponding hydrochloride salt. To confirm this, he treated the initially produced aniline black with either soda or ammonia to remove hydrochloric acid and generate what he viewed to be the free base.[21] This base could then be successfully used to remove acid from aniline salts. That is, if the isolated free base was produced on a piece of cotton, and then treated with aniline salts in the absence of oxidant, the fabric immediately turned green. Treating this again with alkali then returned the fabric to the original blue-violet color. In addition, he showed that the green hydrochloride salt could also be treated with sulfuric acid to release hydrochloride fumes and give a violet solution. When diluted, this solution again gives a black-green precipitate, which he was confident was the sulfuric acid salt.[21]

Rheineck felt that these results confirmed his view that the blue-violet material was a free base (nigraniline), which generated green salts when treated with acid. However, he decided not to follow through with more detailed studies, stating:[21]

> For lack of opportunity and facilities, I have to refrain from further elaboration on this interesting subject in scientific terms, and make other chemists aware of it, to which a well-established laboratory is available.

As such, this remained his only publication on aniline black and he left it to others to expand upon his initial efforts. One such to carry out further efforts was the German chemist Rudolf Nietzki (1847-1917), who reported various studies on aniline black starting in 1876.[30,31]

NIETZKI AND OXIDATIVE DEGRADATION

Rudolf Hugo Nietzki was born on March 9, 1847, in Heilsberg, Prussia (now Lidzbark Warmiński, Poland) to a Protestant family.[32-35] His father, Karl Johann Emil Nietzki, was a pastor, rector and writer.[32,33] In 1854, the family moved to the Prussian town of Zinten (now Kornevo, Russia), where his father served as pastor to the small town.[35] Initially educated by his father, Nietzki was sent to complete his studies at the gymnasium in Königsberg (now Kaliningrad, Russia), as Kinten was too small to have schools for higher education.[32,33,35]

Unhappy with his gymnasium education, he left before completion[32,35] and began the study of pharmacy, beginning with an apprenticeship in Zinten, followed by an internship in Kreuzburg, Prussia (now Kluczbork, Poland).[33,35] After passing the assistant examination in 1865,[32,33] he then worked in a pharmacy in nearby Hirschberg (now Jelenia Góra, Poland),[33,35] before additional studies at the University of Berlin in 1867.[32,33,35] In 1870, he passed the state pharmacy examination[35] and soon after was called to serve as a military pharmacist

in the Franco-Prussian War,[32,33,35] during which he was captured by the French and held as a prisoner of war.[33,35] Following the end of the war in 1871, he was offered a position as private assistant to August Wilhelm Hofmann (1818-1892) at the University of Berlin.[32,33,35] During his spare time, he also carried out some research in plant chemistry,[35] such that he was able to obtain his Dr. phil. at the University of Göttingen in 1874.[32-35] As he did not have a certificate of maturity from a gymnasium, he could not take the degree in Berlin.[35]

After obtaining his doctorate, he worked as a chemist for Matthes & Weber in Duisberg,[32,33,35] but then moved to the University of Leiden in 1876 to became first assistant in the laboratory there,[35] working under Antoine Paul Nicolas Franchimont (1844–1919)[32,33,35] and Jacob Maarten van Bemmelen (1830-1911).[35] In 1879, he began working as a research chemist in the laboratory of Kalle & Co. in Biebrich, Rhineland-Palatinate,[32,33,35] but left in 1883 to rent a place in the laboratory of Dr. Schmidt, in Wiesbaden, with the desire to carry out independent industrial and scientific studies.[35] In the spring of 1884, he moved to Basel, Switzerland, to introduce processes he had developed to the dyestuffs company J. R. Geigy[33,35] and at the same time obtained space in the laboratory at the University of Basel.

At the University, Jules Piccard (1840-1933) quickly recognized the value of having a specialist in dye chemistry at Basel and offered to establish Nietzki as a privatdozent.[35] Nietzki completed his habilitation at the University of Basel on June 30, 1884, after which he was appointed professor extraordinarius in 1887.[32,33,35] He was made Professor of Chemistry in 1895[32-35] and as the university laboratory did not have enough spaces to meet the demand of students, Nietzki established an organic chemistry laboratory at his own expense, in a private house located in the rue du Rhin. The lab initially accommodated 20 students, but was later expanded to allow 36 students. During his third decade at Basel, rapidly developing arteriosclerosis hampered his ability to work and ultimately made laboratory manipulations very difficult.[35] As a result, he resigned as professor in March of 1911,[32,33,35] retiring to Freiburg im Breisgau, in southern Germany, the following year.[35] After a long illness, he died at the Neckargemund Sanatorium on September 28, 1917.[32-35]

It was while at Leiden that Nietzki began reports of his investigations into the nature of aniline black in 1876, beginning with efforts to produce high purity samples for study.[30] Once satisfied with the quality of the samples of aniline black, he then began efforts to analyze its chemical composition. Such efforts resulted in the empirical formula $C_{18}H_{15}N_3 \cdot HCl$. It should be noted that this formula is very similar to that previously reported by Carl Julius Fritzsche (1808-1871) in 1843, although with lower Cl content.[13,14,36] As Nietzki had extensively purified his aniline black samples, it is quite possible that he had partially reduced his sample, thus inadvertently reducing the cationic content and thus the amount of Cl^- counterions. Two additional analysis papers then followed in 1876[31] and 1878[37], but these efforts focused primarily on the blue material generated by boiling isolated aniline black in excess aniline, which Nietzki viewed to be a form of phenylated aniline black. In the 1878 paper, he does conclude that the amount of Cl found during analysis is dependent on the methods of purification and drying of the sample.[37]

It was during the period between the second and third of these papers on the analysis, however, that Nietzki reported a discovery that would have far more impact on the eventual elucidation of the structural nature of aniline black. Thus, in an 1877 report,[38] he found that if aniline black is heated with potassium dichromate ($K_2Cr_2O_7$) in sulfuric acid, copious amounts of quinone was produced. To study the nature of this reaction, he suspended aniline black in dilute sulfuric acid and gradually added potassium dichromate. In the process, the black material was consumed, giving rise to a strong odor of quinone. The brown, liquid mixture was then separated by steam distillation to give a considerable amount of quinone, although not enough to correspond to the initial amount of aniline black. The residual content of the still was then evaporated to give a colorless crystalline material identified as hydroquinone. Thus, Nietzki concluded that aniline black was initially converted to hydroquinone, which was then oxidized to quinone (Figure 3). As aniline black is itself produced via the oxidation of aniline, Nietzki proposed that hydroquinone or quinone could be produced in this way from aniline, in which aniline black was then just an intermediate oxidation product. Treatment of aniline with dichromate in dilute sulfuric acid confirmed this view to be correct, with the ratio of hydroquinone to quinone dictated by the amount of oxidant applied.
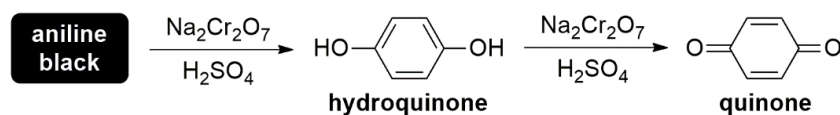
Figure 3. Nietzki's proposed oxidative degradation of aniline black.

Nietzki then followed this initial report with a second paper in 1878, here focusing on optimizing the isolated yield of quinone.[39] While he had previously found that hydroquinone could be produced in good yield, efforts to generate the final quinone always occurred in significantly lower yields, with the exception of attempts carried out at very small scale. As this led him to suspect that the quinone was undergoing further reactivity under heat and oxidation, he steam distilled samples of pure quinone in the presence of oxidant, which resulted in the generation of hydroquinone and a resinous product. He then repeated the process without the oxidant, again getting similar results, which led to the belief that quinone was undergoing condensation under heat. Thus, rather than the application of steam distillation, he found that near quantitative amounts could be generated by the slow addition of potassium dichromate to cooled sulfuric acid solutions of aniline, after which the quinone was isolated by ether extraction.

Of course, the generation of quinone and hydroquinone via the oxidative degradation of aniline black provided some clues as to structural aspects of the initial aniline material. However, this did not seem to be a significant focus for Nietzki, who seemed much more interested in this process as an easy and effective method for the generation of quinone. The next significant step towards an understanding of the structures involved then came from one of the original developers of commercial black aniline dyes, Heinrich Caro (1834-1910).

CARO AND CRITICAL INTERMEDIATES

Heinrich Caro (Figure 4) was born in Posen, Prussia (now Poznań, Poland) on February 13, 1834.[13,40] The family moved to Berlin in 1842, at which point Caro entered the Köllnische Realgymnasium there.[40] He continued his studies at the Köllnische Realgymnasium until 1852, after which he attended the Königliches Gewerbeinstitut (Royal Technical Institute), which trained students for industry.[13,40-42] At the same time, he was also attending lectures at Berlin's Friedrich-Wilhelms-Universität (now the Humboldt University of Berlin).[13,40-42]
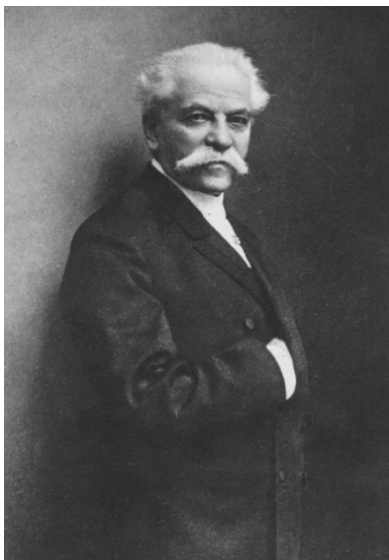
Figure 4. Heinrich Caro (1834-1910) (Edgar Fahs Smith Memorial Collection. Kislak Center for Special Collections, Rare Books and Manuscripts. University of Pennsylvania).

Towards the end of his studies, Caro was encouraged to focus on subjects related to printing and dyeing, as discussion had begun about setting up a state school for the training of technicians in this field, which would thus require teachers.[40] Thus, in April of 1855, Caro took a modest appointment with C. &. F. Troost, a calico printing company in Mülheim an der Ruhr, where he mainly performed analytical work.[13,40,42] In March of 1857, Caro was then sent on a study trip to England, where he was instructed to visit a large number of printing and dyeing factories.[13,40-42] In particular, he visited Roberts, Dale & Co, having previously met the owner John Dale in 1854 during a trip to Germany.[40,41] After Caro's return to Germany, the decision was made to build a larger factory and to transform C. &. F. Troost into a corporation, becoming Luisenthaler Aktiengesellschaft of Mülheim.[40] During this same period, Caro carried out his military service in 1857-1858.[40]

The following year, Caro decided to try his luck in England, moving there in November of 1859. Although his initial efforts were unsuccessful, he was ultimately able to obtain a position with John Dale at the Cornbrook Chemical Works of Roberts, Dale & Co. in Manchester.[40-43] It was during this time that Caro developed a process for making aniline purple in 1860, from which a black residue was isolated as a byproduct. This residue provided an excellent fast black dye for printing on cotton, with this aniline black then commercialized by Roberts, Dale & Co. in 1862.[13,41,42] At least partially due to declining health, Caro dissolved his partnership with Roberts, Dale & Co. in October of 1866, after which he returned to Germany.[41,42]

Once back in Germany, Caro took a post in the laboratory of Robert Bunsen (1811-1899) at the University of Heidelberg, and began private consultancy work, primarily for the newly formed Badische Anilin und Soda Fabrik (BASF).[41] His work with BASF grew to the point that he was hired as a technical director by the end of 1868.[40-43] At BASF, he oversaw the development of various new dyes, including artificial alizarin, eosin, methylene blue, and azo dyes, as well as the initial stages of the indigo synthesis.[41,42] His various contributions to the dye industry resulted in Caro being awarded an honorary doctorate by the University of Munich in 1877.[42] It was also during this time period that Caro started to become involved in the development of German patent law, which had only been recently introduced.[42,43] Caro was then appointed to the company's board of directors in 1884.[43] By the end of 1889, however, the strain of his activities in the fields of both chemistry and patent law, as well as his duties as director, lead to an end of his direct involvement in the work at BASF,[42] although he remained active on the company's supervisory board.[42,43] After a short illness, Caro died on September 11, 1910 in Dresden.[13,40,43]

It was towards the end of his career, in 1896, that Caro published studies that followed up on a previous statement by Nietzki concerning the production of a yellow species from the oxidation of aniline in cold, aqueous alkaline solutions.[44,45] Initial efforts showed that the addition of a permanganate solution to alkaline, aqueous aniline solution resulted in the production of a green solution coupled with precipitation.[44] Filtration isolated a solid mixture of MnO_2 and azobenzene (Figure 5), leaving a yellow solution. Optimized methods utilized a 2% solution of potassium permanganate to an NaOH solution of aniline with vigorous stirring.[45]

The yellow filtrate was then treated with iron sulfite to give a colorless solution, which was then filtered, and evaporated to remove unreacted aniline.[44,45] On cooling, a black tar separated, which was then boiled with dilute sulfuric acid to result in the crystallization of a colorless sulfate salt which was insoluble in cold water. The corresponding base was then crystallized from ligroin as colorless, flat needles which were found to be known species *p*-amidodiphenylamine (Figure 5).[44,45] Oxidation of this base with PbO_2 in cold water then resulted in the isolation of yellow crystals, which were ultimately determined to be *N*-phenylquinonediimine.[45] This final product was believed to be the identity of the original yellow species. Caro recognized that *N*-phenyl-quinonediimine and azobenzene were isomeric species, with both isomers formed during the alkaline oxidation of aniline. The exact mechanism of their formation, however, still remained unknown.[45] Further efforts were then continued in 1906 by the German chemist Richard Willstätter (1872-1942).[46]
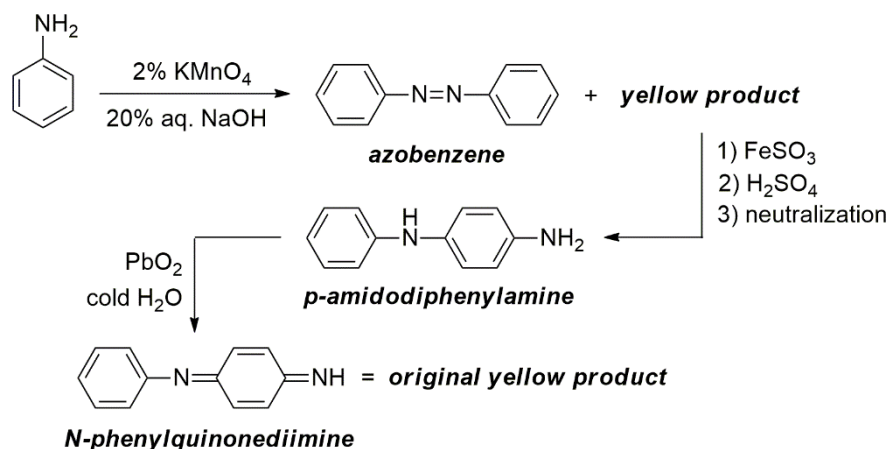
Figure 5. Caro's synthesis and identification of the intermediate oxidation product *N*-phenylquinonediimine.

WILLSTÄTTER AND LINEAR OLIGOANILINE STRUCTURES

Richard Willstätter (Figure 6) was born on August 13, 1872, in Karlsruhe, Germany to Jewish parents.[47-49] After two years in the Gymnasium at Karlsruhe, the family moved to Nürnberg in 1883, where he entered the Realgymnasium with the goal of a commercial career.[48] He then moved to Munich in October 1890, where he studied at the University of Munich while also attending lectures at the Technische Hochschule.[48,49] Although Adolf Baeyer (1835–1917) was Chair at Munich, the bulk of Willstatter's studies were under Eduard Buchner (1860–1917), Johan Rupe (1866-1951) and Eugen Bamberger (1857–1932). He took the pre-doctorate examination in 1893 and was assigned to Alfred Einhorn (1856-1917) as a research student.[48,49]


Figure 6. Richard Willstätter (1872-1942) (Edgar Fahs Smith Memorial Collection. Kislak Center for Special Collections, Rare Books and Manuscripts. University of Pennsylvania).

Willstätter started his independent work in 1894, after which he became privatdozent in 1896.[48-50] He was then made Professor extraordinarius and Head of the Organic Section in 1902.[48,50] In 1905, he accepted the Chair of Chemistry at the Eidgenössische Polytechnische Schule in Zurich (now ETH Zurich).[47-51] He was then appointed

Director of the new Kaiser-Wilhelm-Institut for Chemistry in Dahlem (now the Max Planck Institute for Chemistry), moving to Berlin in 1912.[47-51] He then returned to Munich in 1915 to succeed Baeyer, becoming Professor and Director of the State Chemical Laboratory. That same year, he was also awarded the Nobel Prize for Chemistry for his work on chlorophyll and plant pigments.[47-51] Unfortunately, rising antisemitic views in Germany ultimately led to his resignation on June 24, 1924,[48,49] after which he retained a room to continue some limited research.[48,50] A spate of attractive offers from other institutions followed, but all were declined.[49,51] Recognition for his contributions also continued, including the Davy Medal of the Royal Society of London in 1932 and the Willard Gibbs Medal of the Chicago Section of the American Chemical Society in 1933.[48,50] In late 1938, the Gestapo searched his house and he was later ordered to leave the country, resulting in his move to Muralto-Locarno in southern Switzerland in 1939.[48-51] There, he died of a heart attack on August 3, 1942.[49-51]

Willstätter began his investigation of aniline black and aniline oxidation by revisiting Caro's oxidation of *p*-amidodiphenylamine by lead oxide as discussed above (Figure 5). In analyzing the isolated oxidation product, he found the nitrogen content to be lower than expected for the *N*-phenylquinonediimine proposed by Caro, ultimately concluding that carrying out the reaction in water resulted in a portion of the oxidation product to be hydrolyzed to the corresponding *N*-phenylquinone monoimine (Figure 7), which co-crystallizes with the diimide.[46] In contrast, he found that if the oxidation was carried out in an ether solution using dry silver oxide, pure *N*-phenylquinonediimine could be obtained.
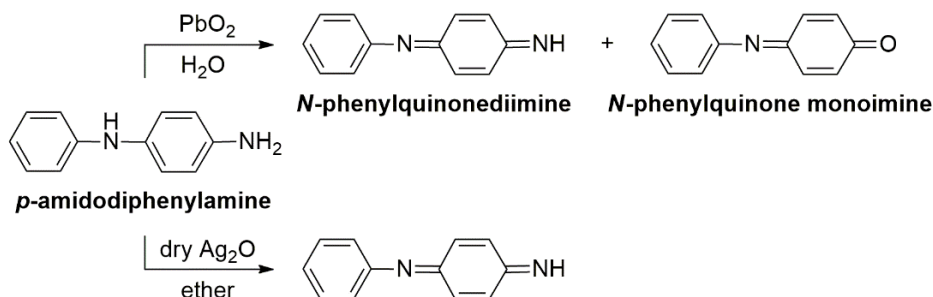

Figure 7. Oxidation of *p*-amidodiphenylamine.

Willstätter then continued with polymerization studies of phenylquinonediimine via treatment with acid.[46] The yellow material first turned red-brown upon protonation, after which it eventually turned into a dark green product. This green product was referred to as *emeraldine* in reference to the commercial name of the green aniline-based dye developed by Frederick Crace-Calvert (1819-1873) and coworkers in 1860.[13] Based on a suggestion from Nietzki, it was found that the same material could be produced more easily by oxidizing *p*-amidodiphenylamine with iron chloride in acidic media. Similar results were also achieved using hydrogen peroxide and a catalytic amount of $FeSO_4$.[46]

From these products, a blue species was isolated that was viewed to be the emeraldine base, also known as the blue aniline-based dye *azurine*. Analysis of the crystallized compound led to a formula of $C_{24}H_{20}N_4$, which was concluded to have been formed from the polymerization of two molecules of phenylquinonediimine.[46,52] Benzene solutions of the blue base were then oxidized with PbO_2 to give a red product with two less hydrogens ($C_{24}H_{18}N_4$). Both the blue and red products could be reduced to give the colorless leuco base ($C_{24}H_{22}N_4$), which could not be reduced any further.[46] As in the case of the oxidation of *p*-amidodiphenylamine in water (Figure 7), oxygen-terminated byproducts were also found in the blue, red, and leuco base species here.

Efforts were then made to determine the structures of the blue, red, and leuco base species, beginning with consideration of what type of bond might link the two phenylquinonediimine units. Of the various new linkages considered, the only option that was viewed to be consistent with the observed results was the formation of new C-N bond between a terminal nitrogen of one unit and a phenyl unit of the other. With the nature of the linkage limited to a simple C-N bond, there still remained various possible structural motifs as illustrated in

Figure 8.[46] Of the three possible structures given, it was viewed that the two branched structures (**II** and **III**) should be easily converted into azine species (**IIb** and **IIIb**) and thus efforts to find evidence of azine content in the blue species was pursued. As no indication of azine content could be found, it was determined that the linear structure (**I**) was the most reasonable structure for the blue species,[46,52] which was also consistent with the initial formation of *p*-amidodiphenylamine from aniline. From this determination, the structures of the three species and their transformations via oxidation or reduction can be summarized as shown in Figure 9.[46]
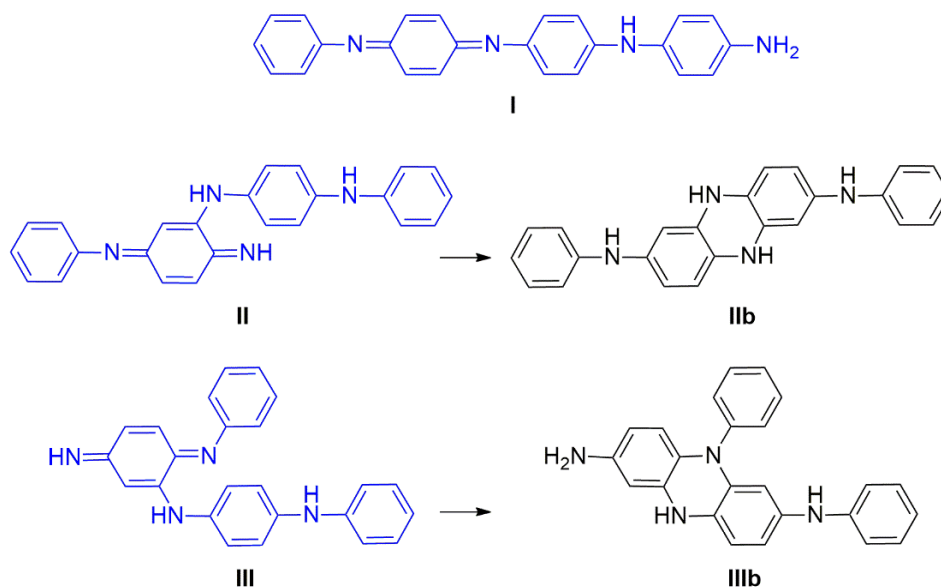
**Figure 8.** Possible structural motifs for the isolated blue product.
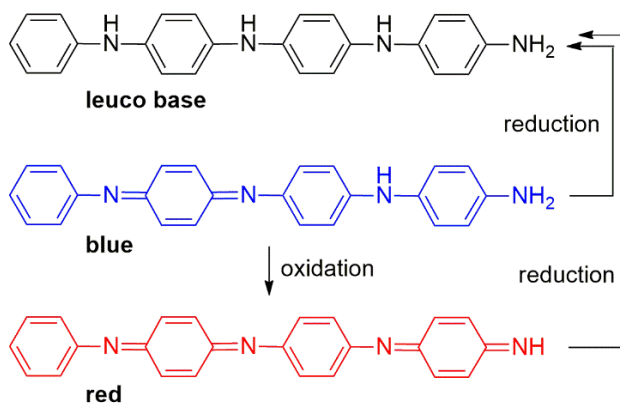
Figure 9. Structures and interconversions of isolated species.

Willstätter viewed his various emeraldine products as intermediates in the formation of aniline black. However, it was found that of the three species given in Figure 9, only the isolated red species could be converted directly to an insoluble black material.[46] In this way, it was found that the red product underwent further polymerization upon heating or treatment with dilute acids to give a black product referred to by Willstätter as *polymerization black*. He acknowledged that the properties of the aniline black prepared from the red intermediate did depend on the exact conditions applied, but examples that produced aniline black without byproducts gave a composition of $(C_6H_{4.5}N)_x$. Thus, he concluded that this composition best represented that of aniline black. As his aniline black was produced from the red intermediate consisting of four units (i.e. *x* = 4),

he concluded that the smallest possible structure for aniline black was where *x* equaled a minimum of 8, with the simplest possible formula being $C_{48}H_{36}N_8$.[46]

Willstätter recognized that this was not a definitive determination of the structure of aniline black, admitting in a second paper published in 1909:[52] "*The way in which the aniline residues are linked in [aniline] black has not yet been determined.*" In fact, the German chemist Hans Theodor Bucherer (1869-1949) had published a paper in 1907 that refuted the proposed structures in Willstätter's initial report, stating that only azine-type structures could explain the significant stability of the aniline black.[53] To further support the linear structures given in Figure 9, Willstätter subjected samples of aniline black to strong oxidation, which had previously been shown by Nietzki to decompose the black material to quinone.[44,45] Various methods were thus studied in order to maximize the experimental yield of quinone from aniline black.[52] The resulting experimental yields were then compared to the theoretical yields of quinone possible from the various proposed structures for aniline black at the time, which showed that the experimental values were ca. 95% of the theoretical value expected for the linear structure proposed by Willstätter, but much higher than that expected for the alternate branched or azine-based structures. In the same study, a more detailed elemental analysis was also performed, resulting in a more detailed average composition of $C_{5.97}H_{4.55}N$. Based on this composition, it was thus proposed that aniline black had a composition consisting of units of the three-fold quinoid derivative given in Figure 10.

In a second 1909 paper,[54] Willstätter continued the study of aniline black to determine the presence and interconversion of two different quinoid species, both of which were derived from the same leuco base (Figure 10). In addition to the three-fold quinoid derivative previously proposed, he now added the fully oxidized four-fold quinoid unit, which could be produced from the three-fold species via further oxidation with hydrogen peroxide. This fully oxidized species was described as blue-black, with salts giving a dark green color. The content of these two oxidized species in aniline black was viewed to be dependent on the oxidation conditions applied. The three-fold quinoid species, which gave a blue-colored base and green materials as the protonated salts, was viewed to represent the traditional material emeraldine. In contrast, the polymerization black previous generated from the heating of his red intermediate (Figure 9) was viewed to be closer to the four-fold quinoid species.
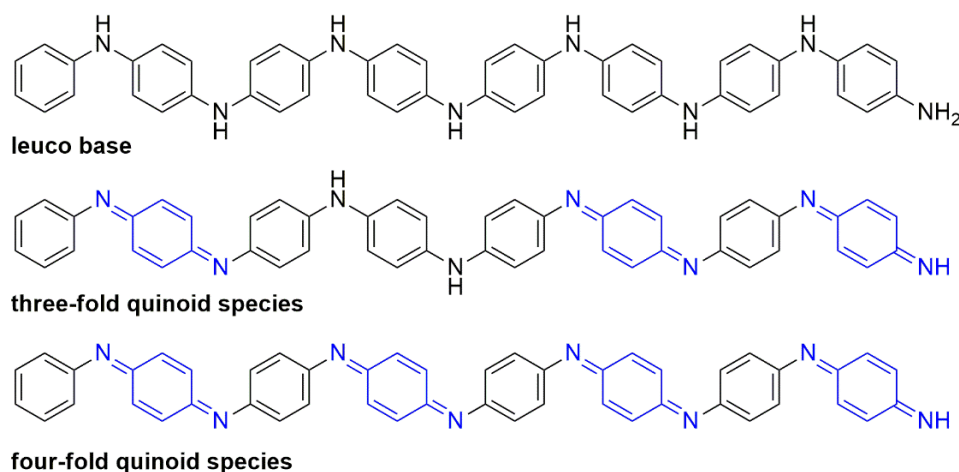
Figure 10. Proposed oxidative states representative of aniline black (quinoid units highlighted in blue).

This was then followed up with a 1910 paper in which the gradual reduction of aniline black was studied via treatment with phenylhydrazine carbamate.[55] In this way, the initial aniline black (viewed to be primarily the three-fold quinoid species) was found to progress through three phases. The initial reduction was observed at 30-45 °C, resulting in a transition from a dark blue base to light blue color. Further heating resulted in another transition at ca. 80 °C to give a gray material. Finally, a colorless product was obtained at temperatures

above 120 °C. The leuco base produced in this manner converted back to the black material under atmospheric oxygen in the presence of a small amount of ferrous salt.

Concurrent with the publication of Willstätter's study on the reduction of aniline black, the English industrial chemists Arthur G. Green (1864-1941) and Arthur E. Woodhead began reporting competing studies. While the first of these papers was reported in 1910,[56] two solo works by Green had also been reported the previous year.[57,58] At least initially, Green had very different ideas concerning the structure of aniline blacks.

GREEN, WOODHEAD, AND FURTHER REFINEMENT

Arthur George Green (Figure 11) was born in 1864, in the town of Ealing, located in West London, and was educated at Lancing College, Sussex. After matriculating in 1880, he entered University College, London.[59,60] In his first year there, he won the gold medal in the junior practical chemistry class and the Clothworkers' Exhibition in chemistry; the next year he won the gold medal for chemical analysis, and in 1883 the Tuffnel Scholarship.[59,61] At the College, Green carried out research under lecturers Henry Forster Morley (1855-1943) and Richard John Friswell (1849-1908),[60,61] and worked as a volunteer during college vacations in the laboratory of Messrs. Williams Bros., aniline dye manufacturers of Hounslow.[60]

Green commenced his industrial career in June 1885, as research chemist with Messrs. Brooke, Simpson & Spiller, Ltd.[59-61] at the Atlas Aniline Dye Works in the east London neighborhood of Hackney Wick, where he had previously carried out his research with Friswell.[62] His initial career was successful and he was awarded the silver medal of the Royal Society of Arts in 1891.[59] He then left in 1894 to became manager at the Clayton Aniline Company, in Manchester.[59,60] In 1901, he decided to become independent and setup in London as a consultant, but accepted an invitation in 1903 to the Chair of Chemistry and Dyeing at the University of Leeds, a position made vacant by the death of John James Hummel (1850–1902).[59] Green was later elected to the Royal Society in 1915.

His time at Leeds was ultimately finite and he resigned the chair in March 1916 to became Director of Research at Levinstein Ltd. in Manchester.[59] He also gave part of his time during 1916-1918 to the College of Technology, Manchester, where he established the Dyestuffs Research Laboratory, with the assistance of Frederick Maurice Rowe (1891-1947), one of his past students.[59,60,63] During this period, Green continued to receive various accolades. He was elected to the Livery of the Worshipful Company of Dyers in 1918 and he received the Dyers' Company gold medal three times, in 1909, 1914 (with W. Johnson), and 1923. He was the Society's Perkin medalist in 1917 and received an honorary M.Sc. from the University of Leeds.[59]
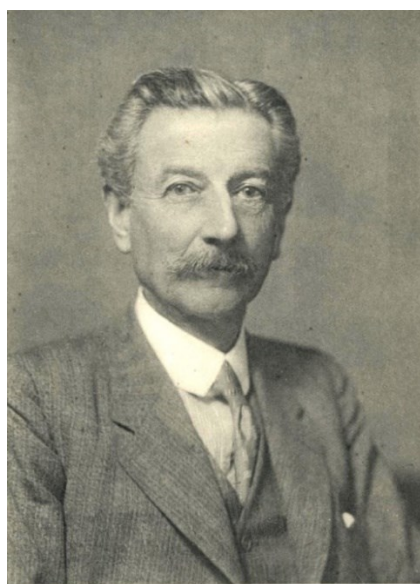

Figure 11. Arthur George Green (1864-1941) (*Obit. Notices Fellows R. Soc.* **1943**, *4*, 251–270; courtesy of JSTOR).

In 1919, Levinstein, Ltd. merged with British Dyes to become the British Dyestuffs Corporation, Ltd, after which Green resigned his position as Director of Research in 1923. At this time, Green returned to his private practice which was considerable both in Europe and America.[59] In 1936, he returned to became consultant to the Dyestuffs Group of Imperial Chemical Industries Ltd., which was established in December 1926 from the merger of British Dyestuffs Corporation with three other British companies: Brunner Mond, Nobel Explosives, the United Alkali Company. Five years later, Green died peacefully in his sleep at his home at Walton-on-Thames on September 12, 1941 at the age of 78.[59,60]

Green's earliest report on the structure of aniline black consisted of a short paper that presented proposed structures for both the emeraldine and nigraniline materials,[57] along with brief comments on the early report by Willstätter and Moore.[46] This was then followed up with a second report covering much of the same material in a bit more detail.[58] As shown in Figure 12, both of Green's structures are cyclic species consisting of three aniline repeat units. It is also important to note that he never designates what the substitution geometry is on various bridging phenyl rings (i.e. ortho, meta, or para). In terms of the report of Willstätter and Moore, Green agrees with the empirical formula of $(C_6H_{4.5}N)_x$. but does not accept any of the rest. As stated by Green:[58]

> *The view expressed by these authors that the product of this so-called "polymerisation" must have a molecule in which x = at least 8, and is to be represented as a complex indamine with a long open chain, appears to me to be very difficult to reconcile with its properties (stability to acids, etc.).*

emeraldine   **nigraniline**
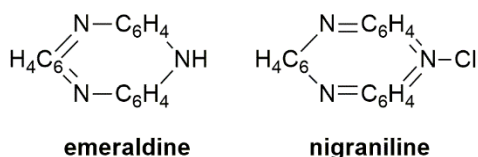
Figure 12. Green's initially proposed structures of emeraldine and nigraniline.

By the publication of the first paper coauthored with Arthur Edmund Woodhead in 1910,[56] however, this stance seems to be somewhat moderated, stating that the work of Willstätter and his coworkers has added much to the knowledge of the complex oxidation products of aniline. Still, they point out that the results of Willstätter can really only apply to the primary oxidation products of aniline (emeraldine or nigraniline), while the most stable form of aniline black, known as *ungreenable aniline-black*, must be an azine. Based on this view, it was then proposed:[56]

> *that the term "aniline-black" should be restricted to the higher condensation products (ungreenable black), whilst the original names "emeraldine" and "nigraniline" should be retained for the primary oxidation products.*

Green and Woodhead then went on to reinterpret some of Willstätter's previous results and attempted to provide additional data to present a more detailed model of the primary oxidation products of aniline. In the process, they retained the general linear octameric structures of Willstätter, even though they felt the question of linear chains vs. ring structures was still undecided. On this point, they state:[56]

> *Assuming the correctness of the eight-nuclear structure for the primary oxidation products, it still remains an undecided question whether the aniline residues are to be regarded as united in an open or in a closed chain, but without attempting to decide this point we shall make use of the open-chain formulae to express provisionally the analytical results.*

These efforts started with the preparation of emeraldine via multiple methods, converted to the corresponding base, and carefully purified to produce an initial material for study. This material was then dissolved in aqueous solutions of either acetic (80%) or formic acid (60%) to give yellowish-green solutions. The addition of a very dilute solution of chromic acid then resulted in the color of the solution changing first

from green to pure blue, and then to violet with the further addition of oxidant, which ultimately gave a violet precipitate.[56] If a very weak solution of sodium hydrogen sulfite was added to the violet solution, these color changes would occur in the opposite direction, from violet to blue to green. Stronger reducing agents (phenylhydrazine, sodium hyposulfite, or titanium trichloride) would convert the green solution to the colorless leuco base. As the initial solution began with the emeraldine, the next sequential colored solution via oxidation was designated nigraniline, with the name *pernigraniline* (Latin *per* "through, entirely, utterly" + *nigraniline*) proposed for the final violet solution. It should be noted here that the prefix *per-* is commonly used in chemistry to denote the highest known oxidation state of various species (i.e. persulfate or permanganate) and thus is added to nigraniline here to denote the fully oxidized form. In a similar fashion, the parent leuco base was given the name *leucoemeraldine* (i.e. the leuco base of the original emeraldine).

Their analysis then continued with efforts to determine the quantity of hydrogen required for conversion of emeraldine into leucoemeraldine via titration of the initial acetic acid solution with titanium trichloride.[56] From these measurements, it was determined that the emeraldine corresponded to a diquinoid species. In a similar manner, the quantity of oxygen consumed in the conversion of emeraldine into nigraniline was then studied by titration of the initial acetic acid solution with a standard solution of chromic acid. In this way, it was concluded that the conversion of emeraldine to nigraniline was the introduction of one additional quinonoid group. This then led to the series as outlined in Figure 13.[56] As the difference between emeraldine and leucoemeraldine was two quinoid units, the additional proposed single quinoid containing species was added between these in the series, which Green gave the name *protoemeraldine* (Greek *prōtos* "first" + *emeraldine*) to denote the first oxidized form.
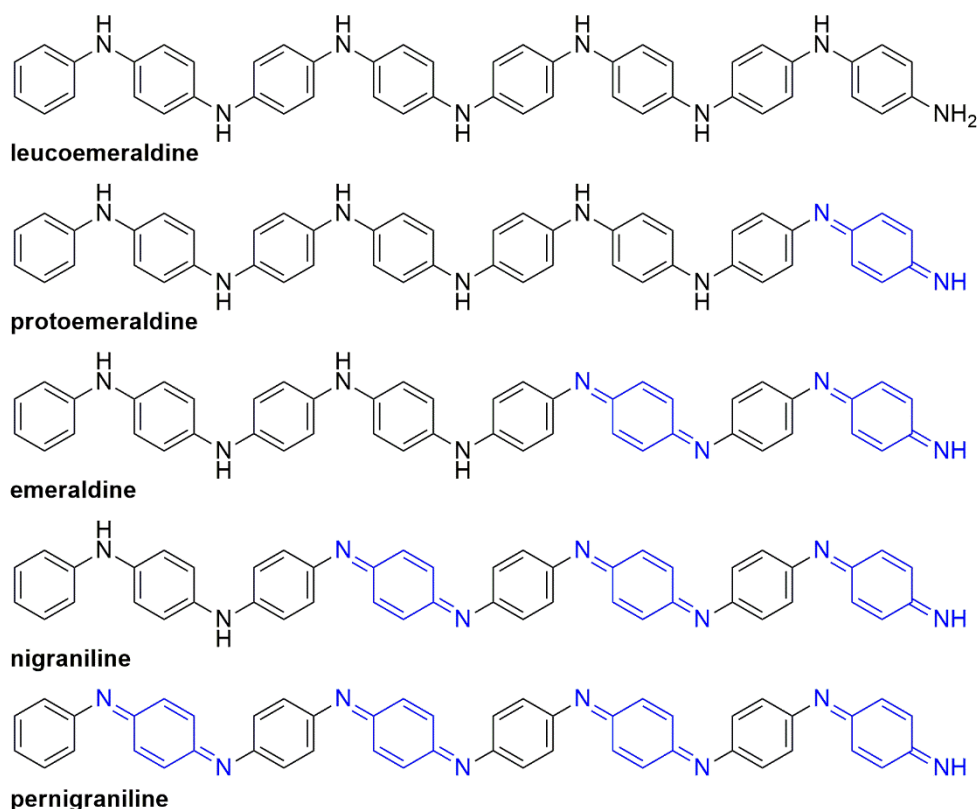
Figure 13. The full series of aniline oxidation products as proposed by Green and Woodhead in 1910.

WILLSTATTER'S RESPONSE AND GREEN'S REBUTTAL

Willstätter then responded to the work of Green and Woodhead in an additional 1911 paper.[64] While he felt that the proposed renaming of the structures provided no improvement over his previous descriptive nomenclature, it was the contradicting views on the quinoid content of emeraldine that dominated his response. The primary point raised by Willstätter was that from their previous attempts at reducing materials to the leuco base, the titanium trichloride required higher temperatures for full reduction than that applied by Green and Woodhead. As such, he felt that the leucoemeraldine reported by Green was actually the monoquinoid product, which he felt was also supported by their description of a "*pale brown amorphous powder*", when it should be completely colorless. Such an assignment would then remove any differences between the studies of the two groups.

Green and Woodhead then provided their own response to Willstätter in 1912.[65,66] Here, they refute Willstätter's claim that full reduction to the leucoemeraldine cannot be accomplished with titanium trichloride at lower temperatures and highlight various points in Willstätter's work that they view as problematic. "*In order to place the matter beyond doubt*", attempts were made to further reduce their leucoemeraldine samples with titanium trichloride at high temperature. Here, leucoemeraldine was prepared from the reduction of emeraldine by phenylhydrazine at a low temperature, after which the leucoemeraldine was treated with boiling titanium trichloride. As the results were not consistent with the further reduction of a mono quinoid species to the full leuco base, it was concluded that their original conclusions were fully supported.

It does not seem that Willstätter had anything further to say on the subject, at least not in the chemical literature. As such, the debate was generally considered decided. This is further supported by the fact that no further modifications to these structural models have been reported since.

CONCLUSIONS

Other than the modern understanding of the macromolecular nature of polyaniline, the final oxidative series as presented by Green and Woodhead still remain the currently accepted structural forms. Although the modern literature typically gives Green and Woodhead the credit for determining the structure and oxidative forms of polyaniline, with little to no mention of Willstätter, it is clear from the historical record that the primary structure determination was really accomplished by Willstätter. This is not to ignore the contributions of Green and Woodhead, who clearly made important corrections and additions to the oxidative series, as well as establishing the traditionally accepted nomenclature, but this was all accomplished by refinement of the previous structural models of Willstätter. Even at the end, Green was not convinced of the linear nature of these materials and only used the linear structures as a convenient working model. In contrast, Willstätter had eliminated other possible structures through careful analysis and fully believed in his linear model. In addition, although these models were presented as linear octomers, Willstätter made it clear that this was the minimum length necessary to explain the presented results and the actual materials could certainly be larger, thus paving the way for the eventual understanding of these materials as macromolecules. As such, Willstatter certainly deserves greater recognition for his important contributions to our modern understanding of polyaniline materials.

ACKNOWLEDGMENT

REFERENCES

1. E. M. Geniès, A. Boyle, M. Lapkowski, C. Tsintavis, Polyaniline: A Historical Survey. *Synth. Met.* **1990**, *36*, 139-182.
2. D. Li, J. Huang, R. B. Kaner, Polyaniline Nanofibers: A Unique Polymer Nanostructure for Versatile Applications. *Acc. Chem. Res.* **2009**, *42*, 135-145.
3. Y. Wang, Preparation and application of polyaniline nanofibers: an overview. *Polym. Intern.* **2018**, *67*, 650-669.
4. P. Zarrintaj, Z. Ahmadi, H. Vahabi, F. Ducos, M. Reza Saeb, M. Mozafari, Polyaniline in retrospect and prospect. *Mater. Today: Proc.* **2018**, *5*, 15852-15860.
5. N. Kumari Jangid, S. Jadoun, N. Kaur, A review on high-throughput synthesis, deposition of thin films and properties of polyaniline. *Euro. Polym. J.* **2020**, *125*, 109485.
6. J. Sebastian, J. M. Samuel, Recent advances in the applications of substituted polyanilines and their blends and composites. *Polym. Bull.* **2020**, *77*, 6641-6669.
7. E. N. Zare, P. Makvandi, B. Ashtari, F. Rossi, A. Motahari, G. Perale, Progress in Conductive Polyaniline-Based Nanocomposites for Biomedical Applications: A Review. *J. Med. Chem.* **2020**, *63*, 1-22.
8. Q. N. Al-Haidary, A. M. Al-Mokaram, F. M. Hussein, A. H. Ismail, Development of polyaniline for sensor applications: a review. *J. Phys.: Conf. Ser.* **2021**, *1853*, 012062.
9. S. C. Rasmussen, Electrically Conducting Plastics: Revising the History of Conjugated Organic Polymers. In *100+ Years of Plastics. Leo Baekeland and Beyond* (Eds.: E. T. Strom, S. C. Rasmussen), American Chemical Society: Washington, DC **2011**, pp. 147-163.
10. S. C. Rasmussen, Early History of Conductive Organic Polymers. In *Conductive Polymers: Electrical Interactions in Cell Biology and Medicine* (Eds.: Z. Zhang, M. Rouabhia, S. Moulton) CRC Press, Boca Raton, FL **2017**, pp. 1-21.
11. S. C. Rasmussen, Early history of Conjugated Polymers: From their Origins to the Handbook of Conducting Polymers. In *Handbook of Conducting Polymers*, 4th Ed (Eds.: J. R. Reynolds, T. A. Skotheim, B. Thompson), CRC Press: Boca Raton, FL **2019**, pp. 1-35.
12. S. C. Rasmussen, Conjugated and Conducting Organic Polymers: The First 150 Years. *ChemPlusChem* **2020**, *85*, 1412-1429.
13. S. C. Rasmussen, The Early History of Polyaniline: Discovery and Origins. *Substantia* **2017**, *1*(2), 99-109.
14. S. C. Rasmussen, Early History of Polyaniline—Revisited: Russian Contributions of Fritzsche and Zinin. *Bull. Hist. Chem.* **2019**, *44*, 123-133.
15. F. F. Runge, Ueber einige Producte der Steinkohlendestillation. *Ann. Phys. Chem.* **1834**, *31*, 513-524.
16. E. Simon, Ueber den flüssigen Storax (Styrax liquidas). *Ann. Pharm.* **1839**, *31*, 265-277.
17. S. C. Rasmussen, Revisiting the Early History of Synthetic Polymers: Critiques and New Insights. *Ambix* **2018**, *65*, 356–372.
18. P. Constantini, G. Belorgey, M. Jozefowicz, R. Buvet, Préparation, propriétés acides et formation de complexes anioniques de polyanilines oligomères. *C. R. Seances Acad. Sci.* **1964**, *258*, 6421-6424.
19. M. Jozefowicz, G. Belorgey, L.-T. Yu, R. Buvet, Oxydation et réduction de polyanilines oligomères. *C. R. Seances Acad. Sci.* **1965**, *260*, 6367-6370.
20. M.-F. Combarel, G. Belorgey, M. Jozefowicz, L.-T. Yu, R. Buvet, Conductivité en courant continu des polyanilines oligomers: Influence de l'état acide-base sur Ia conductivité électronique. *C. R. Seances Acad. Sci.* **1966**, *262*, 459-6370.
21. H. Rheineck, Ein Beitrag zur Kenntniss der Natur des Anilinschwarz. *Dinglers Polytech. J.* **1872**, *203*, 485-489.
22. *Verzeichnis der Beamten, Lehrer und Studirenden der königlich württembergiſchen Universität Tübingen in dem Sommerhalbjahr* **1863**. Tübingen, p. 27.
23. H. Rheineck, Ueber das Verhalten des Allantoïns zu Natrium. *Ann. Chem. Pharm.* **1865**, *134*, 219-228.

24. H. Rheineck, Ein Colorimeter. *Dinglers Polytech. J.* **1871**, *201*, 433-435.
25. H. Rheineck, Ueber die Gührungserscheinungen. *Dinglers Polytech. J.* **1871**, *202*, 282-287.
26. H. Rheineck, Ueber eine maßanalytische Beftimmung des Eisens und Ferrocyans. *Dinglers Polytech. J.* **1871**, *202*, 154-159.
27. H. Rheineck, Ein Beitrag zur Kenntniß der Natur des Anilinschwarz. *Polytech. Centralblatt* **1872**, *38*, 667-670.
28. H. Rheineck, Beitrag zur Kenntniss der Natur des Anilinschwarz. *Chemisches Centralblatt* **1872**, *43*, 295-296.
29. H. Rheineck, berichtet über Versuche, die er betreffs der Bildung von Anilinschwarz auf dem Gewebe angestellt hat. *Jahresbericht Leistungen. Chem. Tech.* **1873**, *18*, 710-711.
30. R. Nietzki, Ueber Anilinschwarz. *Ber. Dtsch. Chem. Ges.* **1876**, *9*, 616-620.
31. R. Nietzki, Ueber Anilinschwarz. *Ber. Dtsch. Chem. Ges.* **1876**, *9*, 1168-1170.
32. H.-D. Schwarz, Nietzki, Rudolf Hugo. *Neue Deutsche Biographie* **1999**, *19*, 248.
33. M. Kurz, Nietzki, Rudolf. *Historisches Lexikon der Schweiz* (HLS), Version 03.06.2010. https://hls-dhs-dss.ch/de/articles/045058/2010-06-03/ (accessed 09, 2021).
34. P. Weinmeister, Ed., *J. C. Poggendorff's Biographisch-Literarisches Handwörterbuch*, Vol. 5, Verlag Chemie: Leipzig, 1925, p 906.
35. E. Noelting, Rudolf Nietski 1847-1917. *Helvetica Chimica Acta* **1918**, *1*, 343-430.
36. J. Fritzsche, Vorläufige Notiz über einige neue Körper aus der lndigoreihe. *J. Prakt. Chem.* **1843**, *28*, 198-204.
37. R. Nietzki, Ueber Anilinschwarz. *Ber. Dtsch. Chem. Ges.* **1878**, *11*, 1093-1102.
38. R. Nietzki, Zur Darstellung der Chinone und Hydrochinone. *Ber. Dtsch. Chem. Ges.* **1877**, *10*, 1934-1935.
39. R. Nietzki, Zur Darstellung des Chinons. *Ber. Dtsch. Chem. Ges.* **1878**, *11*, 1102-1104.
40. A. Bernthsen, Heinrich Caro. *Ber. Dtsch. Chem. Ges.* **1912**, *45*, 1987-2042.
41. A. S. Travis, Heinrich Caro at Roberts, Dale & Co. *Ambix* **1991**, *38*, 113-134.
42. A. Bernthsen, Zum 70. Geburtstage von H. Caro. *Z. Angew. Chem.* **1911**, *24*, 1059-1064.
43. M. Wiedemann, Heinrich Caro. *Chem. Ind.* **1910**, *33*, 561.
44. H. Caro, Die Oxydation des Anilins. *Chemiker Zeitung* **1896**, *20*, 840.
45. H. Caro, Zur Kenntniss der Oxydation des Anilins. *Verh. Ges. Dtsch. Naturforsch. Aerzte* **1896**, *68*, 119-120.
46. R. Willstätter, C. W. Moore, Über Anilinschwarz. I. *Ber. Dtsch. Chem. Ges.* **1907**, *40*, 2665–2689.
47. E. Berl, Richard Willstätter. *Chem. Eng. News* **1942**, *20*, 954.
48. R. Robinson, Richard Willstätter. 1872-1942. *Obit. Notices Fellows R. Soc.*, **1953**, *8*, 609-634.
49. R. Robinson, Richard Willstätter. *J. Chem. Soc.* **1953**, 999-1026.
50. R. Adams, Richard Willstätter. *J. Am. Chem. Soc.* **1943**, *65*, 127-128.
51. R. Huisgen, Richard Willstätter. *J. Chem. Educ.* **1961**, *38*, 10-15.
52. R. Willstätter, S. Dorogi, Über Anilinschwarz. II. *Ber. Dtsch. Chem. Ges.* **1909**, *42*, 2147–2168.
53. H. Th. Bucherer. Über den Mechanismus der Indamin- und Azinsynthese. Bemerkungen zu der Abhandlung R. Willstätters über Anilinschwarz. *Ber. Dtsch. Chem. Ges.* **1907**, *40*, 3412–3419.
54. R. Willstätter, S. Dorogi, Über Anilinschwarz. III. *Ber. Dtsch. Chem. Ges.* **1909**, *42*, 4118–4151.
55. R. Willstätter, C. Cramer, Über Anilinschwarz. IV. *Ber. Dtsch. Chem. Ges.* **1910**, *43*, 2976–2988.
56. A. G. Green, A. E. Woodhead, Aniline-black and Allied Compounds. Part I. *J. Chem. Soc. Trans.* **1910**, *97*, 2388-2403.
57. A. G. Green, The Chemical Technology of Aniline Black. In *Seventh International congress of applied chemistry, London, May 27th to June 2nd, 1909*. Partridge & Cooper, Ltd.: London, **1910**, Sect IVb, pp. 83-84.
58. A. G. Green, The Chemical Technology of Aniline Black. *J. Soc. Dyers Colour.* **1909**, *25*, 188-192.
59. K. H. Saunders, Arthur George Green. *J. Soc. Dyers Colour.* **1941,** *57*, 364-366.
60. J. Baddiley, Arthur George Green. *J. Chem. Soc.* **1946,** 842-852.
61. K. H. Saunders, The Scientific and Technical Work of Professor A. G. Green, F.R.S. *J. Soc. Dyers Colour.* **1944**, *60*, 81-93.

62. R. J. Friswell, A. G. Green, On the Relation of Diaxobenaeneanilide to Anzidoazobenzene. *J. Chem. Soc., Trans.* **1909**, *95*, 2202-2215.
63. E. J. Cross, J. B. Speakman, Prof. F. M. Rowe, F.R.S. *Nature* **1947**, 159, 53.
64. R. Willstätter, C. Cramer, Über Anilinschwarz. V. *Ber. Dtsch. Chem. Ges.* **1911**, 44, 2162–2171.
65. A. G. Green, A. E. Woodhead, Anilinschwarz und seine Zwischenkorper. II.. *Ber. Dtsch. Chem. Ges.* **1912**, *45*, 1955-1958.
66. A. G. Green, A. E. Woodhead, Aniline-black and Allied Compounds. Part II. *J. Chem. Soc. Trans.* **1912**, *101*, 1117-1123.