

EARLY HISTORY OF POLYANILINE— REVISITED: RUSSIAN CONTRIBUTIONS OF FRITZSCHE AND ZININ (1)

Seth C. Rasmussen, Department of Chemistry and Biochemistry, North Dakota State University, Fargo, ND; seth.rasmussen@ndsu.edu

Introduction

Organic polymers and plastics comprise one of the most ubiquitous chemical technologies of modern society. While the bulk of commercial plastics are made of various saturated organic polymers that exhibit insulating behavior, conjugated polymers (Figure 1) are a less common class of organic plastic materials that are native semiconducting materials. In addition, such conjugated materials are capable of enhanced electronic conductivity (in some cases even quasi-metallic) upon either oxidation (p-doping) or reduction (n-doping) (2-5). As a result, conjugated polymers are organic macromolecules that combine the properties of traditional inorganic semiconductors with many of the desirable properties of organic plastics, including low production costs and mechanical flexibility (4, 5). The study and development of these materials has led to the current field of organic electronics, with technological applications including sensors, electrochromic devices, field effect transistors, organic photovoltaics (solar cells), and organic light-emitting diodes (OLEDs) (2-5).

Although conjugated polymers are typically viewed as quite modern materials, the earliest examples of these polymers date back to the early 19th century (4-8). In fact, it has been recently argued that polyaniline not only represents the first reported conjugated polymer, but also the oldest known example of a fully synthetic organic

macromolecule (7, 8). Species consistent with our modern understanding of polyaniline date to the 1834 work of German chemist F. Ferdinand Runge (1794-1867) (9), five years before the more commonly recognized synthesis of polystyrene (10). Of course, the long-chain, polymeric nature of *aniline black* (polyaniline) was not recognized until the early 1900s (5, 7), and the modern concept of the macromolecule was not introduced until the 1920s by the German chemist Hermann Staudinger (1881-1965) (11, 12).

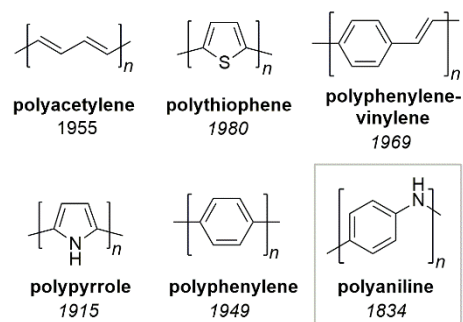


Figure 1. Parent conjugated polymers and the years of their first reports in the literature.

Although an in-depth early history of polyaniline up through the 1870s has been recently reported (7), that paper only touched on the aniline work of Nikolai Zinin in passing. In particular, neither the effect of greater accessibility of aniline via reduction of nitrobenzene nor Zinin's potential contributions to polyaniline itself were discussed. Thus, it seemed worthwhile to revisit

the Russian contributions to early polyaniline in greater detail, particularly as the bulk of discussions on early polyaniline history tend to focus on either German or English contributions. In order to fully recognize Russian contributions during the formative years of aniline polymerizations, the following will present the work of Carl Julius Fritzsche (1808-1871) and Nikolai Nikolaevich Zinin (1812-1880) over the period of 1840-1845, along with a discussion on the impact of these efforts on later polyaniline studies.

Polymerization of Aniline

As the efforts of Fritzsche and Zinin discussed below predate all knowledge of the polymerization processes involved, as well as the molecular structures of the polymeric materials in question, it is worthwhile to briefly review our modern understanding of aniline polymerization. The following thus presents what is currently known about the mechanistic details of the polymerization methods under discussion, as well as a brief introduction of both redox- and acid-doping of

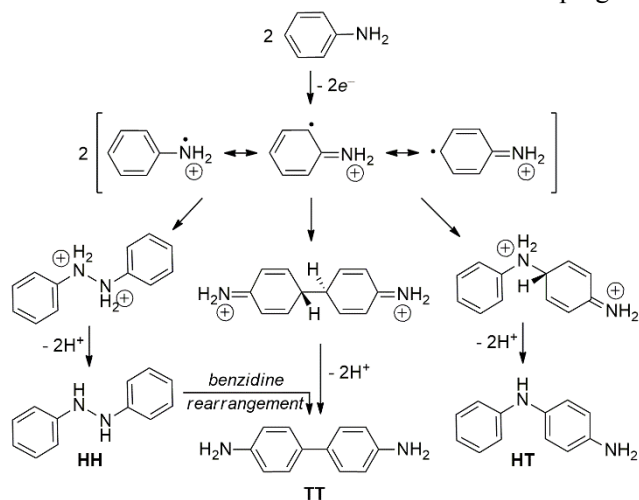


Figure 2. Initial dimerization of aniline.

polyaniline, in order to provide context to what will be presented in the subsequent sections.

Polyaniline is generated almost exclusively via oxidative polymerization (7, 13-18), which is a form of step-growth polymerization (19). In this process, the electron-rich aniline polymerizes anodically via either chemical or electrochemical oxidation of the π -system to form the corresponding radical cation, which can exist in multiple resonance forms (Figure 2). Spin density studies predict nearly equal distribution of the unpaired electron between the aniline nitrogen and the *para*-carbon

of the benzene ring (18), which can result in three possible couplings: nitrogen-nitrogen (head-to-head, HH); nitrogen-arene (head-to-tail, HT); and arene-arene (tail-to-tail, TT) (13-18). This initial coupling is then followed by deprotonation to generate the neutral dimer.

Diarylhydrazine products formed via HH coupling are not stable, particularly under acidic conditions. Under these conditions, the HH dimer is converted to the TT dimer via the benzidine rearrangement (14). Alternately, two equivalents of the HH dimer can be converted to azobenzene (Ph-N=N-Ph) and two equivalents of aniline via disproportionation. As such, HH units do not contribute to the production of polyaniline (15). Of the remaining two possible regiocouplings, TT coupling is favored over HT coupling at the high radical cation concentrations typical of most polymerization conditions (i.e. large excess of oxidant and low pH) (16, 17).

Polymerization then continues through oxidation of the neutral dimers to form new radical cations (Figure 3). The oligomeric radical cations again undergo coupling, either with simple monomeric radical cations or radical cations of other oligoanilines, to generate still larger oligoaniline species after deprotonation. Thus, the overall step-growth process propagates via sequential oxidation, coupling, and deprotonation steps to ultimately give polymeric products (7, 13-18).

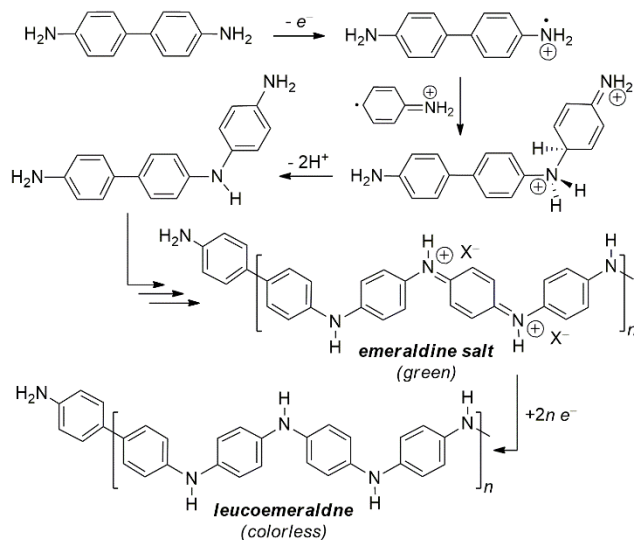


Figure 3. Continued polymerization mechanism from the initially produced dimer intermediates

As the polymer products undergo oxidation at lower potentials than either aniline or smaller oligomers, the materials generated via oxidative polymerization are initially produced in their oxidized state and require reduction in order to isolate the neutral form of the

polymer. The most common oxidized form of polyaniline is the half-oxidized emeraldine (Figure 3), which can exist as both the violet-blue emeraldine base or the green emeraldine salt. As strongly acidic media are most commonly used for aniline polymerizations, however, the emeraldine salt is the typical product initially generated.

Fritzsche – From Germany to Russia

Carl Julius Fritzsche (Figure 4) was born on October 29, 1808 (20) in Neustadt, Saxony (7, 21-26) (now part of Germany), near the city of Stolpen (21, 22). His father was a physician and the district medical officer for the cities of Stolpen and Hohenstein. His mother was from the prominent Struve family (22). Although his given name was Carl, he appeared to go by his middle name Julius as neither Carl nor the initial C is found among any of his many publications, the majority of which he authored as simply J. Fritzsche (27).



Figure 4. Carl Julius Fritzsche (1808-1871).

In the city where Fritzsche spent his childhood, there was no Gymnasium, so he was educated through private lessons until the age of 14. Choosing to pursue pharmacy, he then moved to nearby Dresden to become apprentice to his uncle Friedrich Adolph August Struve (1781-1840) at the Salomons-Apotheke (22, 23). Five years later, he moved to Berlin to manage the laboratory of Johann Gottfried August Helming (1770–1830) (22).

Although this was not strictly a scientific position, it enabled him to acquire a position as assistant to Eilhard Mitscherlich (1794-1863) at the University of Berlin in 1830 (7, 21-25).

It was in this position that Fritzsche is said to have developed his passion for science over the next two and a half years, largely due to his close relationship with Mitscherlich. It is also thought that Mitscherlich probably persuaded Fritzsche to enroll at Berlin in 1831 (22, 23), where he had already been attending lectures the previous year. In 1833, he acquired the Doctor of Philosophy (Dr. Phil.) degree with his “dissertatio de plantarum polline” (dissertation on plant pollen) (7, 21-25). As the subject of his doctorate was not chemistry, but botany, Mitscherlich is credited with all of Fritzsche’s chemical training (7, 24). In his dissertation, Fritzsche clearly expressed his strong appreciation of Mitscherlich (22):

In these times, I express the greatest affection for Mitscherlich. With the deepest gratitude I will remember him to the grave. With paternal precaution, he led my occupations and gave me the opportunity to complete my knowledge.

Fritzsche then emigrated to Russia in 1834 (7, 21-24), where he became the head of Struve’s Institute of Artificial Mineral Waters (7, 28) established by his uncle Friedrich in St. Petersburg (21). Here, he continued his scientific pursuits, with his name appearing for the first time in the *Mémoires des savants étrangers* of the St. Petersburg Academy of Sciences in 1836 (22). From that point on, all of his papers appeared initially in the publications of the Academy of Sciences, of which he became an adjunct member in 1838 (6, 21-23, 25). He was granted status as an extraordinary member in 1844 (6, 22, 23), and was appointed an academician (full member) in 1852 (7, 22, 23, 25) or 1853 (21). In addition to his decades of scientific activity in the Academy, he contributed his time to the Russian government through a number of service positions. This included serving as a member of the Imperial Commission for the Research and Utilization of the Caucasus Mineral Waters, as a chemist to the Medical Department, and as a consulting member of the Medical Council of the Minister of the Interior (22, 23). He also held various administrative posts within the Academy itself and served as a member of its Administrative Committee for three years (22).

Over the span of his career, he authored more than 60 papers, most covering various topics within organic chemistry (22, 23). His chemical work included research on various heterocyclic aromatic nitrogen compounds such as murexide and uric acid, and the hydrocarbons

of coal tar, as well as the work that is the focus of the current discussion, his studies on indigo and its derivatives (7, 21-25).

All of the efforts discussed below were carried out in a small, modest laboratory next to his residence (7, 21-24). This was largely due to the fact that the laboratory of the St. Petersburg Academy was very primitive, and there were almost no funds for its support (29). However, upon completion of the new and spacious chemical laboratory of the Academy in 1866 (7, 22, 25) or 1867 (23, 29), he outfitted and occupied shared facilities there with Nikolai Zinin (22-25).

Although Fritzsche had always enjoyed excellent health, he suffered a stroke in 1869 (7, 22-25). Afterwards he did recover to some degree, but still suffered from paralysis on one side, and his speech and memory suffered (7, 22, 23, 25). To his friends, who had always known him as sprightly and cheerful, he suddenly changed. Seeing the hopelessness of his situation, Fritzsche even suggested that he preferred death to such a life (22, 23). Nevertheless, he did continue to work for some time (22-24), even if he rarely appeared for Academy sessions after that point (22). In the following year, he returned home to Germany in order to seek physical and spiritual relief (22, 23, 25), finding the latter in the circle of those that gathered around him (22). His health continued to deteriorate, however, and he finally died on June 20, 1871 (7, 22-24, 30) in Dresden (26).

Aniline from Indigo

Indigo has been utilized as a dye and pigment throughout antiquity, with documented reports as far back as 27 BCE (31). The color of this dye originates from the organic species commonly known also as indigo. In addition to being the primary coloring agent of the indigo dye isolated from the indigo plant *Indigofera tinctorial*, it is also largely responsible for the color of the dye isolated from the plant woad, *Isatis tinctorial* (32, 33). Considering its long history, however, the indigo structure (Figure 5) was not determined until 1883 by Adolf Baeyer (1835-1917) (34).

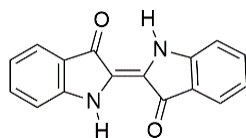


Figure 5. The chemical structure of indigo.

Fritzsche became interested in the chemistry of indigo sometime before 1839 (24), with his first paper on

the reactions of indigo appearing in January of that year (35). However, it is his second indigo paper in 1840, that is of interest here (36). Unlike his first paper, which investigated decomposition products resulting from treatment with acid, his second paper focused on the base-induced decomposition of indigo. In the process, he found that treating indigo with a hot, highly concentrated KOH (or NaOH) solution gave a salt mass of reddish-brown color. If this salt mass is then heated in a retort, it is converted to an oily material with the simultaneous distillation of aqueous ammonia. Further heating of the brown, oily liquid resulted in the distillation of a color-less product to leave a brown, resinous body remaining in the retort. The final colorless product was found to be ca. 18-20% of the original indigo. He decided to call this new product *Anilin* (36) after *anil* (7, 8, 24), an older name for the indigo plant introduced by the Portuguese, which can ultimately be traced back to Sanskrit origins.

Fritzsche went on to characterize the product as an oxygen-free base that formed light and highly crystalline salts when treated with acids. In the process, he reported the corresponding salts generated from HCl and oxalic acid. Fritzsche reported that, in its purest state, Anilin strongly refracts light and exhibits a strongly aromatic, but unpleasant odor. He further determined its specific gravity to be 1.028 and its boiling point to be 228° C (37). Finally, combustion analysis led to the formula C₁₂H₁₄N₂, a doubling of the modern C₆H₇N formula (38).

Although Fritzsche believed Anilin to be a new species, it is now understood that modern aniline was independently discovered by multiple chemists (7, 8, 24, 39-46). The first of these was in 1826 (42), when Otto Unverdorben (1806-1873) reported the isolation of an oil that he named *Crystallin* (43) via the dry distillation of indigo. Then, in 1834, F. Ferdinand Runge isolated a volatile oil from the distillates of coal tar that he named *Kyanol* (44). Thus, Fritzsche's report in 1840 marked the third isolation of this species.

During the publication of Fritzsche's report of Anilin in the *Journal für praktische Chemie* (36b), the editor Otto Erdmann (1804-1869) recognized the similarity of Anilin with Unverdorben's Crystallin, and highlighted this in a postscript published directly following Fritzsche's paper (45). Erdmann began by bemoaning the fact that authors place more effort on the report of new compounds resulting from the decomposition of natural species than investigation of the chemical processes involved in their production. To drive this point home, he then followed this with a list of the unknowns not

addressed by Fritzsche's publication, before going on to state (45):

These and other questions that have to be imposed remain undecided. However, the last of these can almost certainly be answered. Anilin is most probably no other body than *Krystallin* described by Unverdorben already 14 years ago... Unverdorben's description of *Krystallin* is not complete. However, the agreement between the properties of *Krystallin* and of Anilin given by him is so great that Herr Fritzsche, if there is a difference, had the obligation to prove it by specific experiments.

Erdmann then concluded his postscript with a side-by-side comparison of the known properties of the two species.

When Fritzsche's report was then republished in *Annalen der Chemie und Pharmacie* (36c), Justus von Liebig (1803-1873) added his own note to the end of the paper (46). This repeated Erdmann's paraphrased comments with Liebig's full agreement. Liebig, however, went even further than Erdmann, stating (46):

Herr Erdmann... must not be surprised at the methods of Herr Fritzsche. Herr Fritzsche is one of those who mines by robbery; when he learns that some chemist is engaged in an investigation promising him valuable results, he undertakes not to help or render him any services, or to help carry the burden, but, like the corsairs, tries to unburden him in a quite particular way.

It is interesting to note here that neither Erdmann or Liebig mention Runge's Kyanol. It could be concluded that it was the fact that Anilin and Crystallin were both isolated from indigo that drew the ready comparison and the fact that Kyanol came from another source made its relationship less obvious. Still, confirmation that Crystallin, Kyanol, and Anilin were indeed all the same species had to wait until 1843, when August Wilhelm Hoffmann (1818-1892) presented conclusive evidence to support this conclusion (39).

Fritzsche's Oxidation Products of Aniline

Regardless of any criticisms relating to his "rediscovery" of aniline, Fritzsche did go on to study the oxidation products of his Anilin, something Unverdorben did not pursue in his previous isolation of Crystallin. Both Unverdorben (42) and Fritzsche (36) had observed the air oxidation of aniline to give a yellow color. Fritzsche, however, found that this yellow product was just an intermediate, with longer exposure times leading to a transition of the yellow color to brown, ultimately leading to the production of a resinous dark mass.

Extending this to the purposeful addition of oxidizing agents, Fritzsche found that the addition of nitric acid to aniline resulted in the formation of a blue or green material (36). This formation depended on the specific reaction conditions, but the resulting material did not appear to be indigo. However, its study was limited by the small quantities formed, and the fact that the solid continued to react with nitric acid resulting in decomposition.

Continuing his investigations, he found that dissolving aniline salts in chromic acid (H_2CrO_4 , usually as a H_2SO_4 solution) resulted in the formation of a dark green precipitate, which ultimately became a dark blue-black (36). Unlike the case of nitric acid, the colored solid could be reproducibly produced under a variety of conditions, even in fairly dilute solutions. Combustion analysis revealed that the precipitate contained significant amounts of chromium, however, even for samples obtained from acid solutions.

Lastly, he treated aniline salts with potassium permanganate, resulting in the deposition of a brown precipitate containing manganese oxide. Fritzsche admitted that he had not been able to study these various color-forming reactions in much detail and planned to return to these in later publications (36).

While he did not follow up on most of these specific observations reported in 1840 (36), he did return to the treatment of aniline with chromic acid in 1843 (47). In this second report, he admitted that while he was able to reproducibly obtain the previously reported green product via the treatment of aniline with chromic acid, he was unable to obtain products of consistent composition. However, he did recognize that the product composition was affected by both the amount of chromic acid used, as well as the amount of other acids involved, even if he didn't understand exactly how these variables changed the nature of the products generated. Thus, he stated (47):

Apart from the fact that the products are different in appearance, as one uses more or less chromic acid accordingly, or applies a greater or less excess of another acid, even apparently similar products give very different results in analysis, to which I still miss the key.

Fritzsche was much more successful, however, with the treatment of aniline with potassium chlorate (47). Thus, he found that the addition of an HCl solution of potassium chlorate to an aniline salt in alcohol resulted in the formation of a beautiful blue precipitate. If this product was then filtered and washed with alcohol, the blue color turned green, becoming dark green upon dry-

ing. Analysis of the product's composition 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 ($X = Cl^-$) (47).

Lastly, Fritzsche reported that he had also produced analogous products via the successful application of H_2SO_4 solutions of either potassium bromate or potassium iodate (47). This 1843 report, however, seemed to be the last of Fritzsche's efforts concerning the oxidation products of aniline. Afterwards, he moved onto other subjects and focused his efforts elsewhere.

Zinin – Chemist by Dictate

Nikolai Nikolaevich Zinin (Figure 6) was born on August 25, 1812 (29, 48-50) in Shusha, a small town in the far southeast of the Russian Empire, located in the Caucasus mountains (29, 49-52). Shortly after his birth, both of his parents died (29, 50, 51), leaving him in the care of his step-sisters (50). These too, he lost a few years later in an epidemic (29, 50), after which Zinin was sent to live with his uncle in Saratov, on the Volga River (29, 50-53). It was in Saratov that Zinin received his early education, where it has been said that he excelled in Latin, mathematics, and physics (50, 51).



Figure 6. Nikolai Nikolaevich Zinin (1812-1880).

Although he initially planned to attend the St. Petersburg School of Engineering and Communication, the sudden death of his uncle left him without the necessary

funds. Instead, he entered Kazan University in 1830 (29, 50-52), which was much less expensive than an institution in the northern capital. Zinin began his work at Kazan in the mathematical division under Lobachevskii, ultimately taking his *kandidat* degree in physics and mathematics in 1833 (29, 50-53), with a dissertation on the perturbation of the elliptical motions of planets (51-53). He was then appointed assistant in physics, before being made lecturer in analytical mechanics six months later. Teaching duties in hydrostatics and hydrodynamics were then added the following year (29, 50, 53).

About this time, however, the administration of the university had decided that the current professor of chemistry, Ivan Ivanovich Dunaev, needed to be replaced (51-54). Zinin had previously taken some courses in chemistry under Dunaev (51), and the administration determined that Zinin should be Dunaev's replacement (51-54). Thus, Zinin was relieved of his other teaching duties in 1835 and was ordered to teach only chemistry (50, 51).

Meanwhile Zinin was also preparing for his examinations for the *magistr* degree (i.e., master's degree), which he passed in April 1835 (51). For his subsequent *magistr* dissertation, the faculty then gave Zinin the topic "The Phenomena of Chemical Affinity and the Superiority of Berzelius's Theory about Constant Chemical Proportions over the Chemical Statics of Berthollet" (51, 53). His resulting dissertation, which he successfully defended in October 1836, was theoretical in nature and involved no laboratory work (51-53, 55). Zinin thus received the degree *magistr* of physical-mathematical sciences and was then quickly appointed as adjunct in 1837 (50-53).

Permission was then requested from the Ministry of Education in early 1837 to send Zinin abroad for two years for advanced training in chemistry (50, 51, 53). The request was granted and Zinin was sent to Europe in September 1837 (29, 51, 52). For the next three years, he visited chemical laboratories in Germany, Switzerland, France, and England, and also devoted attention to the current developments in medicine. In the process, he spent considerable time in Liebig's laboratory in Giessen (29, 50-55). Zinin's experience in Liebig's laboratory profoundly affected him and it was here that he began his career in chemical research (52), studying the reactions of benzoyl compounds (29, 55).

Zinin returned to Russia in late 1840, arriving in St. Petersburg in September (29, 50, 51, 53). There he sat

for examinations for the doctoral degree at St. Petersburg University. By early November, Zinin had successfully completed the examinations and then quickly began to write his dissertation (51-53). He defended a dissertation based on the work he had carried out in Liebig's laboratory at the end of January 1841 (29, 50, 51, 53), for which he received his doctorate from St. Petersburg. Zinin then returned to Kazan where he was appointed to the chair of chemical technology (29, 49-55).

Zinin only remained at Kazan until 1847, when he was offered the chair in chemistry at the Medical-Surgical Academy in St. Petersburg (29, 50-55). He thus moved to St. Petersburg in 1848, during which time Zinin carried out his research in his private laboratory at home (29, 50), a room described as overflowing with apparatus, books, chemicals and equipment (29). He continued to work in his private laboratory until the Academy of Sciences built a new chemical laboratory in 1867 (50) and he was appointed to be Director of the Chemical Laboratory (29, 52).

Zinin played an active role in the formation of the Russian Physico-Chemical Society in 1868, and served as its President for the first ten years (52, 54). He retired from the Medical-Surgical Academy in 1874 and devoted himself to work in the St. Petersburg Academy of Sciences (29), of which he had been elected adjunct in chemistry in 1855 (50, 53). He was then elected extraordinary member in 1858 (50, 53) and academician in 1865 (50, 52, 53). Zinin continued active chemical work until the autumn of 1878, at which time he became ill (29, 50). He continued to hope that he would be able to return to his studies, but he gradually grew worse, and ultimately died on February 6, 1880 (29, 50).

Reduction of Nitrobenzene

Upon his return to Kazan in 1841, Zinin was faced with developing new research projects. The previous work he had carried out in Liebig's laboratory had utilized oil of bitter almonds (primarily benzaldehyde) as a key reagent, a material whose import into Russia was prohibited due to its toxicity (51, 52, 56). As a result, he instead began investigations of other related organic compounds, beginning with the action of hydrogen sulfide on nitroaromatics such as nitrobenzene and nitronaphthalene.

First reported in the spring of 1842 (57a), Zinin found that the addition of hydrogen sulfide (H_2S) to nitrobenzene in ammonia-saturated ethanol resulted

in the formation of a mixture of elemental sulfur and yellow needles (57). After cooling at 0°C , this mixture "almost completely solidified to a mass of fine, yellow needles." Letting this stand for a day, he then boiled the initial mixture and decanted the resulting solution from any solid sulfur. This isolated liquid fraction was then distilled to give an oil described as heavier than water and yellowish in color (57). Our modern understanding of this chemical process is outlined in Figure 7.

Zinin characterized the oil as an oxygen-free base that was insoluble in water, but miscible in either alcohol or ether, and distilled with a boiling point of ca. 200°C (37). Combustion analysis led to the formula $\text{C}_{12}\text{H}_{14}\text{N}_2$, a doubling of the modern $\text{C}_6\text{H}_7\text{N}$ (38), and he was also able to successfully form and characterize several salts of the base (sulphate, HCl , and mercuric chloride) (57). He ultimately named the oil *Benzidam*, based on its determined composition (57).

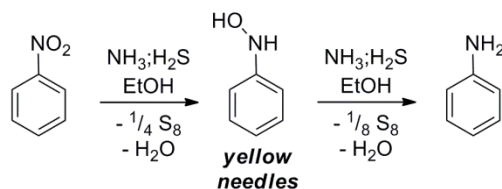


Figure 7. Modern representation of Zinin's reduction of nitrobenzene.

After reading Zinin's initial paper for the St. Petersburg Academy of Science (57a), Fritzsche added a short note on Zinin's paper when it was then published in the *Journal für praktische Chemie* (57b). In its entirety, Fritzsche's note stated (58):

To the most interesting treatise of Mr. Zinin, I must add the remark that the base designated as new under the name of *Benzidam* is nothing but *Anilin*. In its properties, as well as in its composition and the composition of the salts, *Benzidam* agrees so perfectly with *Anilin* that there can be no doubt about its identity.

Of course, one can imagine that Fritzsche's own rebukes from Erdmann (45) and Liebig (46) might have been on his mind as he composed this statement. However, it is also interesting to note that Fritzsche speaks only of his own *Anilin* here and includes no mention of Unverdorben's *Crystallin* (42) or Runge's *Kyanol* (44). Nevertheless, all of these comparisons were confirmed the following year when Hoffmann presented strong evidence that *Crystallin*, *Kyanol*, *Anilin*, and *Benzidam* were indeed all the same compound (39). It should also be pointed out that while Fritzsche and Zinin ultimately shared space in the Academy of Sciences laboratory (22-25), in 1842 they were still separated by over 700

miles (Zinin in Kazan; Fritzsche in St. Petersburg) and Fritzsche's note may have been their first professional interaction.

Zinin's Oxidation of Aniline

Although Zinin did not specifically investigate the oxidation of aniline in the same way that Fritzsche did, he does make reference to reactivity in his papers which likely refer to oxidation processes. The first such statement occurs when he provides the basic properties of his isolated Benzidam, in particular its air stability. Thus, he states (57) that it is

preserved after some time in contact with atmospheric air, but instantly turns red with strong nitric acid.

This is in contrast with the previous report of Fritzsche that nitric acid caused the conversion of aniline to a blue or green material (36).

The second statement comes when discussing the stability of the isolated aniline salts. In this case, he notes that the sulfate salt is not all that air stable, stating: "[The crystals] turn rose red in air, especially when wet" (57).

It should be pointed out that this is in stark contrast to the analogous HCl salt, which does not show this reactivity.

Thus, Zinin reports the formation of red products under two separate cases when aniline is under the influence of both air (i.e., oxygen) and an oxidizing acid. However, the identities of these red species are unknown and Zinin reported no attempts to analyze these products. What is clear is that these are not examples of polyaniline, as the macromolecule does not possess red forms under any known conditions (13).

A potential answer could come from later studies by first Heinrich Caro (1834-1910) in 1896 (59) and then Richard Willstätter (1872-1942) in the early 1900s (60). In efforts to determine the structure and identity of aniline black and other aniline oxidation products, they oxidized aniline under non-optimal conditions and then tried to identify products as potential intermediates in the production of aniline black. In the process, Caro successfully identified the yellow oxidized dimer phenylquinonediimide (Figure 8) (59), while Willstätter later isolated a blue compound which he concluded to be the half-oxidized tetramer (60). This tetramer could then be further oxidized to a red form (Figure 8).

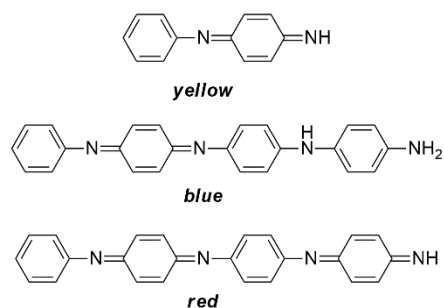


Figure 8. Oligoanilines known between 1896-1907.

The conditions under which Zinin observed his red species could be viewed as consistent with low levels of oxidant that could result in oligomeric, rather than polymeric, products. For this reason, Zinin's red product could well be the same as Willstätter's. Of course, this is only a proposed identity and it is not feasible to confirm this possibility with any certainty.

Impact of Fritzsche and Zinin on Later Polyaniline Work

At the most basic level, both Fritzsche and Zinin contributed to monomeric aniline, an obvious critical factor in the production of its macromolecule. Of the two methods for the production of aniline, Zinin's had by far the greatest impact, as this represented the first viable method for the mass production of aniline. As pointed out by others (40, 51, 53), Zinin's synthesis of aniline later became the key step in the synthesis of many coal tar dyes. This is true of polyaniline as well, which coincidentally represents the very first synthetic aniline dyes, as demonstrated by Runge in 1834 (9). Both Runge and Fritzsche made specific comments that their efforts were limited by the small quantities of the materials generated, with Runge specifically referring to the fact that significant amounts of aniline salts would be needed to make his dyes viable (9).

Interestingly, after Hoffmann had confirmed that Crystallin, Kyanol, Anilin, and Benzidam were all the same compound, he felt that only the original name Crystallin might be retained, although he favored the name *Phenamid* (39). Still, by 1845 Zinin was also using Fritzsche's name Anilin (61) and ultimately it was the name that endured as the modern aniline, the preferred IUPAC name for this aromatic amine. Thus, both men left lasting marks on the chemistry of aniline.

In terms of the aniline oxidation products, although Runge was the first to report materials now recognized as polyaniline (9), Fritzsche was still only the second to do so (36, 47). Furthermore, he was the first to produce these materials via potassium chlorate (47), which later became the basis for the production of the first commercial polyaniline dyes in the early 1860s (7). In addition, Fritzsche was the first ever to determine the chemical composition of a polyaniline sample (47) and did so with an empirical formula nearly identical to that expected by our modern knowledge of these materials (5, 7). As such, this was the first step in the ultimate determination of the structure and identity of these materials, even if it did take another 60 years for such determinations to really begin to take shape (4-8).

Acknowledgements

I would like to thank David Lewis for inviting me to participate in his HIST Award Symposium at the 256th ACS Meeting in Boston, thus leading to the current manuscript. In addition, thanks to Alan J. Rocke (Case Western Reserve University) and Ian Rae (University of Melbourne) for helpful feedback during the oral presentation of this work. Lastly, I would like to thank the Department of Chemistry and Biochemistry of North Dakota State University (NDSU) for continued support of my historical research, and the NDSU Interlibrary Loan Department, that always helps to track down various elusive and somewhat obscure sources.

References and Notes

- Presented at the 256th National Meeting of the American Chemical Society, Boston, MA, Aug. 21, 2018, HIST 23 in the HIST Award Symposium Honoring David Lewis.
- T. A. Skotheim and J. R. Reynolds, Eds., *Handbook of Conducting Polymers*, 3rd ed., CRC Press, Boca Raton, FL, 2007.
- I. F. Perepichka and D. F. Perepichka, Eds., *Handbook of Thiophene-based Materials*, John Wiley & Sons, Hoboken, NJ, 2009.
- S. C. Rasmussen, "Early History of Conductive Organic Polymers," in Z. Zhang, M. Rouabhia and S. Moulton, Eds., *Conductive Polymers: Electrical Interactions in Cell Biology and Medicine*, CRC Press, Boca Raton, FL, 2016, Ch. 1, pp 1-21.
- S. C. Rasmussen, "Early history of Conjugated Polymers: From their Origins to the Handbook of Conducting Polymers," in J. R. Reynolds, B. Thompson and T. Skotheim, Eds., *Handbook of Conducting Polymers*, 4th Ed., CRC Press, Boca Raton, FL, 2019, Ch. 1.
- S. C. Rasmussen, "Electrically Conducting Plastics: Revisiting the History of Conjugated Organic Polymers," in E. T. Strom and S. C. Rasmussen, Eds., *100+ Years of Plastics. Leo Baekeland and Beyond*, ACS Symposium Series 1080, American Chemical Society, Washington, DC, 2011, pp 147-163.
- S. C. Rasmussen, "The Early History of Polyaniline: Discovery and Origins," *Substantia*, **2017**, 1(2), 99-109.
- S. C. Rasmussen, "Revisiting the Early History of Synthetic Polymers: Critiques and New Insights," *Ambix*, **2018**, 65, 356-372.
- F. F. Runge, "Ueber einige Produkte der Steinkohlendestillation," *Ann. Phys. Chem.*, **1834**, 31, 513-524.
- E. Simon, "Ueber den flüssigen Storax (Styrax liquidas)," *Ann. Pharm.*, **1839**, 31, 265-277.
- D. Feldman, "Polymer History," *Designed Monomers Polym.*, **2008**, 11, 1-15.
- Y. Furukawa, *Inventing Polymer Science: Staudinger, Carothers, and the Emergence of Macromolecular Chemistry*, University of Pennsylvania Press, Philadelphia, 1998, pp 48-92.
- E. M. Geniès, A. Boyle, M. Lapkowski and C. Tsintavis, "Polyaniline: A Historical Survey," *Synth. Met.*, **1990**, 36, 139-182.
- C. L. Heth, D. E. Tallman and S. C. Rasmussen, "Electrochemical Study of 3-(*N*-alkylamino)thiophenes: Experimental and Theoretical Insights into a Unique Mechanism of Oxidative Polymerization," *J. Phys. Chem. B*, **2010**, 114, 5275-5282.
- D. Wei, C. Kyarnstrom, T. Lindfors, L. Kronberg, R. Sjöholm and A. Ivaska, "Electropolymerization Mechanism of *N*-methylaniline," *Synth. Met.*, **2006**, 156, 541-548.
- R. L. Hand and R. F. Nelson, "Anodic Oxidation Pathways of *N*-alkylanilines," *J. Am. Chem. Soc.*, **1974**, 96, 850-860.
- J. Bacon and R. N. Adams, "Anodic Oxidations of Aromatic Amines. III. Substituted Anilines in Aqueous Media," *J. Am. Chem. Soc.*, **1968**, 90, 6596-6599.
- G. D'Aprano, E. Proynov, M. Leboeuf, M. Leclerc and D. R. Salahub, "Spin Densities and Polymerizabilities of Aniline Derivatives Deduced from Density Functional Calculations," *J. Am. Chem. Soc.*, **1996**, 118, 9736-9742.
- The distinction between the two primary polymerization mechanisms, step-growth and chain-growth polymerization, was introduced by Paul J. Flory (1910-1985) in 1953: P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953, p 38.
- October 17, 1808, by the Julian Calendar.
- J. C. Poggendorff, *Biographisch-Literarisches Handwörterbuch zur Geschichte der Exacten Wissenschaften*, Vol. 1. J. A. Barth, Leipzig, 1863, pp 808-809.

22. A. Butlerow, "Carl Julius Fritzsche," *Ber. Dtsch. Chem. Ges.*, **1872**, 5, 132-136.
23. A. V. Harcourt, "Anniversary Meeting, March 30th, 1872," *J. Chem. Soc.*, **1872**, 25, 341-364.
24. F. E. Sheibley, "Carl Julius Fritzsche and the Discovery of Anthranilic Acid, 1841," *J. Chem. Educ.*, **1943**, 20, 115-117.
25. D. E. Lewis, *Early Russian Organic Chemists and Their Legacy*, Springer Briefs in Molecular Science: History of Chemistry, Springer, Heidelberg, 2012, p 45.
26. B. W. Feddersen and A. J. von Oettingen, Eds, *J. C. Poggendorff's Biographisch-Literarisches Handwörterbuch zur Geschichte der Exacten Wissenschaften*, Vol. 3, J. A. Barth, Leipzig, 1898, p 481.
27. Although some publications give the alternate spelling of Fritsche.
28. Fritzsche's uncle Friedrich A. A. Struve, a doctor of medicine and pharmacist from Neustadt, was a pioneer in the commercialization of artificial mineral water. Together with Rudolf Bloch, he established the first institution for artificial mineral water curatives in Dresden in 1818, with additional institutions later added in Leipzig, Berlin, Brighton (England), Königsberg, Warsaw, Moscow, St. Petersburg, and Kiev. All of these later institutes were overseen by students of Struve. See (a) *Allgemeine Deutsche Biographie*, Vol. 36, Duncker & Humblot, Leipzig, 1893, pp 676-677; (b) W. Kirkby, *The Evolution of Artificial Mineral Waters*, Jewsbury & Brown, Manchester, UK, 1902, pp 33, 92-93.
29. H. M. Leicester, "N. N. Zinin, an Early Russian Chemist," *J. Chem. Educ.*, **1940**, 17, 303-306.
30. June 8, 1871, by the Julian Calendar.
31. M. V. Orna, "Historic Mineral Pigments: Colorful Benchmarks of Ancient Civilizations," in Seth C. Rasmussen, Ed., *Chemical Technology in Antiquity*, ACS Symposium Series 1211, American Chemical Society, Washington, DC, 2015, Ch. 2, pp 17-69.
32. P. E. McGovern and R. H. Michel, "Royal Purple Dye: The Chemical Reconstruction of the Ancient Mediterranean Industry," *Acc. Chem. Res.*, **1990**, 23, 152-158.
33. Z. C. Koren, "Modern Chemistry of the Ancient Chemical Processing of Organic Dyes and Pigments," in *Chemical Technology in Antiquity*, Seth C. Rasmussen, Ed., *Chemical Technology in Antiquity*, ACS Symposium Series 1211, American Chemical Society, Washington, DC, 2015, Ch. 7, pp 197-217.
34. A. Baeyer, "Ueber die Verbindungen der Indigogruppe," *Ber. Dtsch. Chem. Ges.*, **1883**, 16, 2188-2204.
35. J. Fritzsche, "Vorläufige Notiz über ein neues Zersetzungsproduct des Indigo durch Salpetersäure," (a) *Bull. Sci. Acad. Imp. Sci. St. Petersb.*, **1839**, 5, 159-160; (b) *J. Prakt. Chem.*, **1839**, 16, 507-508.
36. J. Fritzsche, (a) "Ueber das Anilin, ein neues Zersetzungsproduct des Indigo," *Bull. Sci. Acad. Imp. Sci. St. Petersb.*, **1840**, 7, 161-165; (b) "Ueber das Anilin, ein neues Zersetzungsproduct des Indigo," *J. Prakt. Chem.*, **1840**, 20, 453-457; (c) "Ueber das Anilin, ein neues Zersetzungsproduct des Indigo," *Ann. Chem. Pharm.*, **1840**, 36, 84-88.
37. As determined by modern means, the density of aniline is 1.0297 g/mL, with a boiling point of 184.13 °C.
38. Such doubling of formulas was typical of the time period, usually the result of utilizing an atomic weight of 6 for carbon.
39. A. W. Hofmann, "Chemische Untersuchung der organischen Basen im Steinkohlen-Theeröl," *Ann. Chem. Pharm.*, **1843**, 47, 37-87.
40. H. Dussauce, "Aniline—Its History, Properties, and Preparation," *Sci. Am.*, **1867**, 17, 321-322.
41. C. M. Jackson, "Synthetical Experiments and Alkaloid Analogues: Liebig, Hofmann, and the Origins of Organic Synthesis," *Hist. Stud. Nat. Sci.*, **2014**, 44, 319-363.
42. O. Unverdorben, "Ueber das Verhalten der organischen Körper in höheren Temperaturen," *Ann. Phys. Chem.*, **1826**, 8, 397-410.
43. Although most authors give the name as *Krystallin*, Unverdorben clearly spelled it *Crystallin* in his original 1826 paper. The use of the more common alternate spelling dates as far back as the 1840 postscript by Erdmann (see Ref. 45).
44. F. F. Runge, "Ueber einige Produkte der Steinkohlendestillation," *Ann. Phys. Chem.*, **1834**, 31, 65-78.
45. [O.] Erdmann, "Nachschrift," *J. Prakt. Chem.*, **1840**, 20, 457-459.
46. J. Liebig, "Bemerkung zu vorstehender Notiz," *Ann. Chem. Pharm.*, **1840**, 36, 88-90.
47. J. Fritzsche, "Vorläufige Notiz über einige neue Körper aus der Indigoreihe," (a) *Bull. Classe phys.-math. Acad. Sci. St.-Petersbourg*, **1843**, 1, 103-108; (b) *J. Prakt. Chem.* **1843**, 28, 198-204.
48. August 13, 1812, by the Julian Calendar.
49. J. C. Poggendorff, *Biographisch-Literarisches Handwörterbuch zur Geschichte der Exacten Wissenschaften*, Vol. 2, J. A. Barth, Leipzig, 1863, p 1415.
50. A. M. Butlerow and A. P. Borodin, "Nikolaus Nikolajewitsch Zinin," *Ber. Dtsch. Chem. Ges.*, **1881**, 14, 2887-2908.
51. N. M. Brooks, "Nikolai Zinin and Synthetic Dyes: The Road not Taken," *Bull. Hist. Chem.*, **2002**, 27, 26-36.
52. Ref. 25, pp 42-44.
53. N. M. Brooks, "Nikolai Zinin At Kazan University," *Ambix*, **1995**, 42, 129-142.

54. S. N. Vinogradov, "Chemistry at Kazan University in the Nineteenth Century: A Case History of Intellectual Lineage," *Isis*, **1965**, *56*, 168-173.
55. D. E. Lewis, "The University of Kazan-Provincial Cradle of Russian Organic Chemistry. Part I: Nikolai Zinin and the Butlerov School," *J. Chem. Educ.*, **1994**, *71*, 39-42.
56. The toxicity of oil of bitter almonds is due to a small amount of cyanide content (ca. 0.5% by weight).
57. (a) N. Sinin, "Beschreibung einiger neuer organischer Basen, dargestellt durch die Einwirkung des Schwefelwasserstoffs auf Verbindungen der Kohlenwasserstoffe mit Untersalpetersäure," *Bull. Sci. Acad. Imp. Sci. St. Petersb.*, **1842**, *10*, 273-285; (b) N. Zinin, "Beschreibung einiger neuer organischer Basen, dargestellt durch die Einwirkung des Schwefelwasserstoffs auf Verbindungen der Kohlenwasserstoffe mit Untersalpetersäure," *J. Prakt. Chem.*, **1842**, *27*, 140-153; (c) N. Zinin, "Organische Salzbasen, aus Nitronaphtalose und Nitrobenzid mittelst Schwefelwasserstoff entstehend," *Ann. Chem. Pharm.*, **1842**, *44*, 283-287.
58. J. Fritzsche, "Bemerkung zu vorstehender Abhandlung des Hrn. Zinin," *J. Prakt. Chem.*, **1842**, *27*, 153.
59. H. Caro, "Zur Kenntniss der Oxydation des Anilins," *Verh. Ges. Dtsch. Naturforsch. Ärzte*, **1896**, *68*(part II, 1st half), 119-120.
60. R. Willstätter, and C. W. Moore, "Über Anilinschwarz. I.," *Ber. Dtsch. Chem. Ges.*, **1907**, *40*, 2665-2689.
61. N. Zinin, "Ueber das Azobenzid und die Nitrobenzinsäure," *J. Prakt. Chem.*, **1845**, *36*, 93-107.

About the Author

Seth C. Rasmussen is Professor of Chemistry at North Dakota State University (NDSU) in Fargo. He received his B.S in chemistry from Washington State University in 1990, before continuing his graduate studies at Clemson University under Prof. John D. Petersen. After completing his Ph.D. in 1994, he moved to the University of Oregon to study conjugated organic polymers as a postdoctoral associate under Prof. James E. Hutchison. He then accepted a teaching position at the University of Oregon in 1997, before moving to join the faculty at NDSU in 1999. Attaining the rank of full professor in 2012, Prof. Rasmussen also spent the spring of 2018 as a Fulbright Senior Scholar and visiting professor at the Centre for Organic Electronics of the University of Newcastle, Australia. Active in the fields of materials chemistry and the history of chemistry, his research interests include the design and synthesis of conjugated materials, photovoltaics (solar cells), organic light emitting diodes, the history of materials, chemical technology in antiquity, and the application of history to chemical education. Prof. Rasmussen served as the Program Chair for the History of Chemistry (HIST) division of the American Chemical Society from 2008 to 2017 and currently serves as the HIST Chair-Elect. In addition, he serves as the series editor for the book series *Springer Briefs in Molecular Science: History of Chemistry* and *Perspectives on the History of Chemistry*, as an editor of the journal *Cogent Chemistry*, and on the advisory board for the journal *Substantia: An International Journal of the History of Chemistry*.

Erratum

In the article "On the Origins of a Tool for Chemists, The Dean-Stark Apparatus," (this Journal, **2013**, *38*(1), 67-72), one of the inventors of the apparatus was named incorrectly. The Dean of the apparatus was Ernest Woodward Dean (1888-1959), not Edward Woodward Dean as printed in the article.