From Manchester to Massachusetts via Mulhouse: The Transatlantic Voyage of Aniline Black

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During the 18th and 19th centuries the introduction of new technologies into countries anxious to industrialize or retain their competitiveness in existing markets was the principal feature of modernization in Europe and North America, especially in the textile industry.[1] The routes of this technology transfer were varied. They involved industrial espionage, legal and illegal exports of machinery and designs, patent agreements (and infringements), and cartel arrangements. Sometimes transfer occurred because a particular invention was not appreciated, or readily applicable, in the country of its origins. In the case of the dyestuff (or pigment) known as "aniline black," many of these elements are present. Its discovery in Lancashire, Great Britain, was a consequence of the rise of a new high-technology industry, the production of synthetic dyestuffs. However, its widespread application was delayed for over a decade because the process was much better suited to the traditional methods of printing with hand blocks than to the new high-speed steam-driven roller printing machines to be found in Britain's northwest and, in increasing numbers, in the United States (see fig. 1). The result was that

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[1]Nathan Rosenberg first tackled the issue of technology transfer in "Economic Development and Transfer of Technology: Some Historical Perspectives," *Technology and Culture* 11 (October 1970): 551–75. For the impact on the early U.S. textile industry, see David J. Jeremy, *Transatlantic Industrial Revolution: The Diffusion of Textile Technologies between Britain and America, 1790–1830* (Cambridge, Mass., 1981). A useful survey of the 19th century will be found in David J. Jeremy, ed., *International Technology Transfer* (Aldershot, Hampshire, 1990).

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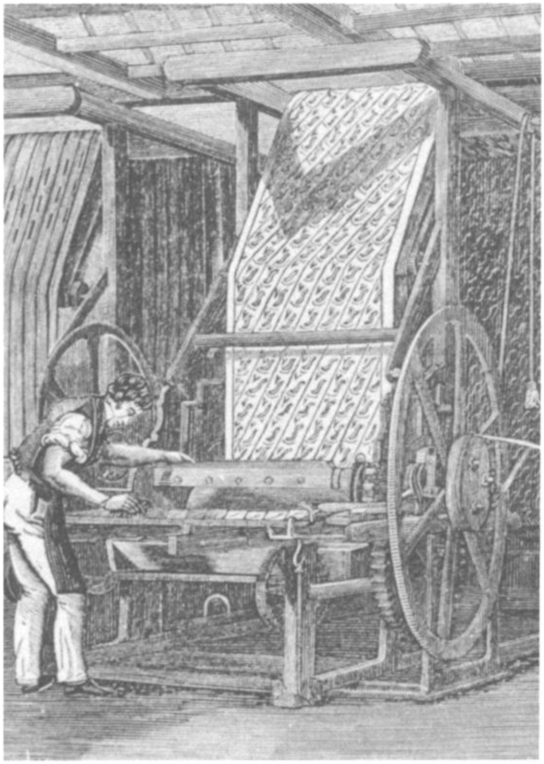

FIG. 1.—Mass production of printed cotton goods was based on the adoption of power-driven machinery in the early 1800s. Mechanized calico (cotton) printing was quickly established in Britain and the United States, but less rapidly in many parts of mainland Europe, where block printing, which was associated with better-quality goods, remained prevalent until the 1870s. This determined where the first aniline black processes could be introduced with moderate success. (George S. White, *Memoir of Samuel Slater, the Father of American Manufactures. Connected with a History of the Rise and Progress of the Cotton Manufacture in England and America. With Remarks on the Moral Influence of Manufactories in the United States* [Philadelphia, 1836], p. 395, detail.)

aniline black first became popular among printers on mainland Europe, where mechanization was less rapid, from as early as 1862–63. These printers were not slow in appreciating, and profiting from, the beneficial qualities of the brilliant black, that unlike the other coal-tar colors was far more suited to cellulosic material (cotton) than to animal fibers (wool and silk).

The earliest true synthetic dyestuffs were prepared by oxidizing the amino compound aniline, made in two steps from benzene that was extracted from coal tar (since the benzene was contaminated with other hydrocarbons, additional amino compounds, especially toluidine, were also present). William Perkin discovered the first aniline colorant, later known as "mauve," in 1856. It was formed in low yield, and the main product was an intractable black precipitate. Three years later a brilliant aniline red, known as "fuchsine" in France and "Magenta" in Britain, appeared in the streets of Paris and London and was soon transformed into no less fashionable blues and violets. The violets, obtained by August Wilhelm Hofmann in his laboratory at the Royal College of Chemistry in London during 1863, were the consequences of theory-inspired experimentation. Hofmann researched aniline and other amino compounds and their oxidation products. At the end of the 1860s, Carl Graebe and Carl Liebermann worked on the constitution and laboratory synthesis of the important natural dye alizarin. This heralded the move toward science-based industries, academic research into industrial problems, and the establishment of industrial research laboratories.[2]

Aniline black has been neglected by historians probably because the romance of coal-tar dyestuffs is fixed on the rainbow of novel colors that became available from new chemical theories, especially after 1865. Although the development of aniline black was made possible by these industrial advances, it benefited little from the growth of scientific theory fostered by the demands of the dye makers. Yet, in commercial terms, aniline black was a success story that rivaled the triumphs of artificial alizarin and indigo, and it outlived many of the original aniline colors.[3] This success was confirmed in the writings of textile printers, especially in the Alsace region of northeast France, where, in 1877, Camille Koechlin, of the Mulhouse-based Koechlin Frères, commented: "When a colour appears, fashion takes possession of it, and it has its run. This run was for a time more lavish for aniline black than for any other. The solidity and the distinction of this shade allowed a use so varied, so general, that what was formerly a mark of mourning has become a novelty."[4]

[2]John J. Beer, *The Emergence of the German Dye Industry* (Urbana, Ill., 1959; reprint, New York, 1981); Anthony S. Travis, *The Rainbow Makers: The Origins of the Synthetic Dyestuffs Industry in Western Europe* (Bethlehem, Pa., 1993); and Anthony S. Travis, Willem J. Hornix, and Robert Bud, eds., "Organic Chemistry and High Technology, 1850–1950," a special issue of *British Journal for the History of Science,* vol. 25, pt. 1 (March 1992).

[3]Even in 1920, and after new synthetic blacks had appeared, some 50–60 percent of aniline produced was destined for aniline black dyeing and printing. See Hans Eduard Fierz, *Grundlegende Operationen der Farbenchemie* (Zurich, 1920), p. 71.

[4]Camille Koechlin, "Aniline Blacks Turning Green," *Chemical Review* 6 (February 1877): 87–88. This was a translation from the French of an article in the *Industriel Alsacien.*

Dyeing with aniline black was much more difficult to achieve than printing, but once mastered it enabled the run on the colorant to continue well into the 20th century. The popularity of aniline black derived from wide usage in a variety of cotton goods, including sunblinds and umbrella fabrics (because of resistance to fading), and cotton velvets, socks, and lining materials (since black is a good contrast color for reds and violets). More unusual uses included dyeing cloth for Muslim clothing.[5]

The discovery of aniline black dates from the end of 1859, and its decline from the 1930s, with the introduction of new blacks that were easier to apply, concern over health risks, and changing fashions. Its importance, especially in the two decades after 1860, is reflected in trade agreements, claims over priority, and lengthy litigation over patents in Europe and the United States. In this article, an account of one of these suits is used to provide evidence of how aniline black first reached the United States. For more general background, I rely on the promotional activities of, and chemists at, the main British manufacturer of the raw material after 1876, the Clayton Aniline Company Ltd. of Clayton, Manchester.[6] In both cases, chemists from the French town of Mulhouse and its environs play important roles.

Aniline Blacks from Lancashire

In the early days there were in fact two ways of achieving a printed black on fabrics. One produced the color directly through the application of aniline salts and various reagents; the other employed a mixture of uncertain composition that was supplied to the printers. The first was the work of John Lightfoot (1832–72) of Accrington, about 20 miles north of Manchester. In 1859 he applied the hydrochloride salt of aniline to cotton in the presence of the oxidizing agent potassium chlorate (chlorate of potash) using the engraved copper printing rollers and found that he could print a dark green. When a

[5]Bernard Kramrisch, "Dyeing Cotton with Aniline Black," *American Dyestuff Reporter* 75 (March 1986): 30–31, 41.

[6]The source material on the history of aniline black before 1875 is very limited. It consists mainly of archival holdings in the Caro Nachlass, held in the Special Collection, the Deutsches Museum, Munich; John Lightfoot's *The Chemical History and Progress of Aniline Black* (Burnley, 1871); Lightfoot's recipe books and papers, reference M/75 in Manchester Central Library; and a book of printed samples, the 1880 volume of *American Chemist,* and a copy of Lightfoot's book, all, apparently, formerly belonging to Merrick & Gray of Boston, consultant for the plaintiff in the U.S. court case described here and to be found in the Edelstein Collection in the Jewish National and University Library, the Hebrew University, Jerusalem. See also Moshe Ron, *Bibliotheca Tinctoria: Annotated Catalog of the Sidney M. Edelstein Collection in the History of Bleaching, Dyeing, Finishing and Spot Removing* (Jerusalem, 1991).

salt of copper was added to the printing mixture a fast and brilliant black was obtained. Lightfoot's process was not a success at first in Britain, or in Alsace, because of the corrosive action on the rollers and other parts of the printing machines, which also caused streaking on the fabric. The second aniline black was the outcome of work done at Roberts, Dale & Co. in Manchester by the German colorist Heinrich Caro, who later became the technical expert at Badische Anilin und Soda Fabrik (BASF).[7] In 1860, he developed a process for making aniline purple (mauve) by the oxidation of aniline with copper salts, which left a black residue after alcoholic extraction of the purple. Roberts, Dale & Co. prepared the residue and sold it to printers from 1862. It also played havoc with the machinery. However, it could be printed with wooden hand blocks, as used extensively in most European centers of textile production. Not long after Caro's black was introduced, the dye manufacturer J. J. Müller & Co. of Basel took on the mainland European agency.

The pioneering work of Roberts, Dale & Co. established the very favorable advantages of aniline black over other black colorants then in use (such as logwoods and madder preparations). This probably acted as the spur that encouraged Lightfoot to patent his process in 1863, which, despite its disadvantages, opened the field to both imitators and those prepared to invest time in making aniline black suitable for roller printing. Lightfoot's patent specified the use of copper chloride.

There were other early attempts to apply aniline directly to fabric and obtain fast colors. In Manchester during 1860, the chemical manufacturer Frederick Crace-Calvert, the tar distiller Samuel Clift, and their assistant Charles Lowe had filed a joint patent for dyeing cotton goods with the hydrochloride salt of aniline and potassium chlorate. This gave a green color ("emeraldine") that, on treatment with soap or alkali, afforded a not very brilliant blue ("azurine"). Although this process was not brought into industrial use, it was the first of its kind to be the subject of a patent application, a fact that was used by the defense in the U.S. lawsuit that is the main subject of this article.

John Lightfoot and Charles Lauth

In 1871, John Lightfoot published his monograph on aniline black. He described how in November 1859 he had produced the black while undertaking experiments with aniline for Richard Dugdale Kay

[7]A. S. Travis, "Heinrich Caro at Roberts, Dale & Co.," *Ambix* 38 (November 1991): 113–34.

of the Broad Oak Print Works, Accrington. Aniline was made from coal-tar benzene and was the vital intermediate used to produce the first coal-tar dyes. However, according to Lightfoot, "Because of the high price of aniline I did not take this up."[8]

Nevertheless, experiments were carried out with calico printing at the Broad Oak works during July 1860, and at the end of 1862 Lightfoot gave details of his process to J. J. Müller-Pack, the proprietor of J. J. Müller & Co. Lightfoot took out British, French, and United States patents on January 17 and 28, and May 19, 1863, respectively, and rights for all these were assigned to Müller-Pack. Through control of Lightfoot's process, Müller-Pack attempted to profit from aniline black printing. This was from royalties on chemicals supplied by one manufacturer in Britain and from the direct sale of chemicals to French and Swiss printers (and also, presumably, to printers in the German states). The popularity of the black was such that over 50,000 pieces were printed with hand blocks in Germany and Switzerland not long after Lightfoot had ceded the rights of his patents to Müller-Pack for 25,000 francs in April 1863. Müller-Pack's attentions were soon directed toward the United States, where, though the Confederate States had returned to homespun methods as a result of the Union blockade,[9] the North was still eager to learn all it could about the latest European technologies.

In the meantime, research by the French chemists and colorists Emile Kopp and Charles Lauth, working on behalf of printers in Mulhouse, made the process more applicable to calico printing with machinery. On June 7, 1864, Lauth's British patent agent registered a patent in London that specified the use of insoluble copper sulfide ("sulphuret of copper"), which was converted to soluble copper sulfate only after impression on the fabric. This reduced dramatically the harmful action on the rollers of the printing machines.

The importance of Lauth's copper sulfide process for aniline black printing was recognized immediately in Basel, where Müller-Pack purchased the British patent rights, and in Mulhouse, where Koechlin Frères pioneered its use. Müller-Pack also retained the option to patent Lauth's improvements in France and America. On January 4, 1865, Lauth read a memoir on the subject to the Société Industrielle de Mulhouse, and its Comité de Chimie began an investigation into the processes of Lightfoot, Lauth, Honoré Cordillot (whose red prussiate of ammonia, or "ferridcyanide of ammonium" [ferricyanammonium,

[8]Lightfoot, p. 1.

[9]Sidney M. Edelstein, "Dyes and Dyeing in the Confederacy," in *Historical Notes on the Wet-Processing Industry* (New York, 1972), pp. 115–19 (reprinted from *American Dyestuff Reporter* 51 [April 16, 1962]: 35–39).

or ammonium ferrocyanide] aniline black process was discovered in April 1863),[10] and others. In April, Théodore Schneider presented a report to the society of his and Paul Schützenberger's opinions on Lauth's memoir. They were sufficiently impressed by the natures of the new inventions to recommend the medal of honor for Lightfoot and the first-class medal for Lauth.

Müller-Pack and Control of the Market

Chemical processes that led to a given novel product were more readily patentable in Britain than in France and the United States, where the product took precedence. This was especially true after 1863, when one French company gained absolute control over all the processes for the important aniline red product known as "fuchsine." For this reason, Müller-Pack did not patent Lauth's process in France ("acting under express advice of the most eminent counsel, and chemists of France")[11] or in the United States. The product came too close to Lightfoot's to warrant the risk of rejection. Instead, every attempt was made to merge the two inventions by demonstrating that "the Lauth improvement is an integral part of the Lightfoot Patent, and can only reach its ultimate result, by passage through the stages and processes, to which the Lightfoot Patent lays claim . . . we assert, that Lauth's process cannot be used without direct infringement upon Lightfoot, for it arrives at the same result by passing through stages of chemical action which are the grounds of Lightfoot's claim, and it produces a new product of which Lightfoot is the inventor."[12]

Details of the approach to the marketing of aniline black in the United States were made available when existing arrangements with the British and French came to an end around 1869–70. From that time on, it was proposed that customers in all three countries should pay a royalty for use of the Lightfoot and Lauth processes. In February 1870, Morgan-Brown of Brandon & Morgan-Brown, the Paris-based attorney of J. J. Müller-Pack, advised the public in a

[10]Cordillot was a colorist at the print works of Huguenin-Schwartz & Conilleau (the La Mer-Rouge works) of Mulhouse. This firm offered Cordillot's process to Müller-Pack, who, following trials by his manager, Albert Schlumberger, agreed to purchase it. See E. Noelting and A. Lehne, *Anilinschwarz und seine Anwendung in Färberei und Zeugdruck* (Berlin, 1904), pp. 37–38. This was the second edition of the German version of Noelting's *Histoire scientifique et industrielle du noir d'aniline* (Mulhouse, 1889).

[11]*Aniline Black: Explanatory Statement to Manufacturers and Calico Printers of the Patent Rights and Claims of J-J Müller Pack* (Paris: Imprimierie de Dubuisson & Cie, 1870), reference M/75, "Records Deposited in Manchester Central Library by the Calico Printers' Association," item no. 58, Local Studies Unit, Manchester Central Library, p. 15.

[12]Ibid.

pamphlet entitled *Aniline Black* that he was dealing with all legal matters concerning aniline black, including in the United States, where "we are arranging the terms of settlement for M. Muller-Pack."[13] The British were to be approached in the same way as the

> American manufacturers, viz: to give copies of the Patents, a short history of the case, extracts from well known works relative to the chemistry of Aniline Black, reports of law cases, decisions of judges [neither the reports nor the decisions had anything to do with aniline black], etc. . . . The Lightfoot patent is an original one for an original article, viz: Aniline Black; consequently, whether Mr. Muller-Pack were the possessor of the Lauth patent, or not, it would make no difference to his rights, for the Lauth Patent which contains the formula chiefly adopted by manufacturers, is clearly dependent on, and an infringement of, the Lightfoot Patent. For these reasons we have adopted nearly the same extracts, that we have applied to Mr. Muller Pack's position in America.[14]

This new arrangement, based on royalty payments, worked satisfactorily in France, "and we feel sure that American manufacturers, will act equally honourably."[15] Lightfoot's "historical" monograph appeared one year later, incorporating much of the material in the pamphlet, and was undoubtedly intended to spell out the message to users of aniline black who were now directly confronted with claims for royalty payments.[16]

Printing Aniline Black

A typical 1870s recipe for making up the printing mixture, according to Lauth's process, required thickening pastes, aniline salt, and

[13]Ibid.

[14]Ibid.

[15]Ibid.

[16]Another patent was taken out in 1865 by Boboeuf for dyeing, rather than printing, a black with aniline, and this process was still in use in France in the 1890s. The chemist Edmond Willm informed the Société Industrielle de Mulhouse that the use of chlorate of potash and aniline hydrochloride gave a result similar to that of Crace-Calvert, Lowe, and Clift's green (emeraldine) process. Other aniline black processes were developed, often without patent registration. In 1879, Justus Wolff described the various types of aniline black in *Chemical News*, including his nigrosine, which had found application in the dyeing of sunblinds. Wolff claimed to have invented nigrosine in the laboratory of Appold Frères of Salzbach, near Saarbrücken, in 1862. By the mid-1870s he appears to have joined Read Holliday & Sons of Huddersfield, a major British tar distiller. Notes on Wolff, and later progress in aniline black, will be found in Maurice R. Fox, *Dye-Makers of Great Britain: A History of Chemists, Companies, Products and Changes* (Manchester, 1987).

other ingredients.[17] This mixture was transferred from a color box to the engraved copper roller by means of a color furnisher, a roller covered with short bristles. A steel or composition doctor blade (color doctor) removed excess color from the engraved roller. Printing was followed by drying at 70° Fahrenheit, "with the ordinary amount of moisture," and the aging step, in which the impregnated cloth was subjected to heat or left to hang. After two days the cloth was of a dark olive green shade as a result of the oxidation. The green afforded black by treatment with alkali and soaping, and "[a] certain experience is required for knowing all the properties of this Black." Aniline black was noted to withstand soaping and scouring, and "its fastness is its only inconvenience."[18]

In the United States, Müller-Pack obtained a reissue of Lightfoot's patent on February 6, 1872, which provided an opportunity to introduce into the specification a wide range of copper and iron salts, based on Lightfoot's more recent researches, and, to some extent, it also embodied Lauth's modification.[19] Although the metal salt could be varied, and the necessity of the metals was hotly debated, the procedures were similar. Thus, at the Merrimack Manufacturing Company of Lowell, Massachusetts, which had no arrangements with Müller-Pack, the printing of aniline black on cloth was followed by several operations: aging, raising, rinsing, soaping, drying, bluing, starching, calendering, folding, and packing.

The Mulhouse Connection: Alfred Paraf and Charles Dreyfus

Müller-Pack's introduction of aniline black into the United States was soon followed by the more personal transfer of a similar, but rival, process. This was the result of the efforts of a much-traveled chemist from the Mulhouse region, Alfred Paraf (fig. 2). Little is known about the life of Paraf, except what is revealed about his inventions in patent

[17]This was made up of a boiled mixture of 2 gallons of starch paste, 1 gallon of gum tragacanth paste, and 1 gallon of British gum paste, to which was added 16 ounces of chlorate of potash and 14 ounces of "black paste" (perhaps containing the copper sulfide). After cooling, 4 ounces of a salt of aniline and 12 ounces of sal ammoniac were added. See "Aniline Black. Lauth's Patent Improvement on Lightfoot's Black," undated leaflet in Caro Nachlass, Special Collection, Deutsches Museum.

[18]In the 1930s, similar methods were still in use. For calico printing, the doctors had to be protected, so insoluble copper sulfide or sulfocyanide (or a salt of vanadium, as introduced around 1875) was employed. Arthur G. Green, "Landmarks in the Evolution of the Dyestuffs Industry during the Past Half Century," *Journal of the Society of Dyers and Colourists* 50 (1934): 61–62.

[19]For the purpose of the reissue in broadening a patentee's claims, see Kendall J. Dood, "Pursuing the Essence of Inventions: Reissuing Patents in the 19th Century," *Technology and Culture* 32 (1991): 999–1017.

FIG. 2.—Alfred Paraf in 1866. Enlargement from a miniature photograph attached to a letter from Paraf, in New York, to Heinrich Caro, September 27, 1866. (Uncataloged item, Caro Nachlass, Special Collection, Deutsches Museum.)

applications and the court case described here. His family was closely involved in the textile industry and became engaged in the development of new chemical-based processes. Alfred and Mathias Paraf, for example, filed patents for dyeing and dye-making processes from 1860, and Mathias became a member of the Comité de Chimie of the Société Industrielle de Mulhouse. They were related to the Paraf-Javal family, whose print works at Thann, in Alsace, exhibited its products at the 1862 International Exhibition in London, including the fast purple made from "alizarenate of iron and oxidised aniline." From February 1864 until October 1869, Paraf-Javal & Cie purchased Müller-Pack's chemicals for aniline black printing. The Paraf-Javals filed an aniline black patent, based on chromic acid with aniline or toluidine, in Paris on November 8, 1865, and another Paraf-Javal aniline black process, which employed manganese salts, was patented in London by Alfred Paraf in 1866.[20]

Alfred Paraf appears to have started his career as a textile colorist and was, no doubt, influenced by the environment of Mulhouse, especially the activities of his relatives, and the prestige and high income associated with the profession.[21] By 1860, the study of chemistry to a high level was an essential prerequisite for entry into this field of activity, and Paraf moved on to become a student and associate of Paul Schützenberger at the Collège de France in Paris. He then took up employment in Manchester with Roberts, Dale & Co. and became friendly with Heinrich Caro. Paraf took out a number of patents for natural and synthetic dyes and their application in Britain, one for aniline purple (mauve), several with John Dale, cofounder of Roberts, Dale & Co., and one, in 1866, with the English chemist James Alfred Wanklyn (one of Dale's consultants), for converting aniline violets to greens with ethyl iodide and alcohol. Paraf must have acquired a strong interest in aniline black after witnessing the large amounts supplied by Roberts, Dale & Co. to Müller-Pack in Basel and the wider application following Lauth's improvement. In Manchester, Paraf formulated an aniline black process based on fluosilicic acid (hydrofluosilicic acid), and this was prepared at Roberts, Dale & Co.[22]

It was probably in 1864 that Alfred Paraf left Roberts, Dale & Co. for the United States, where he introduced his fluosilicic acid process to American printers. Paraf's first assignment was for the Riverpoint works in Rhode Island. This would have been facilitated by the availability of aniline, manufactured by Thomas and Charles Holliday (formerly of Huddersfield, England) in New York from 1864. Since no copper was specified in Paraf's patented recipe, there was considerable concern at the Müller establishment, where the manager, Albert Schlumberger, called in Charles Lauth to investigate. The latter concluded that the black formed during Paraf's process was due to the use of copper in the apparatus and equipment. In other words, Paraf's process was not considered to be in any way new. It was also criticized by Schneider in his 1865 report, which stated that the

[20]See also Noelting and Lehne (n. 10 above), pp. 122–23.

[21]Ernst Homburg, "The Influence of Demand on the Emergence of the Dye Industry: The Roles of Chemists and Colourists," *Journal of the Society of Dyers and Colourists* 99 (1983): 325–33.

[22]Alfred Paraf, Great Britain Patent no. 804 of March 22, 1865. Hydrofluosilicic acid was made by decomposing fluorspar and sand with sulfuric acid. For the black process, the aniline salt was dissolved in the acid, the solution was thickened, and then printed on fabric prepared with potassium chlorate.

method was "perfectly impracticable" unless copper was present. Paraf made a trip to Europe in order, among other things, to answer his opponents. On August 30, 1865, Paraf described his process to the Société Industrielle de Mulhouse, and details were published in its bulletin.

Paraf kept in touch with Caro after returning to the United States and in 1866 gave his business address as the dyestuff merchant and manufacturer F. Brett & Co. of 178 Fulton Street, New York.[23] In April 1866, Paraf took out a patent for a second aniline black process, which specified chromium compounds, and in the following year this was licensed to the Merrimack Manufacturing Company. It was a time of growing interest in the new black, and Paraf remained in the United States where he continued with research into improved ways of using natural dyestuffs, like madder.[24] Paraf also studied under Charles F. Chandler at the Columbia School of Mines, New York, founded in 1866.

By the late 1860s several color makers in Manchester were realizing considerable profits from the sale of aniline salts for black, including Ivan Levinstein of Blackley. In the inaugural issue of his *Chemical Review,* published in October 1871, Levinstein explained that although aniline black was used by almost every calico printer on the Continent, it "is in this country almost discarded."[25] The problems with the adverse action on rollers, and of loss of color through "greening" (considered to be caused by sulfurous vapors), were not completely solved.[26] Iron compounds had been introduced with some success in the 1860s, but the application of vanadium was considered

[23]Paraf was an imaginative inventor, and his interests were not restricted to the textile industry. He proposed that calcium chloride could be employed to attract moisture from the atmosphere, especially in hot climates, which would be released to provide water for agricultural purposes. This was heralded as a great discovery by the American press.

[24]Aniline black had become increasingly important in Europe, especially in France, since most aniline dye patents in that country were controlled by one firm, Renard Frères (La Fuchsine from late 1863). *Noir d'Anilin Lucas,* as it was known in England, was made by F. Pétersen of Pétersen & Sichler in Paris, where Jean Théodore Coupier adapted his nitrobenzene oxidation of aniline by the addition of copper to afford a black. In 1867 Karl Stalars of Lille managed to dye cloth by immersion, and in the following year, trading as Stalars Frères, took up aniline black dyeing on a large scale. By 1870, aniline black was employed at three print works in Rouen. From 1865, the firm of Nahrath had sold throughout Europe a preparation composed of aniline and dichromate of potash for aniline black dyeing and printing.

[25]"Aniline Blacks for Printing Cotton," *Chemical Review* 1 (October 1871): 3.

[26]Aniline black dyeing was far more problematic at this time, especially for wool and silk, as well as for cotton. Logwood blacks for dyeing were still popular in the 1920s, and the raw materials were imported from Honduras, Santo Domingo, and Jamaica.

a major breakthrough since the corrosive action was reduced considerably. Vanadium had become available in Manchester during 1870 and was tried by John Lightfoot and by Robert Pinkney of London. Despite its high cost, several Lancashire printers were employing this metal in the aniline black process from 1875, as were dyers and printers in Rouen, where wool, silk, cotton, and linen were treated with aniline. The most popular salts were vanadium chloride and ammonium vanadate. Pinkney promoted the use of vanadium and uranium, patented by him in October 1871, in *Chemical Review, Chemical News,* the Philadelphia-based *Textile Colorist,* the *American Chemist,* and elsewhere from 1875–76 on. Vanadium was noted to minimize corrosion of the doctors and rollers, as well as greening, and since only small amounts were required (one hundred thousand parts, or less, of vanadium to one part of the aniline salt) the cost was considered to be one-eleventh that of using Lauth's copper sulfide process.

At this time, the chemist Charles Dreyfus was setting up a business in Manchester. Dreyfus, also of a Mulhouse textile family, arrived in Manchester during 1869, after gaining his Ph.D. in Paris. In 1876, he formed the Clayton Aniline Company Ltd. to manufacture intermediates for the coal-tar dye industry, especially aniline and its salts for the black. It was an opportune moment since the aniline black market was expanding rapidly, especially in Lancashire. Dreyfus and his chemist, Julius B. Cohen, in their efforts to promote the sale of chemicals for aniline black, provided some of the most useful accounts of the history of the color. Aniline black, according to Cohen in 1887, had "engaged the attention of scientists as well as dyers and printers for nearly a quarter of a century, and its importance may be measured by the almost seismic effect on the dyeing industry on the Continent induced by the recent patent litigation."[27] Cohen pointed out that aniline black, unlike other aniline colors, could be obtained fast without the aid of a mordant and was noted for its greater affinity for cotton than for wool or silk, quite the reverse of aniline dyes. There had been many attempts to solve the technical problem of

[27]Julius B. Cohen, "Aniline Black: Its History and Its Application to Dyeing and Printing," *Journal of the Society of Dyers and Colourists* 3 (July 25, 1887): 104–12. For a major British patent case involving aniline black, which began in 1886 (Thomas Holliday, patentee of Samuel Grawitz's processes vs. Heppenstall Brothers, dyers, of Huddersfield), see "Notes of the Month, Aniline Black," *Journal of the Society of Dyers and Colourists* 3 (August 25, 1887): 129. Read Holliday engaged in further litigation over processes for black early in the 20th century. Details will be found in the papers and correspondence concerning the Vidal Dyes Syndicate case (1900–1902) and the Schoellkopf Black case (1910–12), Historical Archives, Zeneca, Blackley, Manchester.

greening, notably in Rouen and Mulhouse. Chemists had also attempted to unravel the constitution, but without much success. What was generally agreed was the necessity of the presence of metallic salts, especially those of copper, for the oxidation to occur.

Litigation in the United States

The most complete account of the introduction of aniline black by Müller-Pack and Paraf into the United States derives from a case of patent litigation in the United States Circuit Court, District of Massachusetts, that began in 1872 and was brought to an end four years later. One of the witnesses was S. Dana Hayes, the state assayer of Massachusetts, who published an extensive report in the *American Chemist* in July 1876.

Hayes represented J. J. Müller-Pack, who, as the assignee and proprietor of the U.S. patents granted to John Lightfoot, had taken out a bill of complaint against the Merrimack Manufacturing Company, "to restrain them from making or developing aniline black in textile fabrics, and from selling or using fabrics in which aniline black has been developed."[28] In response, Merrimack, which employed machine printing, put forward the claim that the invention was not Lightfoot's, but that it was covered by the 1860 British patent of Crace-Calvert, Lowe, and Clift for emeraldine.

Müller-Pack's bill was filed in February 1872, at the same time as the reissue of Lightfoot's patent was granted.[29] The first evidence was taken one year later. Throughout, the argument put forward by the plaintiff was that, since copper was necessary for producing the black, infringement of Lightfoot's original process took place even if the metal only entered the mixture from the apparatus employed in preparing the dye and printing it. The defense drew on the inventions of Paraf, Crace-Calvert, and others in attempts to play down the general, and specific, roles of metals. The last evidence was taken in December 1874, the arguments were presented in December 1875, and the decision of the court was rendered in April 1876. "The actual preparation and chemical work extended through nearly three years, and resulted in the production of a printed volume of 370 pages of

[28] S. Dana Hayes, "Aniline Black in Court," *American Chemist* 3 (July 1876): 1–13, quote from p. 1.

[29] In the meantime, Müller-Pack was continuing to control new aniline black processes, mainly of French origins. In June 1872, jointly with Jarossen, he filed a patent in Paris that was almost identical to the process of Alland, who, following legal action, had his name added to the patent. In June 1873, Müller-Pack acquired the process of L. Bretonniere. See Noelting and Lehne (n. 10 above), pp. 126–27.

evidence, given almost entirely by chemists and practical color-printers."[30]

Following the presentation to the court of aniline black prints made at Merrimack (see fig. 3), the first evidence for the plaintiff was given by Hayes. The differences between aniline black and other aniline colors, and its probable constitution, were discussed, while the distinction between aniline black and common mordanted colors was explained. According to Hayes, aniline black could not be produced on the fabric without the aid of a metal, although the metal did not form any part of the composition of the color: "cloths printed with it, as found in commerce, always contain part of the metal used . . . [and] it may be determined by analysis. The infringing prints were analyzed, and found to contain as much copper as other aniline black prints known to have been produced by the Lightfoot process."[31]

Hayes described the nature and peculiarities of the new color or pigment: "Aniline black forms, in the class of aniline colors, a group by itself; the method of its generation and its resistance to physical and chemical agents give it special characters. Instead of being prepared in the laboratories of chemical products, like the purples, reds, violets, etc. . . . it is produced from a nearly colorless mixture in the fabric by entirely different processes, and is there 'fixed' by this particular mode of generation."[32]

Aniline black was declared to be a nearly fast color that was not affected by sunlight and could be boiled in strong solutions of chemical agents without being discharged: "it is one of the most, if not *the* most, durable color known in the arts. . . . Aniline black is an oxidised aniline oil; the accepted authorities state its composition to be that of aniline with oxygen; it is thus an individual coloring matter, and does not contain any mordant, as a part of its composition."

The critical role of the metal was emphasized further, even though it "does not enter into the composition of the black color itself." This was shown by removing the salt from printed fabric "without destroying, and in some cases without injuring, the aniline black color." The metal, in the form of its salt, acted only as a "vehicle" for the oxygen: "The fabrics as ordinarily prepared for the market, having been imperfectly washed in their manufacture, always contain a considerable

[30]Hayes (n. 28 above), p. 1. See also "Aniline Black, A, M & G," "Samples of Cloth—Printed with aniline black and other colors illustrating the case of J. J. Müller-Pack vs. The Merrimack Manufacturing Co.," John Merrick, Massachusetts College of Pharmacy, December 18, 1873, Edelstein Collection, Jewish National and University Library, the Hebrew University of Jerusalem.

[31]Hayes, p. 1.

[32]Ibid., pp. 2–3.

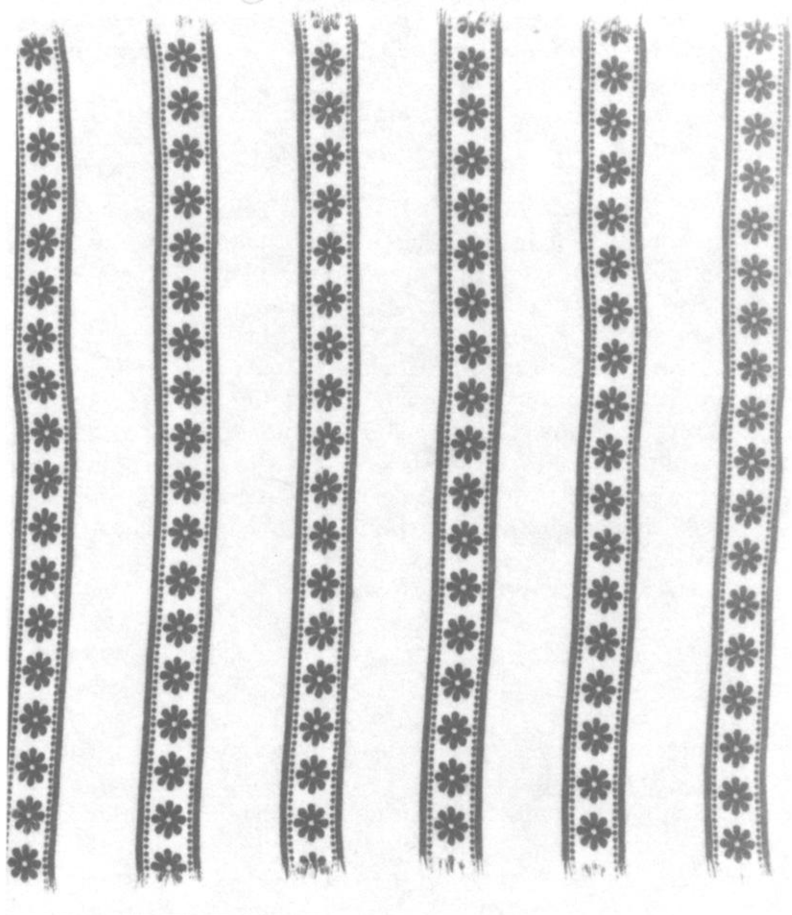

FIG. 3.—Sample of cloth printed at the Merrimack print works, November 4, 1873. ("Aniline Black, A, M & G," "Samples of Cloth—Printed with aniline black and other colors illustrating the case of J. J. Müller-Pack vs. The Merrimack Manufacturing Co.," John Merrick, Massachusetts College of Pharmacy, December 18, 1873, Edelstein Collection, Jewish National and University Library, the Hebrew University of Jerusalem.)

quantity of the materials employed for printing them, and the products of their decomposition . . . [in the case of the Lightfoot process] contain a notable quantity of copper existing as an incidental impurity."

Hayes had tested and analyzed prints from the Merrimack works sent to him in October 1872. All contained salts of copper, which were partially soluble in water, "and the whole of which may be removed without destroying the aniline black color. . . . In my judgment, these specimens have been printed by a process substantially the same as that described in the Lightfoot patents already referred to . . . these blacks have been produced in the fabric by the aid of an aniline salt, an oxidizing agent and copper salts. . . . I have a small printing machine furnished me by the complaintant for the purposes of my investigations."[33]

Details of the plaintiff's patents, those of Lightfoot, were then introduced, followed by a standard recipe for producing aniline black, with starch as thickening agent, aniline salt (generally the [hydro]chloride, also referred to as the muriate), and perchloride of copper (cupric chloride), as specified in the original 1863 patent.

The first witness for the defendant was Henry Burrows, superintendent, from 1855, of the Merrimack "Print Works." (See fig. 4.) He showed the court various black prints, including a black "emeraldine" (Crace-Calvert's color) said to have been made without copper or other metallic salts, and also described fully the processes and modes of working practiced by Merrimack. The "regular Merrimack standard black" that was found to be the best was claimed to be a "chlorate of aniline" mixture.

James Duckworth, assistant to Burrows (and superintendent at Merrimack from 1875), gave the recipe for the color mixture used to make the samples presented in court. It was a combination of both chloride and chlorate salts of aniline, the latter containing the oxygen that brought about the black reaction. No metal salts were added: "The chlorate of aniline mixture was made by bringing together a solution of tartaric acid and a solution of chlorate of potash, then adding aniline oil and filtering. The chlorate of aniline obtained in this way was mixed with a solution of chloride of aniline, and thickened for printing."[34]

Professor John M. Ordway, of the Massachusetts Institute of Technology, represented Merrimack and read out portions of the literature dealing with aniline blacks and greens. He also discussed the theories for the production of these colors. Ordway's opinion was that emeraldine and aniline black were identical.

The Case for Copper

For the plaintiff, Robert Reoch, superintendent of the print works at Riverpoint, Rhode Island, "testified to the excellence and value of aniline black . . . and had not been able to produce aniline black prints suitable for market, practically, without some copper salt." Reoch referred to the recently reported use of the salts of vanadium, instead

[33]Ibid., p. 3.
[34]Ibid., p. 1.

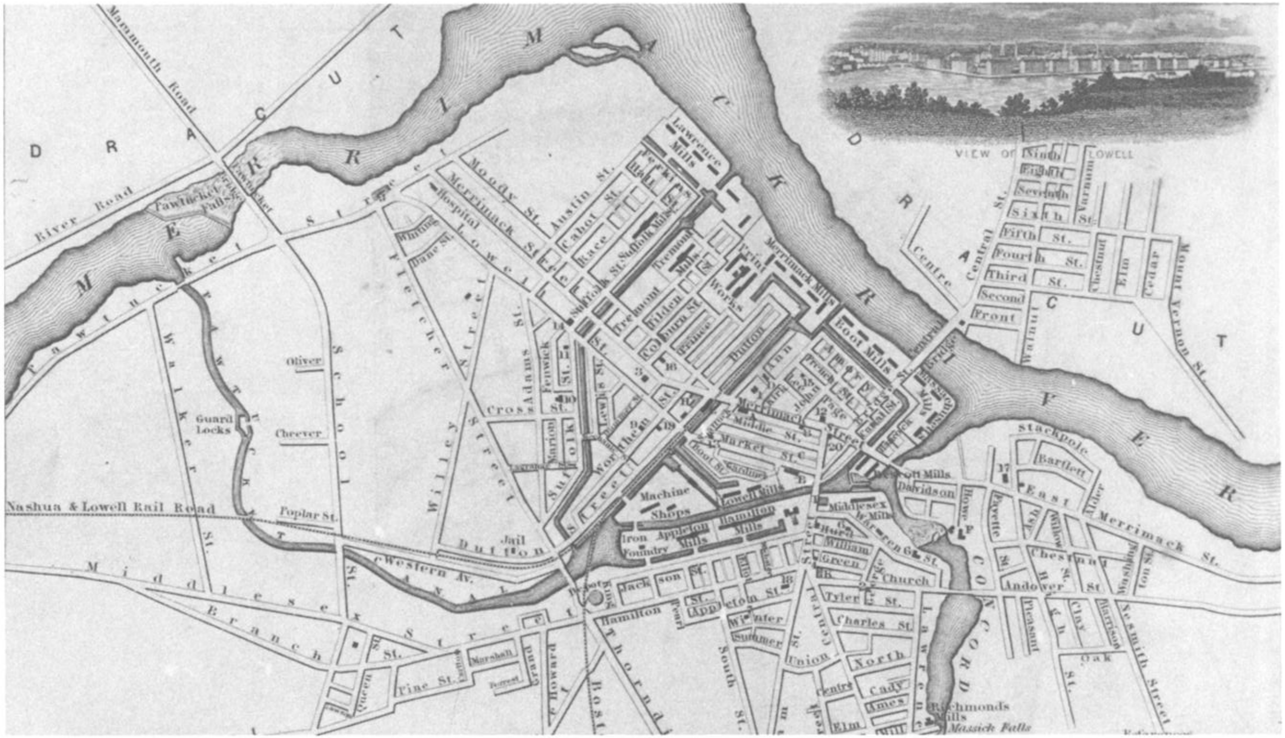

FIG. 4.—The textile manufacturing district of Lowell, Massachusetts, including the Merrimack "Print Works," in 1845. (From "Plan of the City of Lowell by G. W. Boynton. From a Survey Ordered by the City," reproduced as the frontispiece in Henry A. Miles, *Lowell, As It Was, and As It Is* [Lowell, Mass., 1847].)

of copper, and pointed out the distinct advantages brought about by using aniline black in printing, as compared with madder and logwood blacks. "The amount of single color black prints was very limited before the introduction of aniline black, on account of the instability of the logwood black, which in former years was commonly produced, and on account of the expense of the madder black, and the want of purity of the whites [the unprinted part]." Aniline black "is applicable to madder and garancine colors, steam and pigment colors, chrome and soda colors, Turkey reds, and, in short, to every style of work known to the calico printing art."[35]

In 1864, Paraf had brought Reoch in as an expert to introduce aniline black made with fluosilicic acid at the Riverpoint works, and trials continued beyond 1866, when Paraf's chromate process was introduced: "I am well acquainted with the Paraf patent for obtaining aniline black by means of chromate of chromium," stated Reoch, "but never was successful in obtaining a satisfactory black. . . . Mr. Paraf was the means of bringing me here for the purpose of carrying out successfully his process of aniline black. But the only way in which I was able to use the Paraf patent and produce satisfactory results, was by the addition of a very small proportion of sulpho-muriate of copper [a salt of copper containing sulfur and chlorine] to Paraf's formula; the proportion of the above copper salt I then used was one part of sulpho-muriate of copper to 320 parts of Paraf's aniline black formula." With this recipe for black—in the presence of a small amount of copper—the Riverpoint works made aniline prints successfully for two years ("from the beginning of 1868 more particularly"). "We tried a good many experiments under the superintendence of Mr. Alfred Paraf in 1864, and printed quite a number of pieces under the formula patented by M. Cordillot using the ferridcyanide of ammonia. We did not succeed to our satisfaction in either of these directions."[36] James Hunter, a Philadelphia-based calico printer, testified to the tremendous importance of aniline black, and also stated that he used a salt of copper.

Hayes was then recalled and gave the results of analyses, which showed the presence of copper in prints submitted by Burrows. Hayes visited the Merrimack works in June, July, and November 1875 and had "analyzed many samples taken there. The raw materials used were all free from metals; but the color-mixtures, containing free chloric acid, as used there, acted rapidly upon the copper vessels in which they were made and dissolved enough copper to give aniline

[35]Ibid., pp. 1, 5, 6.

[36]Ibid., p. 6. The Cordillot process belonged to Müller-Pack (n. 10 above).

black by the ordinary modes of ageing, even with the emeraldine formula . . . but when the same color-mixtures were made, without contact with metals, they failed to produce good blacks by the same ageing processes."[37]

Professor John M. Merrick, of the Massachusetts College of Pharmacy, representing Müller-Pack, referred to portions of the literature on aniline black. Merrick was a consultant in the Boston-based partnership of Merrick & Gray and had visited the Merrimack works and made quantitative analyses and experimental trials, confirming the evidence of Hayes. The majority of their trials, at least those made during 1873, were carried out with block printing at the Pacific Mills and Print Works of Lawrence, Massachusetts (see fig. 5). As part of his background reading on the subject, Merrick acquired a copy of Lightfoot's book early in 1874.[38]

The Case against Copper

Additional evidence was now introduced for the Merrimack works. Burrows presented new specimens of black prints, claimed to have been made without contact with copper, including some produced "from chlorate of aniline, which was made by means of sulphate of alumina, instead of the tartaric acid used in the other chlorate of aniline mixture. A description of the hot ageing process employed at Lowell was also given. The evidence was confirmed by Mr. Duckworth."[39] Burrows gave his version of the early history of aniline black at Merrimack. He had also tried experiments based on Crace-Calvert, Clift, and Lowe's emeraldine. After aging and soaping, the results were compared with Lightfoot's black. Crace-Calvert, Clift, and Lowe's process afforded azurine (not the emeraldine), which, said Burrows, was simply a reduced black (a weaker color, of paler shade). In the summer of 1865 he tried Lightfoot's method, which was abandoned because of the severe action on the machinery, namely the corrosive action on the doctor, and the liability to tender the cloth, caused by the action of acid during aging.[40] Burrows did not, however, refer to Lauth's improvement of 1864.

In 1866, according to Burrows, Merrimack used muriate of alumina (aluminum chloride) on a small scale. "In 1867 and 1868," he said, "we printed a few blacks, also using the muriate of alumina in

[37]Ibid., p. 2.

[38]Copy of Lightfoot's *The Chemical History and Progress of Aniline Black* in Edelstein Collection, Jewish National and University Library, the Hebrew University. This contains the inscription "Merrick & Gray, 59 Broad Street, Boston, Jany 1874."

[39]Hayes, p. 2.

[40]Ibid., p. 4.

FIG. 5.—Sample of cloth printed with aniline black at the Pacific Mills and Print Works for S. Dana Hayes, consultant to J. J. Müller-Pack of Basel. ("Aniline Black, A, M & G," "Samples of Cloth—Printed with aniline black and other colors illustrating the case of J. J. Müller-Pack vs. The Merrimack Manufacturing Co.," John Merrick, Massachusetts College of Pharmacy, December 18, 1873, Edelstein Collection, Jewish National and University Library, the Hebrew University of Jerusalem.)

place of copper. In 1869 and 1870, we printed a few more blacks than in previous years, still using muriate of alumina in place of the copper salt." Burrows pointed out that in 1867 Merrimack had acquired a right under the Paraf patent for the so-called chromate of chromium black. Four years later the works used mainly an insoluble copper salt patented—in England but not in the United States—by James Higgin, a Manchester-based chemical manufacturer:

> I thought this was a little better black than the muriate of alumina black. I then used chromate of chromium, so called, which I had previously used experimentally, being Paraf's patent. We kept on with the chromate of chromium until March, 1873, and then we began to change gradually to a black, which we have used ever since, using it entirely from the middle of May, or, say May 16, 1873. This black is made with chlorate of aniline and hydrochlorate of aniline, chlorate of potash and thickening. It contains no metallic salt whatever. It requires only twelve hours' age in the ageing room, is raised with soap and water in the usual manner, and is very much the best black we have ever used.

Burrows ended by reiterating his claim that blacks could be made without any metal or metallic salts.[41]

Ordway moved the debate from industrial application to scientific discourse. He discussed the literature on the subject again and presented specimens of prints made by himself in June 1875, in the presence of Hayes, Merrick, and F. P. Pearson (the works chemist at Merrimack), in which there was no copper, and some of the blacks obtained were good. Analyses of aniline black produced in apparatus made of infusorial silica were given, and Ordway concluded that the presence of copper was entirely unnecessary. He also commented on the constitution of the black, especially the results published in 1872 by Armand Müller at the Zurich Federal Polytechnic: "there has been no analysis of aniline black published, worthy of any confidence whatever, except that of Fritzsche. My own experiments have satisfied me that the substance made according to Müller's direction has not the composition assigned to it by Müller. It contains a much larger proportion of carbon. Müller has left out of account altogether the chlorine, which enters into this black to the amount of several per cent. Precisely how the copper acts, I do not know."[42]

As far as Ordway was concerned, Crace-Calvert, Clift, and Lowe's emeraldine and azurine and Lightfoot's and Lauth's aniline blacks were essentially the same. Crace-Calvert, Clift, and Lowe's process afforded "a green insoluble coloring matter," while Lauth's process used copper sulfide and iron sulfide in the mixture, instead of the

[41]Ibid., pp. 4, 5.

[42]Ibid. See also p. 10, where Müller's formula is given as $C_{12}H_{14}N_2O_{11}$; but is considered to be "more nearly" $C_{12}H_8N_2 + H_2O$.

soluble salts of Lightfoot. These were just technical differences that had no bearing on the chemical identity of the "blacks."

The Case Is Proved

The plaintiff responded with further evidence for the necessity of copper. On a visit to Merrimack with Merrick early in November 1875, Hayes had observed that none of the materials used to make the mixtures for aniline black contained copper, but the products did. It was established that the copper had come from the apparatus employed, namely, the copper dippers, the mixing kettle, the copper rollers, and the copper color box. The color mixtures also contained some iron, from the commercial sulfate of alumina used to make the chloride salt of aniline, as this was found to contain nearly 2 percent of sulfate of iron: "The value of the metal taken from the copper vessels was proved and illustrated by the exhibits, and the difference in effect obtained by the respondent's mode of *hot* ageing, and the mode of ageing commonly practiced by calico printers was shown."

Ordway's trials came under attack from Hayes:

> the results were shown to be unmerchantable prints. I described a mode devised for testing the strength of threads of printed cloth, by weighting them until they broke, and then gave the results of many tests made in this way, proving that all the prints put into this case, in which blacks were produced without metals by high and long continued heats in the ageing, were commercially worthless, because the threads were so weakened by the corrosive action of the chlorate of aniline. It was shown that the respondents were benefited by the copper contained in their color mixture, in obtaining a better black, in saving time, and in saving the strength of the fabrics. I recognized the possibility of making aniline black in such indestructible substances as infusorial silica, without metallic salts, but was convinced of the value of copper salts in the modes of working practiced by calico printers, for producing this color.[43]

Merrick was recalled, and corroborated the statements of Hayes by submitting the results of his further experimental trials. In July 1875, Hayes and Merrick had undertaken experiments at Merrimack with roller printing machinery. They made up the "Merrimack standard color mixture precisely as we had seen it made by Prof. Ordway, in porcelain and wooden vessels, and printed it with a wooden roller and doctor, from a wooden color-box, on a regular printing machine,

[43]Ibid., p. 2.

without contact with metals; and we made precisely the same color-mixture in copper vessels, using copper utensils . . . and printed this mixture from a copper roller in the ordinary way as practised there." These experiments, according to Merrick, proved "conclusively the action of copper salts, even in small quantity, in developing aniline black." Merrick presented the results of his chemical analyses, and accounts of aniline black by various authors, and "closed the evidence."[44] According to Hayes, "The case was very ably argued by eminent counsel, who had made themselves familiar with the chemistry of the subject, as well as with all the evidence in the record, and it was fully and faithfully presented in the Court."

In April 1876, the judge ruled in favor of Müller-Pack. Infringement of Lightfoot's patented process had taken place: "Without the use of a copper salt, or its equivalent, a perfect aniline black was not developed. The defendants cannot avoid the charge of infringement by reason of their obtaining the metallic salt from their copper utensils. The second patent [that of Lightfoot] is valid, for that portion of the fabric or yarn in which aniline black is developed as a dye or stain, and the invention is not anticipated by the prior use of aniline black *pigment* cemented on to the fabric [such as the product first marketed by Roberts, Dale & Co.]."[45]

Although Müller-Pack won the Merrimack case, it was not the end of disputes and rival claims over processes for obtaining aniline black in the United States (or, for that matter, in Europe). Müller-Pack's stranglehold on the use of aniline black, through the Lightfoot patent and its reissue, and the acquisition of rights to other processes, did not put off everyone. New aniline black processes, invariably of European origins, became available in the United States, and were the subjects of further wrangling, not all inside the courthouse. By 1900, eleven patents for aniline black had been taken out in the United States, three in the period 1860–69, five between 1870 and 1879, and three during the following decade. These provided plenty of room for claimants who thought they might be able to preempt the field, or at least deceive printers and dyers. A letter in the May 1879 issue of the *Textile Colorist* from the Eddystone Manufacturing Company, of Eddystone, near Philadelphia (formerly the bleaching and calico print works of William Simpson, Senior), implied that it was in possession of patent rights for dyeing with aniline black. Read Holliday & Sons retorted that they held the patent rights to the color (although they

[44]Ibid., pp. 11–12.
[45]Ibid., p. 2.

only possessed rights to the disputed process of Samuel Grawitz).[46] P. Prunier admonished the Eddystone company over its far-reaching claims, and the dyer F. J. Bird described Read Holliday & Sons as "manly" for the manner in which it had responded.[47]

The Nature of Aniline Black

In Europe, the many cases of litigation, as well as interest in better methods of application, stimulated research into the chemical nature of aniline black and the processes for its production.[48] The renewed interest in the scientific debate, in which several leading chemists were involved, caused the technical press to inform its readers of more recent, if not up-to-date, progress. An article "On Aniline Black" in the October 1880 issue of *Chemical Review* noted: "few procedures have given scope for so many discussions, and even lawsuits, as the formation of this black. Every one would have the best process, and kept his system a secret, and all, without knowing it, worked almost in the same manner."[49] The *Textile Colorist* considered the article to be "of

[46]During 1877–79, Read Holliday & Sons had taken up the British and U.S. patent rights to a chrome aniline black process of William Jules Samuel Grawitz of Paris. Because two of Holliday's sons were already established in the aniline dye business in the United States, where the market was dominated by German imports of finished colorants, the transatlantic aniline-black market offered a useful means for diversification. From July 1879 to April 1881, Read Holliday & Sons advertised in *Chemical Review* that it granted "licenses to dye Grawitz's Patent Fast Aniline Black. This black is ESPECIALLY ADAPTED FOR COTTONS; it resists Acids, Alkalies, Age, and mordant bleachings; it does not become Brown or Grey."

[47]"Correspondence," *Textile Colorist* 1 (1879): 71, 87, and 104.

[48]Most notable was an 1879 dispute between Grawitz, who had taken out his first aniline black patent in Paris on September 30, 1874, and Alexander Schultz. It arose from an investigation commissioned by the Société Industrielle de Rouen into Grawtiz's claim that chromium compounds (as also patented by Paraf) could be used in place of vanadium. The study was undertaken by a committee headed by the chemist and aniline black expert Georges Witz and was closely followed in the trade and scientific press, where several articles on the subject appeared. Schultz had publicly made it known, in the *Moniteur Scientifique* and elsewhere, that he would "pay the sum of 10,000 francs to M. Grawitz if he can produce a single metre of black cloth as he affirms." "Report on the Use of Chrome in Aniline Blacks," *Chemical Review* 7 (May 1879): 144–46. It was claimed that Grawitz had stolen the 1876 process of Koechlin Frères, and he also came under attack from M. Blondeau, editor of *Moniteur de la Teinture*. This case was eventually settled in the favor of Grawitz, at a cost of 10,000 francs to Schultz, by the Paris Tribunal of Commerce during July 1880. See "Grawitz and Blondeau," *Textile Colorist* 2 (November 1880): 255. See also *Affaire Wibaux-Florin et Gaydet Père et Fils contre Samuel Grawitz. Teinture et impression en noir d'aniline. Mémoire de refutation* (Paris, 1882). This includes an account of Müller-Pack's misappropriation of Alland's process (p. 36).

[49]"On Aniline Black," *Chemical Review* 9 (October 1880): 268–71, esp. 268.

such interest to the great body of American dyers that we take the liberty of transferring it to our columns."[50] It was in fact a translation from the *Teinturier Pratique,* which in turn had freely adapted an 1876 contribution from Auguste Rosenstiehl of Mulhouse to the *Bulletin de la Société Chimique de Paris.*

Rosenstiehl noted that three substances were required to form the black: a salt of aniline, chlorates, and a metallic salt; "the latter have attracted most attention, in consequence of the especial part which they appear to play." For blacks developed by exposure to air, the preferred metal was copper. The oldest theory was based on the property of copper that enabled it to form two salts: the oxide (cupric oxide) and suboxide (cuprous oxide). Rosenstiehl had shown "more than ten years ago that the theory on which this is based is not correct. My experiments were published in the *Bulletin de la Société Industrielle de Mulhouse.*"[51]

The article then highlighted Paraf's contribution to the scientific debate. Paraf's process was, after Lightfoot's, the first process known to Rosenstiehl: "According to the author, this [chloric] acid, as well as the chlorine and the intermediate oxides of chlorine, produce the black by their action on the muriate of aniline. . . . The idea which has served M. Paraf as a guide is correct, in part at least . . . but things do not happen as he supposes, and the chloric acid does not suffice to transform the muriate of aniline into black in the conditions of practical working."[52]

Rosenstiehl concluded that for textile printing a small quantity of copper was necessary, and a good result was obtained with a mixture of one part of copper to one hundred parts of aniline. He considered that aniline black was a mixture of two blacks, and concluded "that aniline black is produced at common temperatures whenever muriate of aniline is placed in a dehydrogenising medium, such as active oxygen, chlorine, and its oxides, lower than chloric acid."[53] Of course, as Rosenstiehl had earlier pointed out, industrial practice differed from laboratory experiments, and the presence of a metal was still considered essential in printing and dyeing.[54]

[50]"On Aniline Black," *Textile Colorist* 2 (November 1880): 259–61.

[51]Ibid., p. 259.

[52]Ibid., p. 260.

[53]Ibid., p. 262.

[54]The conditions under which the black was formed had also been studied by Camille Koechlin, Charles Zurcher (of J. J. Zurcher & Cie, Haut-Rhine), and Noelting and Jules Brandt, all of whom, like Rosenstiehl, described their results to the chemistry section of the Société Industrielle de Mulhouse.

Aniline Black after 1890

By the 1890s various methods had been devised for printing aniline black in combination with other colors, mainly through the use of resist and discharge processes. In the latter case, a second color was applied after the aniline salt, but before it had time to oxidize. These were described by Dreyfus in 1894.[55] Beginning that year, the chemist Arthur G. Green worked on aniline black at Clayton Aniline as manager of the color department. In 1934, Green described it as a "pigment produced upon the cotton fibre . . . seldom produced in substance."[56] It was formed when salts of aniline were subjected to oxidation, preferably in the presence of an oxygen carrier, such as a salt of copper, vanadium, or ferrocyanide. There had been little change in the materials and methods of application since the time of Lightfoot, Lauth, Cordillot, and the other pioneers.

At the end of the 19th century, the use of aniline black had reached "enormous dimensions," but since that time, it had "suffered considerable diminution" through the introduction of sulfur blacks, which were cheaper and easier to dye.[57] In spite of its great technical importance, the chemical structure of aniline black remained unknown for a long period. Early work by Crace-Calvert, Rudolf Nietzki, and Liechti and Suida showed that it was produced through a green intermediate. Caro made a further contribution in 1896, and the research was taken up again by Green around 1907, in Leeds,[58] and at the Zurich Federal Polytechnic by Richard Willstätter.[59] In 1913, the constitution and mode of formation were finally elucidated, when Green and Salomon Wolff showed that the "ungreenable" black, the final product of aging and processing, was what they called a "triphenylazonium-octaphenazine" compound, eleven benzene rings linked together through nitrogen atoms.[60] However, this structural knowledge had "brought no extension in this field."[61] The essentially craft-based empiricism that had led to the introduction of aniline black could not be improved by scientific knowledge.

[55]Charles Dreyfus, "On Resist and Discharge Styles with Aniline Black," *Journal of the Society of Chemical Industry* 13 (1894): 485.

[56]Green (n. 18 above), p. 61.

[57]Ibid.

[58]Green left Clayton in 1901 to become a consultant in London. He later accepted the Chair of Colour Chemistry and Dyeing at Leeds, moved to Levinstein Ltd. during World War I, and became research director at the British Dyestuffs Corporation, Blackley, Manchester, resigning in 1923.

[59]Richard Willstätter, *Aus Mein Lieben* (Weinheim, 1949), pp. 185–91.

[60]Arthur G. Green and Salomon Wolff, "The Constitution of Aniline Black," *Journal of the Society of Dyers and Colourists* 29 (April 1913): 105–16.

[61]Green (n. 18 above), pp. 61–62.

Conclusion

Industrial processes are often shrouded in secrecy, even if much relevant information is revealed in patent specifications. It is only natural for a manufacturer to try and prevent the escape of fine details about how a product is made, especially if the process might be close to that of a rival's. This makes the work of the historian of technology particularly difficult, unless there are available details of much-dreaded and expensive patent infringement suits and the accompanying literature put about by protagonists and other interested parties. Despite their obviously partisan nature, reports and statements by witnesses and participants do reveal much of what has become known about how and where a new process was introduced, with wider implications for the diffusion of new technologies. What becomes apparent here is that the personal nature of technology transfer began to decline as powerful manufacturers and agents acquired patent rights from individual inventors. Science-based innovation became increasingly controlled through corporate litigation, even in cases where extensive research in academic and industrial laboratories failed to afford satisfactory fundamental knowledge about novel processes.

The Merrimack case shows how Alfred Paraf was a principal carrier of knowledge about aniline black to North America. He was continuing the traditions of the Mulhouse colorists and chemists, who, for this colorant, remained at the forefront of chemical explanation, technical improvements, and transfer of technology until the late 1880s. However, throughout the 1860s and 1870s, Müller-Pack had acquired rights to the major outcomes of their inventiveness, which meant that users of alternative processes in the United States came under rapid attack from the Basel firm.

Significantly, aniline black arrived in the United States in the same year that aniline manufacture was commenced there. But whereas the range of aniline and coal-tar dyes expanded rapidly because of new chemical theories (and availability of intermediates), the nature of aniline black, and the mode of its formation, remained only partially understood throughout the rest of the 19th century.

Although disputes promoted scientific research into the black, this was to little avail. Witnesses for plaintiffs and defendants might both make reasonable speculations on the chemical constitution of aniline black, or on the chemical reactions involved, but these did not materially affect industrial considerations. Their main purpose was to sidestep other issues in the hope that, by merging uncertain science with well-tried and proven technology, an argument might appear convincing. In the United States, as in Europe, litigation over chemical products was an uncertain and costly business, most especially when scientific explanation was not available.[62]

In 1875, Ordway considered that emeraldine, azurine, and aniline black were identical. In 1880, Levinstein implied that the industrial processes were almost the same. They were not far wrong. In 1887, as Cohen explained, emeraldine was thought to be an intermediate product in the formation of aniline black, and this was confirmed by Green and others in the early 1900s. The state of knowledge about aniline black before the 1880s was about the same as that of natural dye- and metal-making processes. As the *Textile Colorist* put it, "Vanadium and copper do not stay in the black composition after the dyeing or printing: their action seems to be merely 'influential,' and the insignificant quantity required for a powerful effect is still a wonder in chemistry. It is an unexplained phenomena like that of a few shots changing the whole character of a cast iron fusion."[63] Developments in aniline black remained decidedly empirical and craft based.

On a more general level, this story of the introduction of aniline black into the United States provides an insight into the patterns of 19th-century technology transfer, with special reference to the textile industry. Patents held by European firms became increasingly important in securing control of U.S. markets. Commonly, transfer began with correspondence between European entrepreneurs and inventors that turned to licensing arrangements. This mechanism for technology transfer was common throughout Europe and was the means, for example, whereby Alfred Mond introduced the Belgian Solvay process into Britain during the 1870s.[64] Moreover, before the late 1870s the geographically most wide-ranging, and the most effective, patent systems were those of Britain, France, and the United States, which is why Müller-Pack and others could monopolize control of new inventions in these countries alone.[65] For *chemical products* the situation was more straightforward in France and the United States than in Britain, where improved *chemical processes* for a given product could be patented.

In summary, the role of the individual in the creation and transfer of new knowledge remained paramount until the third quarter of the

[62]Henk van den Belt, "Action at a Distance: A. W. Hofmann and the French Patent Disputes about Aniline Red (1860–63); Or, How a Scientist May Influence Legal Decisions without Appearing in Court," in *Expert Evidence: Interpreting Science in the Law*, ed. R. Smith and B. Wynne (London, 1989), pp. 185–209.

[63]"Vanadium and Black Aniline," *Textile Colorist* 2 (June 1880): 137.

[64]Peter J. T. Morris, "Ludwig Mond," *Endeavour* 13 (1989): 34–40. See also Jeremy, ed., *International Technology Transfer* (n. 1 above).

[65]In Switzerland and Germany during the 1860s, Müller-Pack relied on the income from sales of the products used in aniline black printing.

19th century. In the case of new dyestuffs, the agent of personal transfer was the colorist, whose job it was to pass on useful information about the latest techniques for dyeing and printing. The colorist moved to and fro across Europe[66] and, in several cases, to the United States. Paraf was treading a well-worn path, but one that is poorly documented (because of the levels of secrecy involved), especially in regard to the transatlantic movements of specialists in the preparation and use of dyes. Only after the 1880s, with changes in national patent systems, and new rulings over chemical products and processes, would the transfer of chemistry-based technology come to rely more and more on the strengths of corporate negotiations over licensing agreements.[67]

[66]Homburg (n. 21 above).

[67]In the 1880s, for example, the BASF company lost its monopoly on artificial alizarin in the United States as the result of a Supreme Court ruling. It was only with the growth of large corporations in the 20th century that the nature of technology transfer, at least for chemical inventions, underwent its own transformation. See, e.g., Peter J. T. Morris on "Transatlantic Transfer of Buna S Synthetic Rubber Technology, 1932–45," in *The Transfer of International Technology: Europe, Japan and the USA in the Twentieth Century*, ed. David J. Jeremy (Aldershot, Hampshire, 1992), pp. 57–89.