150th Anniversary of Mauve and Coal-Tar Dyes

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One-hundred-and-fifty years ago, in March 1856, a teenaged chemical inventor in London discovered in his home laboratory a process that converted aniline, made from coal-tar benzene, into a purple colorant, later known as mauve. The young man was William Henry Perkin, assistant to the German chemist August Wilhelm Hofmann, then head of the Royal College of Chemistry. From Perkin's single serendipitous discovery coal-tar products went on to become a group of organic compounds that would make tremendous contributions to material well-being, not only though synthetic dyestuffs, but pharmaceuticals, products for the processing of rubber, and new polymers. They revolutionized the study of chemistry, and forged academic-industrial collaborations. The enterprise made reputations and attracted the greatest stars of organic chemistry, including Hofmann, Adolf Baeyer, and Emil Fischer. No less profound were the economic and political consequences. The new colorants, as agents of modernity, forced changes in patent law, fostered technology transfer, stimulated the emergence of the modern chemical industry and decimated cultivation of dye yielding plants.

Colorists and Chemists

During the last quarter of the eighteenth century the introduction of power-driven machines for spinning, weaving and printing introduced vast changes in the production of textiles. This created unprecedented demand for dyes and pigments, or colorants, that were applied to textile goods. The supply and efficient application of colorants was critical to the success of the whole endeavor. How this was achieved is the story of the creation of modern science-based industry.

Before the mid-1850s, the experts in the application and improvement of dyes were the colorists. It was their job to analyze the mainly vegetable-based extracts, such as blue from indigo and red from the root of the madder plant, and seek out ways of improving the fastness of dyes. Analysis was applied to dyes, mainly vegetable extracts, and certain metal compounds, called mordants, that fixed the dyes to fabrics and often enabled different colors to be produced. While the stud-

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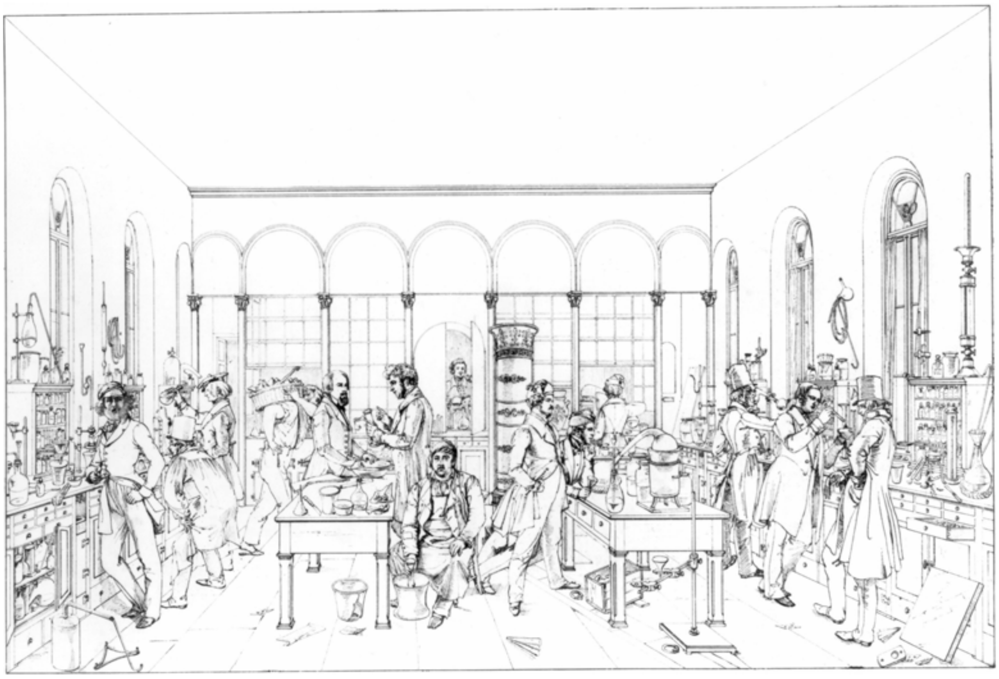
ies were mainly empirical, a vast body of knowledge was built up. However, details of new processes were not always revealed, since there was a long tradition of maintaining dyeing processes, on which the fortunes of dyers relied, as closely guarded secrets. This would change with the introduction of artificial dyes and the greater application of scientific knowledge after 1850.[1]

Leading chemists were drawn into investigations early on, and though they did not have the benefit of equations and formulas, they classified chemicals according to their dyeing properties. This led to considerations of the affinities of different dyes for fabrics, thus setting precedents for later investigations into chemical bonding. From around 1830, elemental analysis, in addition to qualitative tests, was widely employed. There were many disputes, and not just over relative masses. Despite the polemics, a set of well ordered procedures evolved. Some chemical investigators even considered the possibility of creating artificial, or synthetic, colorants from readily available raw materials. One such raw material was coal tar, the unwanted byproduct of coal gas manufacture, used from the early 1800s to light streets. The coal tar was invariably dumped, sometimes into rivers and streams, creating severe environmental problems.



Interior of Justus Liebig's teaching laboratory at the University of Giessen, 1842. At extreme right, wearing a top hat, is August Wilhelm Hofmann. Lithograph by Trautschold and Ritgen, 1842, in: Acht Tafeln zur Beschreibungen der chemischen Laboratoriums in Giessen, by J. P. Hofmann (Heidelberg 1842).

The main studies on coal tar were conducted in the laboratory of Justus Liebig in Giessen. One of his assistants was A. Wilhelm Hofmann, who in the early 1840s isolated several products, including what was later known as aniline. It was the first member of a group of distinctive chemicals that were later known as aromatic amines. In 1845, Hofmann was appointed head of the new Royal College of Chemistry in London, England, and continued with his investigations into aniline and similar products. By then, chemists had mastered a number of simple multi-step syntheses on the laboratory bench. In the mid-1850s Hofmann suggested that quinine might be synthesized from coal tar naphthalene. This inspired his teenaged assistant William Henry Perkin to undertake an experiment involving oxidative condensation of allyltoluidine in his home laboratory. Instead of quinine he obtained a black mass that he discarded. However, though a novice, he did not give up, and drew on experimental skills honed in Hofmann's laboratory. To establish why the reaction did not work, Perkin decided to repeat it, this time with aniline, the simplest analog of the aromatic amine he had used. Again he obtained a black mass, but on treatment with alcohol, he observed a beautiful purple solution that perhaps by accident stained a piece of cloth. Perkin was aware of the need for new dyes to supplement the limited range then available, including of purples, that were all the rage in the world of high fashion. He found that his purple when used as a dye, particularly on silk, resisted the action of light and washing. It was a fast dye.

A. Wilhelm Hofmann, with students and assistants, at the Royal College of Chemistry, London, ca. 1855. William Henry Perkin is in the back row, fifth from right (Edelstein Collection).

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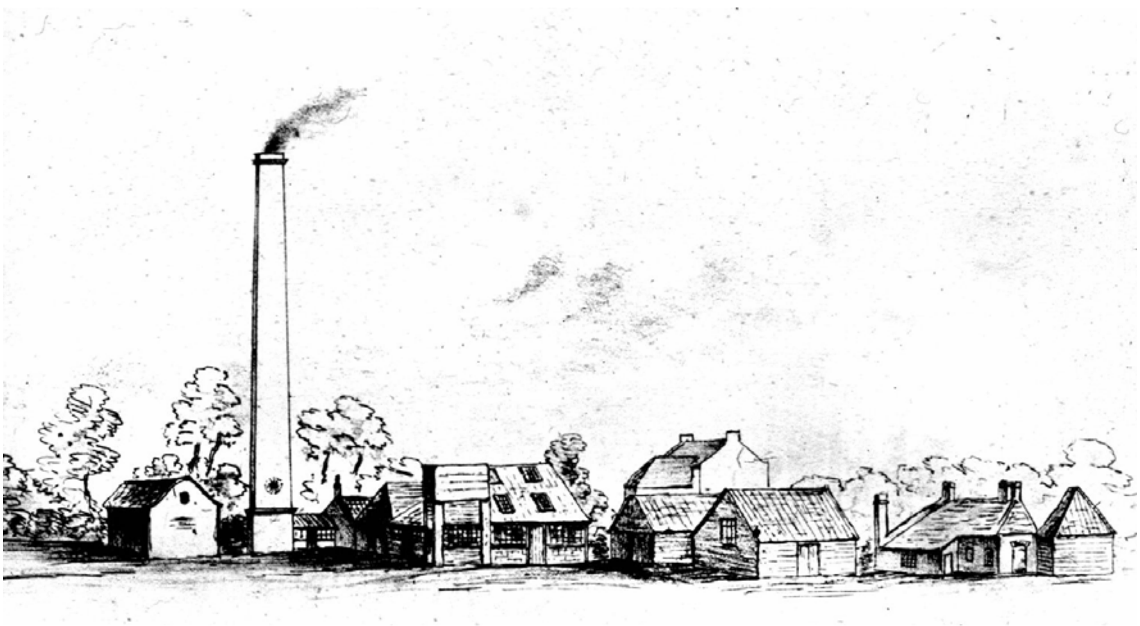

William Henry Perkin's dye-making factory at Greenford Green, northwest of London, in 1858. The first product was Aniline or Tyrian Purple, from 1859 known as Mauve (Edelstein Collection).

A dyer in Perth, Scotland, confirmed the potential of Perkin's novel discovery, and in August 1856, the young inventor filed a patent for the process and product. Though the purple was fast, and superior to other purples, that faded easily, Perkin could not license his process. Rather than give up, Perkin, a brother, and their father, decided to set up in a business as manufacturers of the purple dye. This was not easy. They had to develop a three-step process on a scale beyond that employed at the laboratory bench. First, benzene, distilled out of coal tar, had to be refined, then converted into nitrobenzene, which in turn had to be reduced to aniline. The aniline was then treated with an oxidizing agent, and the colorant, available in about 5 percent yield, was prepared in a form suitable for the users, mainly silk dyers. By 1858, industrial-scale production had begun. Marketing required a name that invoked some level of newness and significance. The purple colorant was called Tyrian purple, to suggest an association with the ancient dye of the Levant. Though it was directly applicable to silk dyeing, the main market, if the business was to flourish, was in cotton printing, as carried out in Lancashire, where machines produced millions of miles of printed fabric. Perkin's color did not take well to cotton, and in any case the printers that he visited were suspicious of anything so completely new, even after Perkin devised a suitable fixing agent. It was only after dyers and printers in France began using the novel purple dye late in 1858 that it caught on. The importance in France arose from the fact that dye users were anxious to break the monopoly on a new lichen-derived purple that was of unprecedented fastness. And Perkin's color was

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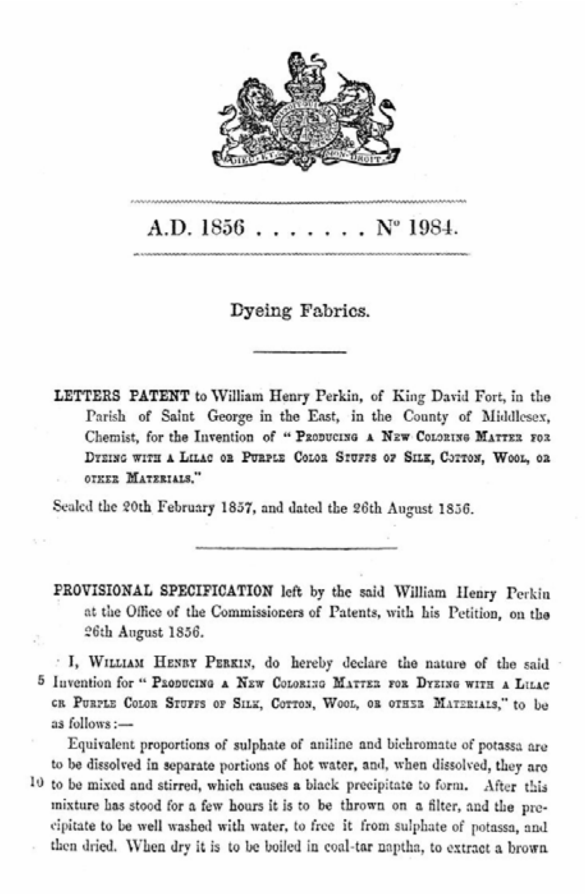
just as fast. By early 1859, it had become the main color of fashion, and the English gave it a more permanent name, mauve, from the French word for the mallow flower.[2]



A.D. 1856 . . . . N° 1984.

Dyeing Fabrics.

LETTERS PATENT to William Henry Perkin, of King David Fort, in the Parish of Saint George in the East, in the County of Middlesex, Chemist, for the Invention of "PRODUCING A NEW COLORING MATTER FOR DYEING WITH A LILAC OR PURPLE COLOR STUFFS OF SILK, COTTON, WOOL, OR OTHER MATERIALS."

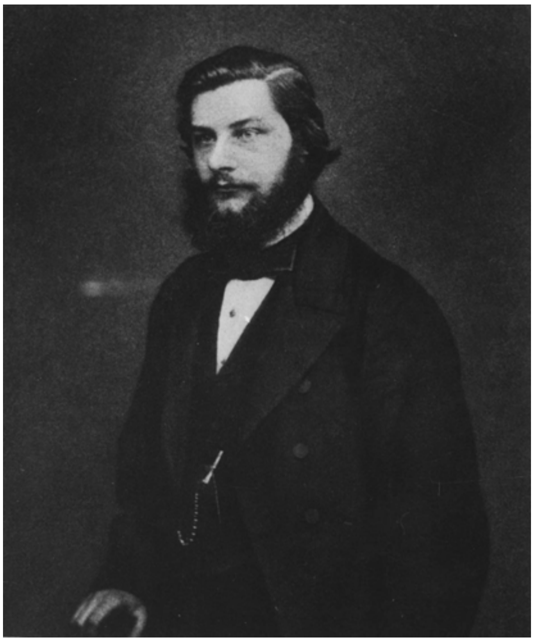
Sealed the 20th February 1857, and dated the 26th August 1856.

PROVISIONAL SPECIFICATION left by the said William Henry Perkin at the Office of the Commissioners of Patents, with his Petition, on the 26th August 1856.

I, WILLIAM HENRY PERKIN, do hereby declare the nature of the said Invention for "PRODUCING A NEW COLORING MATTER FOR DYEING WITH A LILAC OR PURPLE COLOR STUFFS OF SILK, COTTON, WOOL, OR OTHER MATERIALS," to be as follows:—

Equivalent proportions of sulphate of aniline and bichromate of potassa are to be dissolved in separate portions of hot water, and, when dissolved, they are to be mixed and stirred, which causes a black precipitate to form. After this mixture has stood for a few hours it is to be thrown on a filter, and the precipitate to be well washed with water, to free it from sulphate of potassa, and then dried. When dry it is to be boiled in coal-tar naptha, to extract a brown

First page of William Henry Perkin's English patent for aniline purple (Tyrian purple, mauve), no. 1984, 26 August 1856 (Edelstein Collection).



William Henry Perkin (1838-1907), in 1860 (Edelstein Collection).

The success of mauve soon kindled the imaginations of several colorists and chemists, who undertook similar experiments to see if aniline might render other colors. This was soon achieved by a colorist working in Lyon, France, who late in in 1858 or early in 1859 discovered an aniline red dye, called fuchsine (in England it was named magenta). All this work was done without the aid of structural formulas. At best chemists had a system for writing partial, or constitutional, formulas for the coal-tar products, but these were of little use to inventors of novel dyes. One problem was the formula of benzene. The ratio of carbon to hydrogen atoms did not allow a structure to be drawn based on the four-valent carbon theory introduced in 1858.

Once chemists were called in as consultants to the dye makers, they adapted their research agendas to the chemical problems of creating artificial dyes. Most successful was Hofmann in London, who already had two decades of experience with aromatic amines. His approach was so successful that in May 1863 he not only predicted a new color but discovered it (Hofmann's violet). He established empirical formulas, and then partial structural formulas, or constitutional formulas (1864), for the aniline red and its blue and violet derivatives, based on his so-called ammonia-type of 1850. Hofmann gave the free base of aniline red a more scientific name, rosaniline.

Heinrich Caro (1834-1910), technical leader at BASF, 1868-1890 (Edelstein Collection).

Colorists, however, were still important in the early days of the synthetic dye industry, none more so than Heinrich Caro, born in 1834 in the town of Posen (Poznán of modern Poland), then an outpost of eastern Prussia. When he was still a child Caro's family moved west to Berlin, the capital of Prussia. In 1855 he became an apprentice colorist at C. & F. Troost, a calico, or cotton, printer in Mülheim, in the Ruhr Valley. He quickly acquired the knowledge that would later enable him to identify potential novel artificial dyes. His skills in practical textile coloration impressed his employers, who in 1857 sent him to Manchester to investigate the latest developments in textile machinery and the chemicals employed in printing. In 1859, the peak year for Perkin's mauve, Caro left Germany and sailed for Manchester, the center of the vast British textile industry. He joined the firm of Roberts, Dale & Co., that supplied natural dyes and chemicals to textile manufacturers. Caro discovered a new route to the mauve dye that Perkin had discovered, and a novel black colorant that was extracted from the residue of his mauve process. He also investigated all the new coal tar dye processes. Caro's understanding of the special needs of dye users and agents for dyes, and his after-sales service, enabled him to promote and sell the novel products of his employer, and bring about extensive usage of artificial dyes. This he put to good use when he returned to Germany late in 1866, and especially after he joined BASF in 1868.[3]

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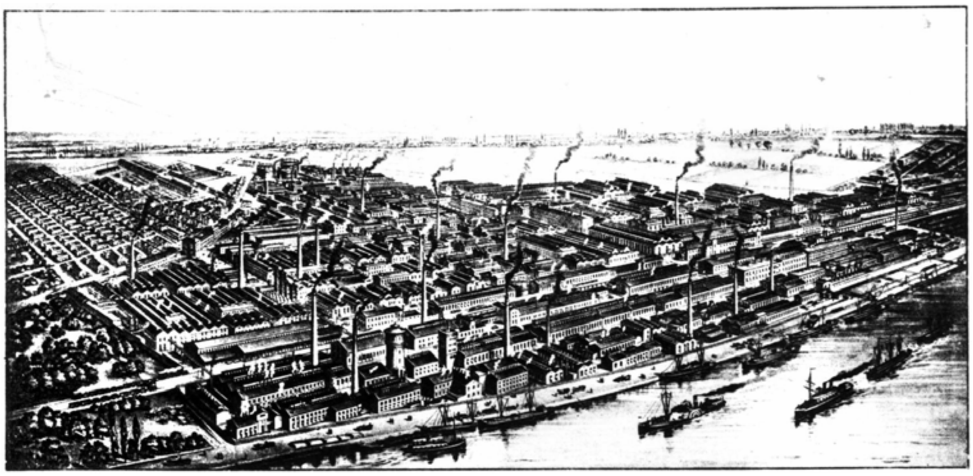
Research for Dyes

The development of new dyes brought together industrial and academic chemists to engage in highly novel synthetic studies. Since the academics were particularly important as consultants, solving problems that might make dye manufacture more profitable, and as expert witnesses in cases of patent litigation, it was in their interests to undertake in-depth studies on processes and products. The scientific foundation of the dye industry was established by Hofmann, the leading consultant and expert witness in court disputes. However, there were limitations as to how far the scientific endeavor could go. That changed after 1865, when F. August Kekulé put forward his benzene theory. This satisfied the empirical formula for benzene. One of the first important applications of the benzene theory was in unraveling the secrets of the dye from the madder plant, a substance called alizarin. This had intrigued chemists and colorists since around 1830, but despite their efforts to create it on the laboratory bench from another coal tar hydrocarbon, naphthalene, all experiments failed. The reason, as discovered in 1867 by Carl Graebe and Carl Liebermann, two young assistants of Adolf Baeyer in Berlin, was that the "mother substance" of madder red was anthracene, another coal tar hydrocarbon. In rapid succession, the formula and partial structure, a dihydroxyanthraquinone, was worked out as was a method of synthesis.[4] It was the first time that a natural product of considerable complexity had been synthesized in a laboratory. The process was sold to the then new BASF (Badische Anilin- & Soda-Fabrik) company, situated at Ludwigshafen, on the River Rhine, and close to Mannheim. There Heinrich Caro established a commercial route independently of and at the same time as William Perkin. They both filed patents in London in June 1869.[5] The outcome was an agreement over marketing and exchange of technical information.



BASF factory, at Ludwigshafen, around 1900 (Edelstein Collection).

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Industrial production began during 1869-70, and soon improvements were introduced based on academic and industrial collaborations into intermediate chemicals and the products. The development of the alizarin synthesis was one of the most important scientific-technical innovations of the 1870s. It was a major achievement in the early period of the second industrial revolution, and enabled the rapid emergence of Germany as the leading nation in the field of synthetic dyestuffs.

Alizarin and Indigo

The alizarin industry became the model for the future relationship between science and technology. This began after Baeyer and Caro in 1874 published the modern structure of alizarin. The outcome was massive expansion in the synthetic dye industry, and demand for trained chemists and new chemical knowledge. This set the academic agenda for chemistry during the remainder of the nineteenth century.

Hofmann returned to Berlin to take up an appointment as professor of chemistry. He also acted as consultant to his former assistant in London, Carl Alexander Martius, co-founder of a forerunner of AGFA.

As a result of interest in synthetic dyes, new methods of synthesis appeared, as did a growing body of concepts and techniques, including a theory of color and constitution suggested in 1875 by Otto N. Witt, then working at a dye firm near London. Witt successfully predicted the existence of an unknown colorant, a yellow of the azo-dye type. He shared information about the new dye with Caro, who had done similar work, and they agreed to keep the details a secret. In 1876 it was marketed by BASF as chrysoidine. However, its structure became public knowledge when Hofmann explained through publication the structure of azo dyes, based on the –N=N– atomic grouping as a linkage between two aromatic moieties. This opened the field of azo dye research throughout the synthetic dye industry.

The diversity of coal-tar colorants, and the fact that for the first time the range of colors was no longer restricted to vegetables and minerals, enabled rapid changes in high street fashions. Moreover, there was a continuous clamor for new dyes, which drove the research programs of both dye companies and their academic consultants. The structural elucidations of synthetic dyes became the basis of PhD programs, and success led to offers of jobs in industry at a time when academic appointments were few. To protect their inventions, German chemists,

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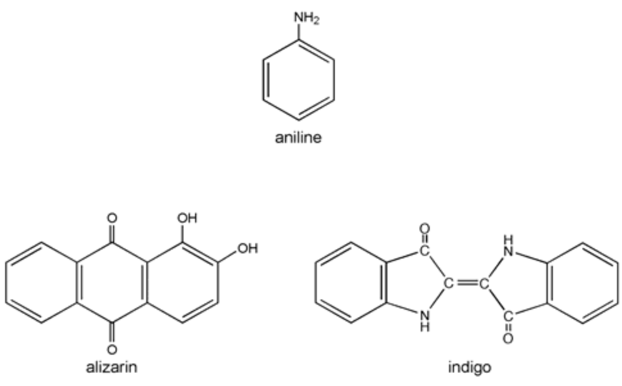
particularly Hofmann, were among those who lobbied for a patent law that was comprehensive throughout Germany. The patent law was introduced in 1877, and created the most advanced system in the world for protection of science-based inventions.[6] It was subsequently amended, including to suit the needs of the coal-tar dye industry. British and French patent systems, while geographically comprehensive, did not adequately protect science-based inventions, which was one of the reasons for the decline of their dye industries. Apart from that, British and French chemists neglected the new structural theories that had in part emerged out of the study of synthetic dyes, and were essential for further progress. Significantly, Emil and Otto Fischer at the end of the 1870s established the structures of rosaniline and its derivatives. This enabled the synthesis of molecules with similar structural features, such as methylene green. Research into azo dyes enabled AGFA to introduce the first benzopurpurine dye, Congo red, in 1884. Meantime the British preferred to rely on their colonial industries, including that of cultivation and processing of indigo, rather than invest in science education and research-based industry.

The Central Research Laboratory in Industry

Heinrich Caro was responsible for the introduction of industrial research as a formal business activity at BASF, and in the late 1880s designed the firm's Central Research Laboratory, prior to retiring from industry at the end of 1889. By then industrial research laboratories had become became established in all research-based industries.[7] Chemists pursued investigations relevant to both fundamental and applied science, as well as in the important activity of patent protection, which often relied on new knowledge. From this time, technical innovations based on industrial research became the source of growth at all science-based industrial concerns.



During the 1870s, Baeyer and Caro had collaborated on research into indigo, work that enabled Baeyer to establish the modern structural formula in 1883. This contributed to his receiving the Nobel Prize for Chemistry in 1905. Following the 1890 discovery by Carl Heumann in Zurich that readily available

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coal-tar benzene and naphthalene could be transformed into indigo, the German firms BASF and Hoechst in 1897 commenced the manufacture of synthetic indigo and soon destroyed the British monopoly on the natural product, with severe implications for colonial trade and the livelihoods of thousands of Indians. In Germany, coal-tar intermediates were converted into medicinal products, notably Aspirin, introduced by Bayer in 1899. In 1901 René Bohn at BASF applied the conditions of the indigo synthesis to an aminoanthraquinone and discovered a fast blue dye, the first member of the Indanthrene range of vat dyes. Profits from dye manufacture enables BASF to diversify into high-pressure chemistry with the Haber-Bosch process, inaugurated at Oppau, next to Ludwigshafen, in 1913. In the mid-1930s, the Bayer laboratories of I.G. Farben, the 1925 merger of BASF, Bayer and Hoechst, developed sulfonamide drugs, the first member (Prontosil) of which was a derivative of an azo dye discovered by Caro when working in England during the 1860s.

The former BASF Central Research Laboratory (Hauptlaboratorium), Ludwigshafen, designed by Heinrich Caro in the mid-1880s, in 1999 (A. S. Travis).

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America and Britain

Before 1915, the United States was not a major manufacturer of synthetic dyes, mainly as a result of the German monopoly, maintained by an aggressive policy of patent protection. However, America was one of the main consumers of dyes for its textile industry, and after World War I broke out in 1914 was faced with a shortage, since Germany requisitioned supplies of dyes for military uniforms, and the British blockaded transatlantic shipping. This forced the Americans to react with the establishment of small dye-making firms, and dye manufacturing departments at major firms such as Du Pont and Dow.[8] One of the most important outcomes was the organization of sophisticated, well-equipped and well-staffed research facilities dedicated to dyes that from the late 1920s were expanded to include investigations into polymers and fibers. The outcomes were products such as nylon (Du Pont).

Despite the severe decline of the British synthetic dye industry, there were two important successes. In 1928, chemists at Scottish Dyes, later part of Imperial Chemical Industries (ICI), discovered by chance a blue pigment that was introduced as Monastral blue. Analysis showed that it was iron phthalocyanine. This was the only completely novel structural class of colorant introduced in the twentieth century. In 1956, ICI introduced the first fiber-reactive dye (Procion range), on the occasion of the 100th anniversary celebrations for the discovery of William Perkin's mauve.

Dye manufacture in Europe and North America was important until the 1970s, which is why in the past the anniversaries for both mauve and Perkin's birth had attracted great attention, as well as extensive participation from the chemical industries. That this was not the case in 2006 is largely due to the fact that the dye industry founded by Perkin has so little presence in Europe and North America. Environmental problems arising from the manufacture of colorants and the shift of the textile industry to Asia have caused the great dye firms to reinvent themselves as agrochemical and pharmaceutical corporations, casting off long heritages that sometimes go back to the 1860s. Today the centers of production are India, China, Japan and eastern Europe, while the main use for aniline is in the manufacture of polyurethane, originally discovered at the end of the 1930s in the Leverkusen laboratories of I. G. Farben.

1 E. Homburg, “The Influence of Demand on the Emergence of the Dye Industry. The

ISSN 0934-8506

Roles of Chemists and Colourists," *Journal of the Society of Dyers and Colourists* 99 (1983): 325-33; Homburg, "From Colour Maker to Chemist: Episodes from the Rise of the Colourist, 1670-1800." In *Natural Dyestuffs and Industrial Culture in Europe, 1750-1880*, eds. R. Fox and A. Nieto-Galan, pp. 219-57. Canton, Mass., Watson International/Science History Publications, 1999.

2 A. S. Travis, The Rainbow Makers: The Origins of the Synthetic Dyestuffs Industry in Western Europe, Lehigh University Press, Bethlehem, PA, 1993.

3 C. Reinhardt and A. S. Travis, Heinrich Caro and the Creation of Modern Chemical Industry, Kluwer, Dordrecht, 2000.

4 E. Vaupel, "Carl Graebe (1841-1927) – Leben, Werk und Wirken im Spiegel seines brieflichen Nachlasses," 2 vols. Ph.D. diss., University of Munich, 1987.

5 C. Schuster, "Heinrich Caro." In *Ludwigshafener Chemiker*, ed. Kurt Oberdorffer, vol. 2, pp. 45-83. Düsseldorf: Econ-Verlag, 1960; Schuster, *Vom Farbenhandel zur Farbenindustrie. Die erste Fusion der BASF*. Ludwigshafen, BASF, 1973; Schuster, *Wissenschaft und Technik. Ihre Begegnung in der BASF während der ersten Jahrzehnte der Unternehmensgeschichte*, Ludwigshafen, BASF, 1976.

6 P. A. Zimmermann, *Patentwesen in der Chemie. Ursprünge, Anfänge, Entwicklung*, Ludwigshafen, BASF, 1965.

7 C. Reinhardt, *Forschung in der chemischen Industrie. Die Entwicklung synthetischer Farbstoffe bei BASF und Hoechst. 1863-1914*, Technische Universität Bergakademie Freiberg, 1997; Reinhardt, "An Instrument of Corporate Strategy: The Central Research Laboratory at BASF, 1868-1890." In *The Chemical Industry in Europe, 1850-1914: Industrial Growth, Pollution, and Professionalization*, eds. E. Homburg, A. S. Travis, and H. G. Schröter, pp. 239-59. Dordrecht: Kluwer 1998. E. Homburg, "The Emergence of Research Laboratories in the Dyestuffs Industry," *British Journal for the History of Science* 25 (1992): 91-111.

8 A. S. Travis, Dyes Made in America, 1915–1980: The Calco Chemical Company, American Cyanamid and the Raritan River, Edelstein Center/Hexagon Press, Jerusalem, 2004.