The Origins of the Synthetic Dye Industry

The synthetic dye industry is regarded as the first science-based industry, which began in 1856 with the discovery of aniline purple, later called mauve, by William Henry Perkin (1838-1907, Fig. 1). Perkin, an eighteen year old student at the Royal College of Chemistry in London, was attempting to synthesize quinine, a natural product important in the treatment of the malaria plaguing British colonists. This followed the suggestion of his mentor, August Wilhelm Hofmann, a German chemist and head of the College. The experiment failed. Perkin then repeated the experiment, this time oxidizing aniline, a coal tar derivative, with potassium dichromate, yielding not quinine, but a tarry residue. The eureka moment occurred when he noticed the solution on workup stained cloth a brilliant purple.

Fig. 1 Sir William Henry Perkin with Mauve Fabric, 1906. By Arthur S. Cope, National Gallery.
From that point on, the stars aligned perfectly for Perkin to commercialize his invention. He provided a sample to Pullar’s dye works in Perth, Scotland. The dye was found suitable for silk, with improved light- and wash-fastness compared to natural purple dyes, based on murexide and lichen, used at the time. Purple was a color of high fashion, renowned for the ancient Tyrian or Roman purple obtained from the murex sea snails. The Tyrian purple was first produced by ancient Phoenicians and was once reserved for royalty.

England was the birthplace of the Industrial Revolution and by the early 1850s the mass production of textiles was expanding rapidly, encouraging Perkin to seek out a market for his purple. He filed a patent for the dye in 1856. Within two years he built a small dye-making factory in northwest London with the help of his older brother Thomas and financial aid from his father, builder George Perkin. The risky venture was called Perkin & Sons.

But Perkin had more than good luck on his side. His genius was the ability to solve manufacturing and marketing problems concurrently. Aniline was not commercially available, so he had to devise a process and set up equipment for the nitration of benzene, followed by reduction and distillation. The cast iron nitration tank was agitated by hand and the workers faced hazards from toxic fumes and explosions. The only control instrument was a thermometer, so the first batches of mauve varied greatly in shade due to impurities and side products. At the same time, Perkin visited skeptical customers to assist in the application of the dye. He found the dye went on silk more evenly with a soap bath and discovered that tannin would serve as a mordant, or binding agent, fixing the dye on cotton and opening up new business with the large calico printers in Lancashire and Scotland.

By the spring of 1859, the purple, now named mauve in England, reached its peak of popularity in London and Paris, the world’s fashion centers. A royal-looking dress was within reach of middle and working class women. But the mauve rage lasted only a few years and demand for the dye declined with the introduction of other brilliant aniline dyes. This was first example of how consumer preferences for color would dictate the fortunes of the synthetic dyes industry. Organic chemistry, however, had begun a prominent role in serving the needs of the textile industry and the two industries, dye manufacture and dye application at printers and dyers, became linked through their inventions.

A rainbow of dyes based on aniline soon appeared on the horizon (Fig. 2). The second aniline color, a brilliant red called fuchsin, was introduced in 1858 or early 1859 by the Lyon factory of Renard Frères. The London dye firm Simpson, Maule & Nicholson purchased the patent rights to an improved process, using arsenic acid as the oxidant, and marketed the dye as magenta. Magenta, known in France as fuchsin, far outsold mauve. The French chemists Girard and de Laire discovered the third color, aniline blue, in 1860 by simply heating magenta with aniline. The patent for the sky blue shade was acquired by Renard Frères and licensed to Simpson, Maule & Nicholson for production in England. The golden dye chrysaniline yellow, suitable for silks and woolens, was discovered as a byproduct of magenta production.
Fig. 2 Early Aniline Based Dyes
Professor Hofmann, who had discouraged Perkin from entering dyestuff manufacture, became involved in the industry when former student Edward Nicholson, of the firm Simpson, Maule & Nicholson, asked him to determine the chemical composition of magenta in 1862. Hofmann found the molecular formula of the base was \( C_{20}H_{19}N_3 \). Although the structural formulas of the dyes were unknown at this time, Hofmann had earlier reasoned that aniline was an ammonia derivative in which one hydrogen was replaced by what is now called a phenyl group. He also determined the aniline blue was a triphenylated magenta.

The discovery led Hofmann to the logical step of adding functional groups to the magenta structure to create new shades. An alkylation reaction afforded brilliant violets, quickly manufactured by Nicholson and named Hofmann’s violets. They were the first dyes made not by accident, but by theory-based scientific research. Hofmann had unlocked the chemical secrets of the class of dyes named triphenylmethane, assuring his role as the premier scientific advisor of the emerging dye industry.

Perkin’s financial success with mauve encouraged competitors to enter the field, expanding the range of available dyes, improving processes and lowering the costs for the textile industry. At the London International Exhibition of 1862, twenty-nine dye makers from Western Europe displayed cottons, silks, cashmeres and even ostrich plumes dyed in brilliant synthetic colors. There were nine firms from England; twelve from France; seven from Germany and Austria; and one from Switzerland.

The early dye firms focused on the triphenylmethane dyes, some blatantly copying patented products and others skirting the patent with a different synthetic route. The patent laws varied throughout Europe and in most German states there was no patent protection at all, as was the case in Switzerland. Patent litigation, based on poor patent law for chemical invention, gave Renard Frères a monopoly on the magenta-related dyes in France. In England, Simpson, Maule & Nicholson lost its patent rights to magenta, again due to poor patent law, and the process went public, expanding competition. By 1864 the price of magenta fell by 90 percent compared to 1860.

The use of toxic arsenic acid as the oxidant in the magenta process had health consequences for both consumers and dye factory workers. Newspapers reported women developed skin rashes after their dresses were exposed to rain or perspiration. Analysis of commercial magenta dyes showed the arsenic content ranged from 2.0 to 6.5 percent, which may have caused the rashes, although this was not scientifically established. Dye workers suffered ulcerations of the nose, lips and lungs. The Swiss dye firm J. J. Muller-Pack was forced to close in 1864 after people living near the Basel factory fell ill from arsenic in well water. In a stinging rebuke, the court ordered the founder of the company to hand deliver clean drinking water to residents. The Renard Frères factory in Lyon ceased production of magenta after poisoned wells caused fatalities. Improvements in equipment design, ventilation and the switch to steam driven agitation reduced worker exposure to chemical hazards. Over time the arsenic process was improved to reduce the residual toxicity of the dye and some firms replaced arsenic with safer oxidants. But the early reports of health and environmental issues were a warning sign of the hazards associated with dye making and the later negative public perception of the industry.

Germany Takes the Lead in Dye Industry

The most notable dye manufacturers in Germany in 1865 were Friedrich Bayer & Co. (Elberfeld); Meister, Lucius & Co. (later Hoechst, Frankfurt); and Badische Aniline & Soda Fabrik (BASF, Ludwigshafen). BASF and Hoechst were located along the River Rhine, useful for cooling water and the barge delivery of heavy chemicals such as sulfuric acid, caustic soda and salt needed for dye production. Bayer later moved to Leverkusen to gain the benefits of a location along the Rhine. German artist Otto Bollhagen painted the plant in a realistic, almost photographic style (Fig. 3). There was a barge dock and a rail line for the efficient delivery of bulk chemicals. Manufacturing buildings for the various product lines were laid out in blocks along streets, in a logical design favored by the German firms.
The earliest dyes from the German firms were imitative of the British, in the same way that German industries like iron, glass, gas, textile and machinery got their start based on British models. A wave of innovation began with the return of German chemists from Britain. Professor Hofmann was recruited by the University of Berlin in 1865 with a higher salary and larger laboratory, where he trained an army of chemists for industry. Heinrich Caro, who had developed new dyes and the aniline black process for cotton printing while at Roberts, Dale & Co. of Manchester, joined the University of Heidelberg in 1866 and later became director of research at BASF. Carl Martius, who had developed Manchester brown, one of the first azo dyes, at Roberts, Dale in 1863, started an intermediates firm in Berlin in 1867 that became the dye maker AGFA.

The race for the leadership of the European dye industry began to favor Germany in the early 1870s. The natural dye alizarin, extracted from the madder root, was used for centuries to dye military uniforms red. Perkin and Caro independently found synthetic routes to the dye based on coal tar derived anthraquinone. Perkin was the first to establish production in 1869 and in 1873 produced 435 tons. The BASF process, however, had higher yield and gave a more desirable shade. Collaboration with university chemists gave BASF a better understanding of the structure of alizarin and how to minimize byproducts. The price dropped by two-thirds in 1873 and the alizarin market was taken over by Germany. Germany soon had over 50 percent of world sales of synthetic dyes.

Another blow to the future of the British dye industry occurred in 1874 when Perkin sold his business to the competing firm Brooke, Simpson & Spiller. He realized his firm was too small to compete with the Germans but was reluctant to expand, which would require raising capital and finding a more advantageous location along a river, with a railroad siding. He had grown weary of the patent litigation necessary to protect his discoveries and tending to the daily problems of manufacturing. His fortune was estimated at £100,000 which is equivalent to $10.2 million today. He retired a wealthy man at just 35 years of age to pursue basic chemistry research in a private laboratory, authoring many scientific papers on the techniques of organic synthesis.

Perkin's exit from the dye industry illustrated two major reasons the German firms leaped ahead—the supply of capital and industrial chemists. British private investors and banks favored businesses with a predictable future, such as shipping, railroads, iron, and textiles which were booming due to a large population and global markets. The synthetic dye industry was based on science and risk; research was needed to continuously introduce new products that might be in demand for only five or ten years. British universities did not train chemists for industry, a fact cited by Perkin as a major obstacle in expanding his business. The situation was the same in France, where the industrial scientist did not enjoy the prestige of an academic scientist. The early innovation in the French dye industry could not be sustained because of the shortage of chemists.
Prussia, the largest state in the German Empire, promoted industrialization with economic policies that encouraged foreign and domestic capital investment. An extensive road, canal and railroad network was built. The state used its own funds to start industries that were too risky or too expensive for private capital. The growth of German textile manufacture, in response to the population increase from 25 million in 1820 to 40 million in 1870, also aided the dye industry.

Germany understood the value of creating technical schools for mechanics and supporting universities and polytechnic institutes to educate scientists and engineers for industry. There was little social or academic bias for chemists to apply their knowledge in a dye laboratory; industry offered good jobs and consultancy fees at a time when few academic posts were available. Relationships with university chemists were actively sought. Bayer had close ties with the University of Göttingen, AGFA was linked to Hofmann at Berlin, and Hoechst and BASF worked with Adolph Baeyer who taught chemists in Berlin, Strasbourg, and Munich. The universities unraveled the chemical structures of new dyes for their partners, giving them a better understanding of the relationship of structure to the shade and dyeing properties.

In the late 1870s, this knowledge allowed the firms to develop the azo class of dyes, discovered by German chemist Peter Griess, working at an English brewery, in 1858. Aromatic amines react with nitrous acid to form a diazo compound, which can react, or couple, with other aromatic compounds. The two compounds are linked with the azo group -N=N- to form dyes, with a full spectrum of shades ranging from yellow to black, depending on the chemical structures of the raw materials. Unlike the triphenylmethane dyes made mainly from aniline, the azo dyes could be made from an almost unlimited number of aromatic amines and coupling compounds. Various functional groups, such as the sulfonic group, could be introduced into the structure, to modify the affinity of the dye for the fiber. Azo dyes could therefore be targeted for application to cotton, wool, silk, paper or leather. The mad scramble for the discovery of these dyes spurred the expansion of the industrial research laboratories. The creation of a uniform patent law throughout Germany in 1877 gave the German firms a monopoly on azos, which became the largest selling dye class, and later all other novel dyes.

The German dye makers were as aggressive in marketing their products as they were in research and manufacture. They excelled at market research and technical service, closely adapting the product to the consumer, and were sensitive to the cultures of foreign countries. An efficient system of market information was established worldwide to collect information for the home office to evaluate and act upon. When reports from China indicated the dyers preferred colors pressed into small cubes, the firms quickly modified their packaging. Dye labels for the containers were designed to appeal to the indigenous population and instructions were often pictorial for countries where illiteracy was high. A Bayer label, dating to about 1900, is shown in Fig. 4. Graphic artists of the company created the labels in the Jugendstil art nouveau style popular at that time.
Handbooks of dyed and printed fabric swatches mounted on stiff paper, called shade cards, were another way to advertise. The books were artistically produced and included technical information and dyeing recipes for customers. They were issued in a dozen languages, including Japanese. Each firm had a department of colorists to produce the dyed samples of textiles, paper, leather, wood, feathers, etc. which were mounted by hand. (Fig. 5).

Fig. 4 Bayer Dye Label for China, ca. 1900.

Fig. 5 Bayer Colorists Produce Dyed Samples for Handbooks, ca. 1900. Photo: E. Verg, G. Plumpe and H. Schultheis, Milestones: The Bayer Story (1863-1988), Bayer AG, Leverkusen, 1988.
Diversification of the German dye industry into pharmaceuticals took place in the 1880s-1890s, starting with the manufacture of the anesthetics chloroform and ether. The need for antiseptics arose with the introduction of the germ theory. These products were derived from the phenol family, used for years as dye intermediates. The first fever and pain reducing drug was Antipyrine, a pyrazolone compound made by Hoechst in 1883. Bayer introduced Phenacetine (p-ethoxyacetanilide) in 1888 and Aspirin (acetylsalicylic acid) in 1898. The sedatives Sulfonal (Bayer) and Hypnal (Hoechst) came next. Koch and Pasteur’s work in immunology led Hoechst into the large scale production of serums and vaccines to control diphtheria, typhus, cholera and tetanus. German scientist Paul Ehrlich, who earlier worked on the cell-staining properties of dyes and their potential therapeutic uses, discovered Salvarsan, a treatment for syphilis, in 1909. The organoarsenic compound, manufactured by Hoechst from a coal tar intermediate, was the first chemotherapeutic drug. Ehrlich called Salvarsan a "magic bullet" because it targeted a specific pathogen. The search for magic bullets would later transform some dye makers into pharmaceutical firms.

In the early 1900s, the German dye industry introduced vat dyes, ideal for application to cotton without the aid of a mordant. Along with azo dyes they were the most important colorants of the 20th century.

The Emergence of the Dye Industry in the United States

In 1913 Germany produced almost 300 million pounds of dyes worth $60 million, with 80 percent exported. The United States was Germany’s largest foreign market, importing 30 million pounds. A handful of dye makers in New York and New Jersey, established in the late 19th century, produced a few million pounds, only ten percent of requirements. The industry was hampered by the lack of organic chemists, limited availability of coal tar intermediates, and low tariff rates on imported dyes that the powerful textile industry lobbied for in Congress. German dye firms were members of cartels that coordinated production, marketing and pricing strategy, frustrating American attempts to enter the market. The outbreak of World War I and the British blockade of German shipping caused a dye famine that dimmed color everywhere. Dyes were in short supply for consumer clothing, military uniforms, postage stamps, and even red ink for accountants.

The panic in the marketplace drove prices to unheard of levels. Rhodamine B for paper dyeing went from $1.00 per pound before the war to $50. Sulfur black for cotton, the largest volume imported dye, rose from $.20 to $3.00 per pound. A few shiploads of dyes arrived from neutral Holland in 1915, but each amounted to only a month’s supply. The German cargo submarine Deutschland eluded British patrols in 1916, arriving in Baltimore with 125 tons of dyes (Fig. 6). The delivery had little impact on the dye famine, serving more as a political statement by the Germans that commerce with the neutral U.S. could not be stopped by the blockade.
In the United States, the dye famine sparked a wave of nationalistic fervor that helped the development of the fledgling dye industry. Newspaper editorials promoted the strategic value of the industry, since the nitration capacity for dye intermediates could be switched to production of high explosives for artillery shells in wartime. Dye manufacturing was now highly profitable, attracting the investments of both private entrepreneurs and large companies. Some of the new firms had improbable beginnings, such as Calco Chemical, founded in 1915 in Bound Brook, New Jersey to manufacture dye intermediates. The firm was previously a manufacturer of fabrics for wall covering. The chemistry to make intermediates was gleaned from German textbooks, trial and error laboratory experiments, and advice from a Yale University professor who was a classmate of founder Robert C. Jeffcott.

The Grasselli Chemical Company produced heavy chemicals, including sulfuric acid for oil refineries, at a plant in Linden, New Jersey. In 1915 it built an adjoining plant to manufacture intermediates and sulfur dyes. Technical advice came from consultant Adolph Wack, a German chemist who worked for a firm in Newark, and by hiring Swiss chemists with dye experience. The company built 300 homes nearby to house workers, many of them Irish and Polish immigrants. This neighborhood remains today and is known as Grasselli Park.

As the supply of dyes dwindled, partially shutting down textile mills, the textile industry now saw the advantages of supporting a domestic dye industry. Tariffs on dyes and intermediates were increased in 1916 and the government published detailed import data so investors could gauge the size and value of the market.

America’s entry into the war in April 1917 spurred further developments in the dye industry. The success of the German firms was based on large scale manufacturing operations that included intermediates and heavy chemicals such as sulfuric and nitric acids. This was the model for the National Aniline & Chemical Company, established in 1917 by merger of the dye firms Schoellkopf Aniline and Chemical and Beckers Aniline and Chemical, along with parts of several coal tar and basic chemical companies. The new company represented the first highly integrated approach to dye manufacture in the U.S. National Aniline then had 75 percent of the dye market. The dye lines of Schoellkopf and Beckers were complimentary since Schoellkopf specialized in cotton, silk, leather, and paper colors while Beckers was strong in colors for woolens. Dye production was consolidated at the former Schoellkopf site in Buffalo, New York. New buildings were constructed including a research department and a massive power plant with soaring brick arches, giving it a cathedral-like appearance (Fig. 7). This was a symbol of the high esteem America placed on industrial progress at the time.
Textile mills and consumers, especially women, were wary of the quality of the American made dyes. National Aniline launched a publicity campaign with newspaper ads and displays at leading department stores, showing fabrics dyed with National and the counterpart German dyes. National proudly announced "Fast American Dyes Are Here" with fabric samples proving the dyes had good light- and wash-fastness.

Synthetic indigo was the Holy Grail of dye makers in the late 19th century, since the natural product from plantations in India was the world's largest selling dye. In 1897, BASF and Hoechst were the first to develop commercial processes, starting from coal tar hydrocarbons. So indigo was a high priority target of U.S. firms like Dow Chemical, which produced heavy chemicals at Midland, Michigan. Dow developed a process starting from aniline, with the help of organic chemist Lee H. Cone from the University of Michigan. After setbacks, Dow began production in 1917 and was soon making 1.5 million pounds annually, capturing 50 percent of the domestic market. This signaled the beginning of the end of the German monopoly on dyes.

Company founder Herbert Dow had an artistic vision of his plant, and commissioned English painter Arthur Knighton-Hammond to paint scenes of Midland (Fig. 8). The oil painting displays the power of the new American chemical industry in a serene pastoral setting, accented by the small boat in the foreground.
Another major step in establishing a dye industry took place in 1917 when Du Pont, the largest explosives maker in the U.S., built a multi-million dollar dye plant in Deepwater, New Jersey along the Delaware River. DuPont selected sulfur black as the first candidate for production, since it was a large volume dye made in one step from dinitrophenol, which Du Pont could easily produce based on its nitration experience. But the production of sulfur black came with poor yield and quality despite the efforts of Du Pont's top chemists. German patents were of little help, since they were masterpieces of obfuscation, omitting information and written in a way to prevent competitors from learning their knowhow. The patents enabled Germany to dominate the global dye market and discourage American manufacturing efforts. It was apparent that a chemist had to be "skilled in the art" to duplicate these patents.

In 1920 Du Pont embarked upon a cloak and dagger mission to obtain the services of German chemists. A DuPont representative in Zurich convinced four Bayer chemists in Leverkusen to bolt Germany and work for Du Pont. The German chemists filled a trunk with process information, equipment drawings, plant layouts and dye samples. At a Dutch border checkpoint the trunk was opened. The suspicious looking contents resulted in seizure of the trunk and notification of German authorities. The Cologne prosecutor issued an arrest warrant for the four chemists for industrial espionage. The charges against the chemists included “illegally appropriating valuable recipes, formulae, etc., to which they had access by virtue of their positions of trust and confidence”. Protection of dye secrets had led Germany to the extreme step of prohibiting the issuance of passports to German chemists. The German public
was outraged about the incident and newspaper headlines screamed “Four Traitors”, “An American Plot Against German Dyestuff Industry”, and “The Power of the Dollar”.

Despite the arrest warrant, two of the German chemists, Dr. Joseph Flachslaender and Dr. Otto Runge, managed to board a Dutch steamer for New York. The remaining two chemists, Dr. Max Engelmann and Dr. Heinrich Jordan, were smuggled out of Germany in 1921. They each signed five-year employment contracts for $25,000 a year, a staggering salary for a chemist at the time. Du Pont now had four talented German dye chemists working in the Jackson Research Laboratory in Deepwater. A wide range of dyes was soon in production.

**Seizure of German Assets in U.S.**

After the U.S. entered the war, anti-German sentiments raged with fears of German spies and sabotage of American industrial and military facilities (Fig. 9). The Chemists Club in New York City advised members not to speak German at the facility.

![Fig. 9 World War I Poster Warned Americans of German Spies. Photo: Library of Congress.](image)

The government seized German owned textile mills, metal foundries, chemical plants and patents. This included the Bayer Company which operated a plant, dating to 1882, on the Hudson River in Rensselaer, New York making dyes and aspirin.

In late 1917 Federal Judge A. Mitchell Palmer, the Alien Property Custodian, announced his intention to "Americanize" the company and named four new members to the board of directors. Palmer claimed that some German board members conspired to violate the Trading with the Enemy Act. In 1918 five company officials were arrested and charged with diverting profits to a dummy American corporation in Rhode Island. The purpose was to enable Bayer to reestablish its dyes and pharmaceuticals business in the U.S. when the war ended. The arrests included Dr. Rudolph Hutz, manager of the Boston sales office. At the time Hutz was staying at his summer home on Pine Island, Lake Winnipesaukee, New Hampshire. Secret Service agents found a boat and rowed out to the island to make his arrest at 1:30 AM. They found him sleeping in bed and immediately handcuffed him. He had four medal decorations from the German government in his possession, along with a large photograph of the
German Emperor. Hutz was charged with espionage and interned first at Ellis Island and then at a prison camp in Fort Oglethorpe, Georgia. The arrests were followed by firing Rensselaer employees suspected of sympathizing with Germany. These draconian actions seem harsh in retrospect but reflected the xenophobic attitude Americans had for Germans during the war, and the tremendous power of German dyes and chemical technology.

In late 1918 the government sold the Bayer plant at auction to the pharmaceuticals firm Sterling Products. Sterling was only interested in the aspirin production and acquired the U.S. rights to the valuable Bayer cross logo, recognized worldwide as a symbol of quality and purity. Sterling immediately sold the dye manufacturing section of the plant to Grasselli Chemical for $2.5 million.

**Post World War I Consolidation of the Dye Industry**

By 1919 the U.S. had invested $466 million in the dye industry, which employed 2,600 chemists compared to only 214 in 1914. The domestic industry was now self-sufficient and even exported $17 million of dyes in 1920. The government took steps to further strengthen the industry by limiting the import of German dyes with a licensing program in 1921 and by increasing tariffs again in 1922.

The business recession of the early 1920s reshaped the industry, forcing the closure of many small dye firms or their merger with larger companies. By 1930 the four largest dye makers were the Allied Chemical and Dye Corporation, which absorbed National Aniline and Chemical; Du Pont; American Cyanamid Corporation, which absorbed Calco Chemical; and the German owned General Aniline Works.

The establishment of General Aniline was a surprising development in view of government actions to prevent Germany from reentering the U.S. market. Grasselli Chemical had acquired 1,200 German patents by purchasing the Rensselaer dye business but lacked the knowhow to work the patents and expand manufacture. Grasselli and Bayer merged in 1924 to form the Grasselli Dyestuff Corporation. In 1925 Bayer, Hoechst and BASF merged to form I.G. Farben, the world’s largest chemical combine. Grasselli Chemical sold its heavy chemicals business to Du Pont and its share of Grasselli Dyestuff to I.G. Farben in 1928, forming the General Aniline Works. The infusion of capital and the transfer of technology from Germany into the Rensselaer and Linden plants made General Aniline a major player in the dyes market.

The war also revitalized the dye industry of Britain, with post war consolidation and import restrictions strengthening its competitive position. The two largest prewar firms, Read Holliday of Huddersfield and Levenstein of Manchester, merged in 1919 to form the British Dyestuffs Corporation which controlled 75 percent of British production (Fig. 10).
In 1926, Imperial Chemical Industries (ICI) was formed when British Dyestuffs merged with the basic chemical companies Brunner, Mond; United Alkali; and explosives maker Nobel Industries. The acquisition of Scottish Dyes in Grangemouth in 1928 added the important class of vat dyes to the ICI range.

Vat dyes, as mentioned earlier, were discovered at BASF in 1901. These complex products are made with multistep syntheses starting with anthraquinone. The dyes are insoluble so they have to be dissolved in a solution of sodium hydrosulfite, called vatting, before application to cotton. Oxidation then locks the color in the fiber, providing extraordinary light- and wash-fastness. Vat dyes spanned the color spectrum and became the largest dye class, eventually surpassing azos. German patents and the difficult chemistry involved prevented British and American firms from entering the field for almost two decades.

James Morton, a Scottish textile manufacturer, imported German vat dyes for fabrics used for clothing, curtains, upholstery and outdoor awnings, all requiring outstanding light-fastness. When the war stopped the supply from Germany, Morton setup a dye manufacturing unit and by 1917 a small range of Caledon vat dyes was in production. A new plant was built at Grangemouth in 1919 and the business was named Scottish Dyes. Morton challenged his chemists to develop a green vat dye, a goal even German dye firms failed at, and in 1920 Caledon Jade Green was discovered (Fig. 11). It quickly became a worldwide best seller. This triumph of British dye chemists was underlined in 1925 when a license was granted to BASF.
Vat dyes were in great demand in the U.S. for heavily laundered items like denims, shirts, and bed linens and outdoor fabrics such as awnings. But production was limited by the supply of anthracene, the precursor to the anthraquinone building block of vats. This was overcome with the commercialization of a new process that made anthraquinone from readily available naphthalene and benzene. The process was developed in 1917 at a government color laboratory established to help the emerging dye industry. By the early 1930s, the leading dye firms were in full production of vats. The U.S. industry now matched every dye class of the German firms and was on an equal technology basis with research and manufacturing capability.

The phthalocyanines, discovered in 1934 by ICI, were the last major dye class discovered in the 20th century. These brilliant blues and greens, with excellent fastness properties, could be produced as either dyes or pigments with a wide range of applications. The Du Pont versions were called "Monastral" colors, samples of which were actually used in 1939 by noted painter N.C. Wyeth in his masterpiece The Island Funeral.

The U.S. Dye Industry Fades in the 1970s

The protective tariff barrier of 1922 shielded U.S. dye makers from global competition for decades. The introduction of synthetic fibers rayon, nylon, acrylic and polyester created consumer demand for new fashions and home furnishings like wall to wall carpeting. New generations of dyes were launched to meet the synthetic fiber applications. The U.S. dye makers owned the huge domestic market, with dye output surpassing Germany in the 1950s. There was little incentive to pursue exports even when the I.G. Farben combine was broken up after World War II. This was a grave error since Bayer, BASF and Hoechst were in chaos after the war. British and Swiss dye firms increased their exports as a result.

The tariff barrier proved to be a two-edged sword, encouraging foreign investment in U.S. dye plants. Ciba built a world-scale vat dyes plant in Toms River, New Jersey in the early 1950s which also supplied partners Geigy and Sandoz (Fig. 12). About the same time, ICI purchased the Arnold, Hoffman dye plant in Dighton, Massachusetts where ICIs new line of reactive dyes for cotton (1956) was introduced. Hoechst acquired the Metro Dyestuff plant in West Warwick, Rhode Island in 1954 which became part of American Hoechst. In 1957 Bayer purchased Verona
Dyestuffs, which in the early 1970s led to building a modern plant for disperse dyes for polyester near Charleston, South Carolina.

The tariff barrier was chipped away by the General Agreement on Tariffs and Trade (GATT) in the mid-1960s, which reduced the rates yearly until their elimination in 1981. I saw the impact on the dye industry firsthand while working at the General Aniline & Film Corporation in Linden, New Jersey. This was the former General Aniline Works, seized as enemy property in World War II and later becoming a U.S. public corporation known as GAF. In the summer of 1966 I was a college student hired as a chemist in the vat dye department. During a tour of the anthraquinone intermediates building I noticed idle equipment. My supervisor said it was now cheaper for GAF and other dye makers to buy intermediates from Europe.

The German dye firms had used Marshall Plan funds to modernize their intermediate manufacturing facilities and were more efficiently backward integrated than U.S. firms. The U.S. dependency on foreign intermediates proved costly after the 1974 oil crisis when the price of crude oil quadrupled. Higher raw material costs and a weakened dollar led to lower profits. The new EPA air and water quality regulations forced the companies to invest millions of dollars in pollution control. Research budgets were slashed in an industry that depended on a constant flow of new products.

During the period 1977-1982, four of the largest U.S. dye makers—Allied Chemical, GAF, DuPont and American Cyanamid exited the business. Although the specific reasons for quitting varied, the firms had diversified into other sectors such as fibers, plastics, rubber chemicals, agricultural chemicals and pharmaceuticals that sprang from the organic chemistry of dye research. So it made sense to prune dyes as the smallest and weakest, as well as most mature, part of their operations. The U.S. dye market, estimated at $1 billion in 1983, was now firmly in control of the German and Swiss firms who invested in plants there.
The European Dye Makers Quit by 2000

The European dye makers outlasted their American rivals with superior research, economies of scale, global marketing expertise and a long range view of their business which dated to the 1860s. But the historical commitment began to erode in the 1980s with structural changes in the textile industry. U.S. dye production in 1986 was 236 million pounds, an 8 percent drop compared to 1976. Dye makers had developed dyes and application methods to exhaust dyes more completely onto the fiber, lowering dye consumption and leaving less in the wastewater of textile mills. Foam dyeing of carpets used 30 percent less dye than older methods. Fiber weight also decreased. Men's suit fabrics, which once weighed up to 20 oz./yard, were reduced to a weight of 12 oz. or less. The heyday years of double-digit growth in dye volume were over.

As the synthetic fiber and textile industry shifted from Europe and the U.S. to the Far East, dye production boomed in China and India. Cheap labor and lower environmental standards gave these producers a significant cost advantage in the global marketplace. At the same time, the European firms were concentrating on the more profitable pharmaceutical, agricultural, and polymer businesses. They began exiting dye manufacture in 1993 when ICI spun off its dye business to Zeneca. DyStar was established in 1995 as a joint venture of the Bayer and Hoechst textile dye businesses. Later the dye businesses of Zeneca and BASF were added. Dystar built a $55 million dye plant in China in 2006 and is now owned by Kin Dyes and Chemicals of Singapore. The Swiss firms Ciba-Geigy and Sandoz exited the dye business after merging in 1996 to form Novartis, a global leader in pharmaceuticals.

Conclusion

The accidental discovery of mauve by a young English chemist in 1856 led to the first science-based industry, synthetic dyes. It was the high-tech industry of the 19th and early 20th century, showing how discoveries in a laboratory could be profitably converted to useful products. World War I demonstrated the political and economic importance of the emerging industry in the United States. The war economy and government protectionist measures enabled the U.S. and British dye industries to become self-sufficient, ending the global domination by Germany.

But the tariff barrier to free trade allowed the American firms to become complacent for decades, neglecting investment and research, and ignoring the global market. When the barrier finally fell in 1981, the German and Swiss firms had taken over the U.S. dye market and led the global industry until 1995.

Today the dye market is mature, with manufacturing centered in the Far East where the textile industry migrated from the U.S. and Europe to take advantage of higher economic growth rates and lower labor costs. The dye industry now represents less than 1 percent of the global chemical industry. The legacy of the dye industry is far greater, however, since the organic chemistry knowhow led to the synthetic fiber, plastics, rubber chemical, agricultural chemical, and pharmaceutical industries. And our world remains as colorful as ever (Fig. 13) irrespective of the location of dye manufacturing.
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