The purple past
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The Purple Past

From its beginning and into the future, our industry revolves around color. BY STEVE HERMAN

The purest and most thoughtful minds are those which love color the most.

—John Ruskin

SHERLOCK HOLMES retired to a quiet life of bee keeping in 1903, but he also found time to rekindle his old interest in chemistry. "The last picture we have of (Holmes) in retirement…shows him still interested in the coal tar derivatives…Holmes was perhaps in the process of isolating some new hydrocarbons of strange properties and values."[1]

Coal tar indeed contains "hydrocarbons of strange properties and values." If one event defines the birth of the chemical industry more than any other, it was the isolation of mauve dye from coal tar in 1856. The discovery by an 18-year-old boy in a primitive laboratory took science from the domain of a few academic researchers and placed it center stage in the world of commerce, where it revolutionized our world. The young lad at the center of the revolution was William Perkin.

FIGURE 1: MAUVEINE A

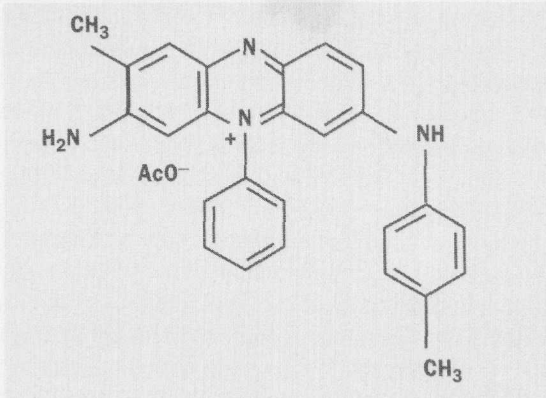
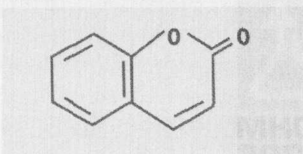


FIGURE 2: COUMARIN



The streets of London were lit by natural gas by the 1840s. Gas is produced by heating coal in closed vessels without oxygen, a process called destructive distillation. The process yielded several undesirable byproducts: foul water, sulfur compounds, and coal tar. Some uses were found for the sulfur, and ammonia was removed from the water, but the coal tar was believed to be without value.

The chemists of the time recognized coal as a highly complex mixture of carbon, hydrogen, oxygen, and a small amount of sulfur and nitrogen. Later research showed coal tar can be distilled to yield several useful organic products, including benzene, toluene, xylene, naphthalene, and anthracene. The component attracting the greatest interest for the early researchers was aniline.

Many of the reaction products were highly colored, but they were considered inconsequential. By contrast, the synthesis of quinine would be of immense importance, since it was the only known treatment for malaria. This was the task that attracted young Perkin, who hoped two alkyltoluidines ($C_{10}H_{12}N$) could be oxidized to yield quinine ($C_{20}H_{21}N_2O_2$) and water. The method used was simple: to begin with a starting molecule similar to the target, and treat it with two processes, distillation and oxidation. The intent was to either add oxygen or remove water.

Young William did not synthesize quinine, as his initial attempt ended with a reddish powder. Beginning again using aniline as a starting material, he got a black product. Only 5 percent of the dark substance was mauve dye, but Perkin succeeded in its isolation. The value of the new material was doubtful.

Dyes of natural origin have been used for thousands of years. Purple has been associated with royalty since antiquity, as the dye extracted from the glands of mollusk found off the Phoenician coast was so costly. Cochineal, a crimson dye extracted from insects, was the

A Perkin Chronology

1838	1853	1856	1868	1873	1906	1907
Born in London	Enters Royal College of Chemistry	Discovers mauveine	Synthesizes coumarin	Sells interest in dye business	Knighted, visits America amid many honors	Dies in Sudbury, UK

other common animal-derived dye. The three common vegetable dyes were woad, madder, and weld. Woad provided the common blue, the same as the indigo used in jeans. Madder is a red dye, with alizarin as the active color principle. Weld, containing the colorant luteolin, was the basic yellow.

Natural dyes were restricted to a limited color palette and tended to fade rapidly, but there was still no great outcry for superior synthetic materials. Most contemporary chemists would have thrown out the new mauve dye, but Perkin colored a piece of silk and noted its stability toward light and resistance to washing. Perkin decided to pursue the commercial application of his color. He received a positive response from a dye works in Scotland, applied for a patent, and obtained financial backing from his father—no bank would fund the endeavor.

The color ignited a fashion trend, spearheaded by Empress Eugénie of France. Soon chemists in France and Germany were duplicating Perkin's results, and making new colors of their own. The ties between industry and academia were strong in Germany, soon giving that country a strong lead in dye production.

Although Perkin made his discovery of mauveine in 1856, its exact structure was not determined until 1994[2]. The dye was found to be a mixture of mauveine A (Figure 1) and a small amount of a similar structure (not shown—it has one more methyl group), mauveine B.

Perkin continued the investigation of color, discovering Britannia Violet and Perkin's Green. The color of the Grand Union Canal near the factory was a different color every week, depending on what dye was being manufactured. In 1869, Perkin synthesized a vivid red dye, Alizarin. BASF beat him to the patent by one day.

Perkin became a wealthy man, but not nearly as wealthy as he might have become without patent infringements and foreign competition. He finally sold his interest in 1873. By the outbreak of World War I, 83 percent of the artificial dyes used in Britain were imported, and it was hard for the army to find enough material to dye its uniforms.

When his work with color ended, Perkin turned his attention to perfume materials. He synthesized coumarin (Figure 2), the first aromatic of natural origin recreated in a laboratory. The synthesis of aromatics from coal tar, especially in the laboratories of Germany, unleashed a flood of new materials into perfumery. The new products, stronger and of greater olfactory variety than the existing plant derivatives, revolutionized the fragrance industry from 1880 to 1910. Fully embracing the new chemicals, François Coty almost single-handedly created the modern cosmetic industry.

Coal tar (and later petroleum) chemistry led to a variety of products beyond dyes: antiseptics, plastics, pesticides, and explosives among them. Aspirin is another well-known example. Bayer began manufacturing aspirin in 1899 from salicylic acid, a dyestuff intermediate. Coal tar chemistry led Paul Ehrlich to pioneer chemotherapy, and aniline dyes allowed the discovery of chromosomes in the cell nucleus by Flemming.

The power of color certainly has dominated history. When the Trojans took up the ashes of Hector on the field of Ilium, he was wrapped in purple. "...they laid what they had gathered up in a golden casket and wrapped this about with soft robes of purple..."[3]

The royal color of antiquity was the ancestor of the technology that this year prompted P&G to spend $4.95 billion for Clairol. From its beginning, and into the future, our industry revolves around color, and no individual influenced its technology more than William Perkin. GCI

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