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## **A History Of The International Dyestuff Industry**

**By Peter J.T. Morris\* and Anthony S. Travis\*\***

*ColorantsHistory.Org thanks Bob McClelland of [Gwelanmor Internet](http://Gwelanmor.Internet) for adapting this article for users of Mozilla Firefox and other modern browsers.*

### **Introduction**

The preparation and use of dyestuffs is one of the oldest of human activities, as evidenced by the unearthing of ancient fabrics at archeological sites, as well as accounts in the Bible and works of classical antiquity. Until two centuries ago, the materials and methods had hardly changed. Then, with the advent of the industrial revolution, chemistry began to play a prominent role in the textile industry. This led to improvements in existing colorants and their methods of application. This article surveys the prehistory of modern dyes, the rise of the synthetic dyestuffs industry during the nineteenth century, when science-based innovations led to artificial products, and the changes brought about in the twentieth century by the challenge of novel fibers, increasing chemical knowledge, and fluctuating economic conditions.

### **Dyestuffs before William Perkin invented Mauve**

*The Orient, the Occident, and Colonial America. The introduction of cochineal, Turkey red and dyewoods into Europe. The first semi-synthetic dyes: picric acid and murexide. The structure of the dye industry in the 1840s.*

In 1630 a Mr. Higginson of Salem, North Carolina, noted of the local vegetation: "here to be divers roots and berries wherewith the Indians dye excellent holiday colors that no rain or washing can alter". <sup>[1]</sup> He, like other colonialists in the New World, marveled at the remarkable variety of dye-yielding trees and plants that were unknown in the Old World.

Until the arrival of these new sources of dyes, Europe relied almost exclusively on the same colorants that had been in use since antiquity, such as woad, madder and indigo. Even the methods of application had changed little from those employed by the ancient Egyptians. Mordants enabled a wide range of colors, especially when used with madder, and different cultures had developed not altogether different technologies.

Notable progress was made in Europe during the thirteenth and fourteenth centuries, especially by Italian and Venetian dyers. Merchants from Genoa established the trade in alum, the most important dye mordant, with the Gulf of Smyrna. There was bitter rivalry with Venice, which brought alum and dyes from the east direct to the low countries. From 1429 Florence also engaged in this trade. By the fifteenth century alum manufacture was commenced at Tolfa, in Italy. <sup>[2]</sup>

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In 1548, the first edition of the earliest book devoted exclusively to professional dyeing was published in Venice. This was Gioanventura Rosetti's *Plictho de larte de tentori che insegna tenger pan[n]i banbasi et sede si Per larthe magiore com per le comvne* [3], which included details of dye recipes and techniques employed in Venice, Genoa, Florence, and elsewhere in Italy. In particular, it provided the most complete record of the dyers craft at the time when the first South American dyewood was becoming available in Europe. [4] Until then three primary colors were employed by dyers. Blue was obtained from indigo, either from woad or the indigo plant. Reds were available from the Kermes insect, from the root of the madder plant, and from so-called brazilwood imported from the Far East.

Yellows were extracted from weld, Persian berries, saffron and dyers broom. These colors were combined to afford greens, browns, violets and other compound shades; they could be varied with the aid of mordants.

Rosetti's publication did not include cochineal, which only later in the sixteenth century displaced Kermes, mainly as a result of the voyages of Cortez (from 1523). Cochineal dyeing was improved in Holland around 1630, and the secrets of the new process were stolen by a German who carried the details to London.

Madder was the basis of Turkey red dyeing, introduced to Europe with the aid of Greek technicians in the eighteenth century. Madder was also important to the emerging calico printing industries of Amsterdam, Basle, Berlin, Elberfeld, Glasgow, Manchester and Mulhouse. Textile printing made great demands on the expertise of the colorist, and encouraged the publication of manuals on calico printing, the first of which was Charles Obrien's, *The British Manufacturers Companion and Calico Printers Assistant*, which appeared in London during 1790. [5]

Occasionally, an intrepid explorer would return with news of new discoveries. Chinese green, Lo-Kao, was not encountered by the Europeans until the end of the eighteenth century, and attracted much attention in the 1850s. [6] Sometimes, colors had fallen out of use, and their secrets had been lost, like the fabled biblical blue and Roman purple, first extracted from the murex snail by the ancient Israelites on the Levantine coast, and then adopted by the Phoenicians and Romans. During the nineteenth century many dyers and scientists attempted to discover the secrets of the colors of antiquity which were imitated using lichens and the New World's products.

While the new dyewoods enriched the ranges of European dyers, the American dyer's needs were met by madder, indigo and other vegetable dyes that were newly cultivated in Virginia from around 1650. Dyes from American woods also displaced those that had been imported. Fustic, cochineal and dyewoods were brought in from the West Indies, while South Carolina and Georgia became significant sources of cochineal. The inner bark of the common ash tree afforded an indigo substitute, while from around 1770 Edward Bancroft found that the inner bark of the American black oak gave the yellow colorant soon known as quercitron. [7]

The development of the colonial natural dye industry in North America coincided with a transatlantic revolution in methods of manufacture, especially of textiles. The rapid growth of the textile industry from the end of the eighteenth century came about through the introduction of mechanized processes, improvements in bleaching, and by the mid-nineteenth century multi-color roller printing. Notably, chlorine became the bleaching agent of choice. These new processes, and the introduction of steam power, enabled rapid and large scale production, and were accompanied by unprecedented demand for dyes. This

encouraged scientific studies, especially new methods for applying dyes in printing, and improved extraction processes notably in France. The Emperor Napoleon I signed a decree calling for madder dyeing on wool to be improved, [8] and in the 1820s the newly formed Societe Industrielle de Mulhouse offered a prize for chemical knowledge about madder This led to the first isolation and analyses of alizarin and purpurin.

The French dyers and printers in Mulhouse and Rouen, and the Germans in Berlin and Elberfeld, had close links with the sites of greatest consumption Lancashire and south-west Scotland, the hubs of the first great Industrial Revolution. Chemists were attracted to these areas, and they assisted the dyers and calico printers, who, in turn, began to appreciate the importance of chemistry.

One consequence of these developments was that the study of chemistry became a respectable activity since it offered possibilities for earning a livelihood.

New sources of dyes were investigated from the 1840s, such as coal tar, the waste of lighting gas works. Nitration of phenol from coal tar yielded yellow picric acid that was a useful dye for over three decades from around 1850. Justus Liebig and Friednch Wohler in Giessen had investigated murexide, a purple product obtained from snake excrement, although in the late 1830s its potential as a dyestuff was not immediately apparent.

The problem, as with many other new colorants, was that there were no known methods available for fixing novel "semi-synthetic" colors. Neither was the raw material abundant. Moreover, dye recipes were secrets that were not, as far as possible, allowed to escape from the confines of the dyehouse.

This situation began to change when chemically trained colorists moved around Europe, and sometimes across the Atlantic, picking up the latest developments and selling their skills to dyers and printers. [9] In the 1840s the dye-making industry was in the hands of the extractors of natural colorants merchants and dyers. The French were particularly successful, and their improved production methods for madder were investigated and imitated by the Dutch. [10] During the 1850s, French colorists and dye-producers, especially Depouilly in Paris managed to surmount the difficulties of making murexide from abundant South American guano, and of applying it to natural fibers, and it was adopted in Britain, France and Germany.

## **Mauve**

*William Perkin's discovery of an aniline purple, and why he succeeded.*

The study of coal tar products that transformed the world of dye-making was spearheaded by August Wilhelm Hofmann, an assistant of Liebig. [11] During the early 1840s, Hofmann demonstrated the identity of a basic compound obtained from various sources, including indigo and coal tar. It was soon named aniline from anil, the Arabic for indigo. After 1845 Hofmann and others prepared this aromatic amino compound in two steps from the coal tar hydrocarbon benzene. There were other coal tar hydrocarbons, such as toluene, naphthalene and anthracene. These were studied because their amino compounds appeared to be related to the alkaloids, above all the important drug quinine.



**August Wilhelm Hofmann, first director of the Royal College of Chemistry, London. An expert in coal tar products, he became a professor at the University of Berlin in 1865 and, two years later, founded the German Chemical Society. Edelstein Collection, Hebrew University.**

Hofmann, from 1845 director of the Royal College of Chemistry in London, and his students and assistants worked on reactions leading to a variety of amino compounds, as well as on the analysis of important natural substances, including dyestuffs. In 1853, the fifteen-year-old William Henry Perkin became one of Hofmann's students.



**Perkin at age 14 (1852) from a photo taken by himself. Edelstein Collection, Hebrew University**

After following the introductory course, Perkin was assigned a research project related to coal tar compounds. This was the preparation of an amino derivative of anthracene. Though the project was a failure, Perkin's interest in aromatic amino compounds led to similar experiments with benzene and naphthalene in 1855-56. Among the products were colored substances. Their dyeing properties were investigated, and noted in the subsequent published reports, which appeared during 1857.

Perkin was also interested in a route to synthetic quinine. He attempted this during the Easter vacation of 1856 in a laboratory that he had set up in a room at his parents' East London home. The idea was to bring about condensation of the amine allyltoluidine under oxidizing conditions with potassium dichromate. The experiment failed. To find out why, Perkin delved into the mysteries of aromatic oxidations. He treated aniline with the same oxidizing agent. The result, a black precipitate, appeared to be no more promising. Treatment with alcohol, however, afforded a purple solution which stained a piece of cloth. This color resisted soaping and the action of light, especially when attached to silk, and Perkin was soon considering its possibilities as a commercial dyestuff.

Perkin sent samples of his colorant to Pullars of Perth, dyers of piece goods with connections throughout Europe, who reported favorably of the novel substance. **[12]** Purple was a popular color, but the alternatives, made from lichens and the guano-derived murexide, were not fast to light, especially in the acidic atmospheres of industrial cities.

Perkin wisely filed a patent for his new invention during August 1856, and, in October, left the Royal College of Chemistry to pursue its improvement.



A.D. 1856 . . . . . N<sup>o</sup> 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."

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

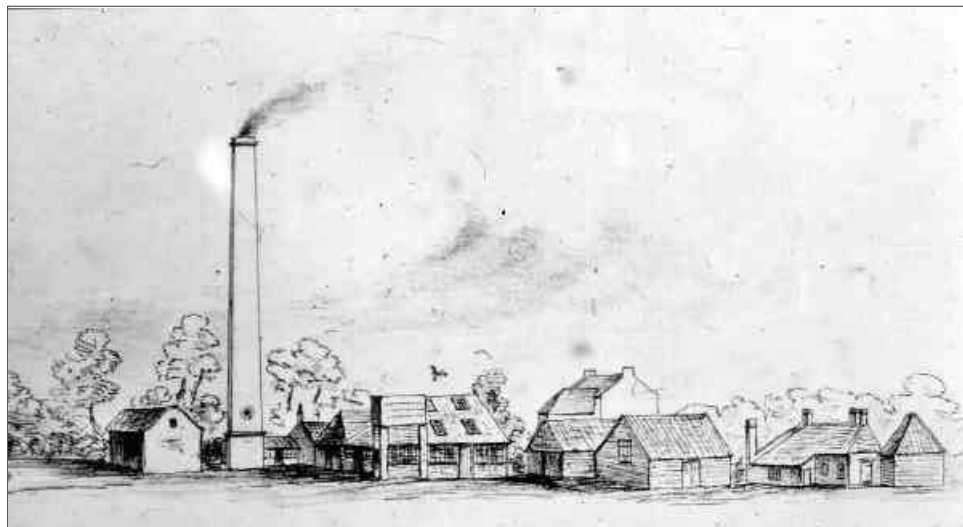
**PROVISIONAL SPECIFICATION** left by the said William Henry Perkin at the Office of the Commissioners of Patents, with his Petition, on the 26th August 1856.

I, WILLIAM HENRY PERKIN, do hereby declare the nature of the said  
5 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  
10 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 naphtha, to extract a brown

**Patent Awarded to William Henry Perkin for Synthetic Dye  
Discovery in 1856. Edelstein Collection, Hebrew University.**

It was in January 1857 that an East London silk dyer named Thomas Keith reported the superior qualities of the aniline color. This encouraged Perkin, his father, and brother Thomas Dix to construct a small factory to manufacture aniline purple at Greenford Green, north-west of London. The first batch of finished product was shipped to Thomas Keith in December 1857. The Perkins were in business.



**Greenford Green Works, 1858. Edelstein Collection, Hebrew University.**

Unfortunately, the product proved difficult to sell, except for the limited application of dyeing silk, because of the difficulties of attachment to cotton. Consequently, there was little enthusiasm from the calico printers in Lancashire and Scotland.

Nevertheless, purple had become the leading color of fashion in Paris and London, probably because of the introduction of a fast and brilliant lichen dye, French purple, manufactured by a firm in Lyon. Perkin was under pressure to develop a suitable mordant for cotton, which he achieved at the same time as Robert Pullar. Then the product had to be sold to the printers, which required considerable travel throughout Britain and trials in the factories of potential consumers. These succeeded, and the synthetic color, at first named Tyrian Purple, after the fabled Levantine dye, became a success early in 1859. [13]



**Perkin at age 22 (1860). Edelstein Collection, Hebrew University.**

The production of the new color required plentiful supplies of aniline, made in two steps—nitration and reduction—from benzene, which was distilled from coal tar. At first the process apparatus was made of glass, but when demand picked up the Perkins introduced small hand stirred iron equipment. These reactors were scaled up, and mechanized, by Edward Chambers Nicholson of the South London chemical manufacturer Simpson, Maule & Nicholson; the partners were also former students of Hofmann. Perkin would not license his patented process to other firms in Britain, which meant that new progress was made elsewhere. Lyon dyers, who specialized in silks, were soon experimenting with the aniline reaction. They and innovative Parisian firms, such as Depouilly and Castelholz, manufactured aniline purple on a considerable scale from the end of 1858, as did one or two German

firms. This caused widespread use in the fashion centers of Europe. In Britain, aniline purple was renamed mauve (French for the mallow flower) during the spring of 1859, when it reached a peak of popularity.

## **Fuchsine**

*A range of synthetic dyestuffs appears in Britain and France. Specialist companies enter the field.*

At the same time as mauve was becoming popular a second aniline color, a brilliant red called fuchsine (after the fuchsia flower), appeared from the factory of the Renard Freres, a dyeing partnership based in Lyon. It was the invention of Francois Emmanuel Verguin, who had joined the Renards early in 1859. The oxidizing agent was stannic chloride, and the product was on sale from May of that year.

During the winter of 1859-60, Nicholson in London discovered a better route to the red, in which arsenic acid was employed in the oxidative condensation of commercial aniline. Henry Medlock, another former student of Hofmann, and consultant to a firm of dyers in Coventry, came across an almost identical process.

In January 1860, Medlock filed his patent, just one week before Nicholson. In October, rights to Medlock's arsenic acid process were purchased from the Coventry firm by Simpson, Maule & Nicholson, which marketed the red as roseine, although it was more generally known as magenta in Britain, after the battle of that name.

The third aniline dye was discovered in 1860 by Charles Girard and Georges de Laire, chemical assistants of Jules Theophile Pelouze at the Paris Mint. Pelouze, an expert in the extraction and reactions of benzene, owned a factory for the preparation of this hydrocarbon and the intermediates nitrobenzene and aniline at Brentford, near London.

While working at Brentford on the aniline red reaction, Girard and de Laire came across a mixture that afforded a blue colorant. They found that the best method was to heat aniline with the red. This was patented early in 1861, and their aniline dye patents were soon acquired by the Renards, who also bought the interests of Pelouze. The Renards were closely connected with Simpson, Maule & Nicholson, which in 1862 was granted a license to manufacture the blue in Britain.

Hofmann was the scientific consultant to the two firms, and studied the constitution of aniline red and blue. [14] Thereafter, the growth of the aniline dye industry was closely linked to Hofmann's work with amino compounds.

Hofmann analyzed the blue for Nicholson, and in May 1863 revealed to the scientific world that it was triphenylated aniline red. This suggested the possibility of colors from other substitutions on the red. He investigated alkylation and came across brilliant violets. The process was patented, licensed to Simpson's firm, the Renards, and a German manufacturer.

The violets became known as Hofmann's violets, and from 1864 displaced Perkin's mauve. Unlike the earlier aniline colors, which had been discovered through empirical methods on the shop floor or in factory laboratories, the Hofmann's violets were a consequence of theory based scientific research. Hofmann's later research into aniline dyes demonstrated that aniline red (fuchsine, magenta, roseine, etc.) was not a product from aniline alone, but from a mixture of toluene and aniline. Moreover, Nicholson found that sulfonation imparted the important property of solubility to aniline blue.

The Renards and Simpson, Maule & Nicholson attempted to control the French and British markets with monopolies based on their patents. A major court case that commenced in Paris during early 1860 was resolved in March 1863, when judgment was given in favor of the Renards. This was a controversial decision. The Renards now controlled all processes to the red, and, therefore, had a monopoly over the supply of its derivatives, aniline blue and the Hofmann's violets. Simpson, Maule & Nicholson was less fortunate. This firm lost its aniline red patent case in 1865, although it managed to retain the monopoly on aniline blue.

Once the red process became public property in Britain, the dye industry there expanded. It was Thomas Holliday, son of the tar distiller Read Holliday of Huddersfield, who had battled

against Simpson, Maule & Nicholson to make free the arsenic acid process for aniline red, and after 1865 his business grew rapidly. This also assisted Ivan Levinstein, from Berlin, who in 1865 began the manufacture of magenta at Blackley, Manchester; Levinstein's factory was a forerunner of the present ICI Specialties.

Litigation and the outcomes of patent disputes were also spurs to new innovative activities. Since routes based on the oxidations of aniline with arsenic acid were held up in Britain (except at Nicholson's firm) until early 1865, because of injunctions, phenol-based colors, naphthalene colors, modifications of mauve, and exploitation of Peter Griess's discovery, what was later called the diazo reaction, were all investigated. Heinrich Caro, a German colorist at Roberts, Dale & Co. in Manchester, the main rival of Simpson, Maule & Nicholson, was instrumental in directing research that led to all these colors. [15]



**Heinrich Caro, colorist, chemist and technical leader, at BASF, from 1868-1888. Edelstein Collection, Hebrew University.**

### **Aniline Black**

Caro invented a process for mauve in 1860, whereby copper salts were used as oxidants. It became the sole competitor to Perkin's dichromate reaction and the Manchester-made mauve was used in Lancashire and Scotland from around 1862. From the residue of the reaction, Roberts, Dale & Co. extracted a black colorant suited to cotton printing. However, in 1862 it was used only to a limited extent by printers in Britain because of the corrosive action on printing machinery. It was more widely applied on the mainland of Europe, where wooden block printing was still popular.

The original discovery of aniline black was made in 1859 by John Lightfoot of Accrington, north of Manchester. He established that the direct application of aniline in the presence of an oxidizing agent to cotton, using the engraved copper plates of cylinders of printing machinery, gave a fast and brilliant black, but, again, this was not wholly satisfactory because of the corrosion problem. Lightfoot eventually patented his process early in 1863. For mainland Europe and the United States patent rights were assigned to J.J. Muller- Pack of Basle.

In 1864 Charles Lauth in Paris came out with the first of the improvements that were to make aniline black printing possible with machinery. This was through the use of insoluble copper salts. For the remainder of the nineteenth century, aniline black printing and dyeing was carried out on a vast scale. [16]

### **Alkylation and phenylation of aniline**

Since the Renards retained exclusive control over the production of aniline red, blue and violet, chemists in Paris and Lyon also sought out new reactions on coal tar products. In addition, the Renards, which became Societe La Fuchsine in 1864 (backed by the Credit Lyonnais bank), had problems with pollution from large scale arsenic acid oxidation (from around 1862). For these reasons, amino group hydrogens of aniline and toluidine were replaced by phenyl and alkyl groups prior to oxidation. This work, inspired by Hofmann's publications on the constitutions of aniline colors, led to the introduction of reactions carried out at high pressures and temperatures by Poirrier in Paris (alkylation, 1866), which enabled the Renards' patents to be circumvented. It also led to the introduction of less

poisonous oxidants. In Britain, Levinstein and Holliday used the substitution reactions to bypass the blue and violet processes licensed to Simpson, Maule & Nicholson.

By 1864, the price of aniline red had fallen to about ten per cent of the 1860 levels, which reflected both the improved methods of large scale production and the high level of competition. A wide range of colors, including yellows, brown, and grey were available from commercial aniline.

**Table 1**

Prices of aniline dyes as quoted in France, 1860-1867, fr. per kg. unless otherwise indicated (1£ =24-25 fr.)

Year Month	Firm	Red	Purple	Blue	Violet	Notes
1859	Casthelaz (Paris)		3,000-4,000			powder
	Depouilly (Paris)		60			paste
	Depouilly		100/l			solution
1860	lager (Barmen)	1,500				
Feb.	Fayolle (Lyon)	100				paste
May		60				paste
"	Depouilly	1,250	900			
Nov.		400				dry
"		700				dry, sol. in water
"		400				'pure'
"		60	50			paste
"		18/l				solution
Dec.			500			
1861						

Jan.	Simpson, Maule & Nicholson (London)			400		
"	Renards			300 (bleu de Lyon)		
Feb.	Poirrier (Paris)		300 (bleu d'aniline)			
	Depouilly	700				
	Renards	800				
July	Renards	800				
	Iager	700				
	Depouilly	500				
				150		
Aug.	Renards	600				
Sept.	Renards			600 (bleu Imperial)		
Dec.	Renards			600 (bleu de Lyon)		
1862						
Jan.	Guinon (Lyon)			450 (azuline)		
	Renards			500 (bleu de Lyon)		
		600				
		700				

July	Renards			400 (bleu de Lyon)		
Oct.	Renards			500		solid, soluble in water
1863						
March	Tillmanns (Krefeld)	190				
"	Muller-Pack (Basle)	180				
June-Nov.		250-300		250-300	250-300	
1864						
Feb.	La Fuchsine (Lyon)	125				
	La Fuchsine			500 (bleu lumiere)		
March	La Fuchsine				1,500	Dahlia Imp, soluble in water
Sept.	La Fuchsine	40		300		
1865						
Feb.	La Fuchsine			300		Hofmann's soluble
	Belgian	55			55	
June	La Fuchsine	80		75	80	

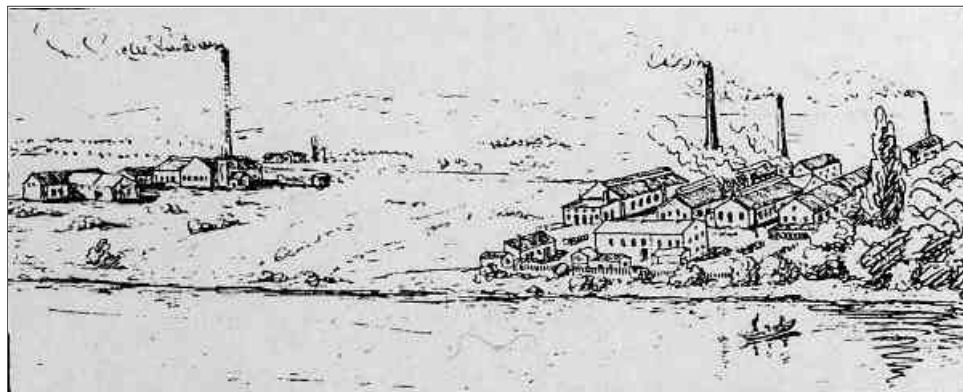
Aug.	Oehler (Offenbch)	45-80			60	
"		55		55	55	
1866						
June	Poirrier				125 (violet de Paris)	
July	Imbert					Hofmann's
1867		10-50		30-250	35-75	
					60	Hofmann's soluble

Sources: Theodore Chateau, *Nouveau Manuel Complet Theorique et Pratique de la Fabrication et de l'Emploi des Couleurs d'Aniline* 2 vols. (Paris, 1868), vol 2, pp 450-462. *Moniteur Scientifique*, 2 (1 November 1859):403. *Le Teinturier Universel*, 1861-1863, inclusive.

Notes to Table 1: The aniline blues listed for the early part of 1861 may have been blue shades of red Aniline purple == mauve (UK) = harmaline (France), etc. Aniline red = magenta (UK) = fuchsine (France), etc. Wide price variations in aniline blues (phenylated reds) and violets (alkylated reds) arose from introduction of improved products, especially the water soluble varieties. Qualities within a given range were designated by additions of capital B's after the name of the dye. Thus, blue BBBB was superior to Blue BBB Aniline greens were made by the reaction of aldehydes on aniline red, and were especially important products for Usebe-Cherpin, Muller-Pack and Meister, Lucius & Co. from 1864. In August 1864, green was quoted at 25 fr per kg, probably of poor quality. By August of the following year a superior product was fetching 350 . fr per kg Aniline yellow was quoted at 400 fr per kg in June 1864, and 250-300 fr per kg in November 1864. In 1867, La Fuchsine's "Durand" yellows, browns, etc. were 15-30 fr per kg. L. Durand was one of the company's chemists and later became a partner in Durand & Huguenin. Prices in Germany in 1860 revealed that aniline purple was the equivalent of about 1,250 fr per kg, and aniline red about 700 fr per kg.

### **The rise of the German and Swiss dye industries**

*German manufacturers of aniline dyes become significant in the early 1860s Swiss dye-making was assisted by the patent monopoly in France.*



**Hoechst dyeworks, commencement of alizarin factory, 1869-1870. Edelstein Collection, Hebrew University.**

A small group of German businessmen and chemists founded the Hoechst dyeworks (Meister, Lucius & Co.) at the village of Hochst, near Frankfurt, in 1863. [17]

In the same year, Friedrich Bayer & Co. was established in Barmen and within a few years had moved to nearby Elberfeld. [18] They tended to imitate French and British processes, a situation encouraged by the absence of a unified patent law throughout the various states and principalities.



**Friedrich Bayer & Co. Dye Label. Edelstein Collection, Hebrew University.**

From 1861, the Clemm brothers had been involved in the manufacture of magenta at Mannheim, and this became the nucleus of the Badische Anilin- & Soda-Fabrik (BASF), formed in 1865.



**BASF factory, Ludwigshafen (ca. 1900). Edelstein Collection,  
Hebrew University.**

In the same year Hofmann left London for the University of Berlin, where Carl Alexander Martius, formerly at Roberts Dale & Co., was one of his assistants and worked on substitutions of amino group hydrogens in aromatic compounds. At the end of 1866, Caro departed from Manchester to work with Bunsen in Heidelberg, and became a consultant, chiefly for BASF.



**Carl Alexander Martius founded an intermediates-making firm in  
Berlin, 1867; from 1873 this traded as the dye-maker AGFA.  
Edelstein Collection, Hebrew University.**

The La Fuchsine monopoly had forced several French chemists and firms to move to Switzerland where that country's fledgling dye industry began to flourish from around 1862. The first Swiss firms to manufacture coal tar dyes were dyers, dye merchants and tar distillers in Basel who entered the field in 1860. This included Alexander Clavel, a French emigre who set up what in 1884 was to become the Gesellschaft für Chemische Industrie Basel (CIBA). [19] J.J. Muller-Pack originally sold dyewares on behalf of the Geigy family, and began the manufacture of mauve and magenta, as well as marketing aniline black, firstly the Roberts, Dale & Co. product, and, later, Lightfoot's and Lauth's processes. In 1862, Muller was taken over by Johann Rudolf Geigy.

### **Alizarin**

*The conquest of a natural product. England versus Germany.*

In 1865, while the young West European dye industry was undergoing many organizational changes, partly as a result of the patent cases in Britain and France, Friedrich Auguste Kekule put forward his benzene ring theory. This transformed the understanding of aromatic compounds, especially by German chemists, including those who had experienced the early growth of the British dye industry. [20] Many had returned to their homeland after 1865 to contribute to the rise of new firms. Martius, for example, in 1867, became a partner in the forerunner of the AGFA corporation. At the end of 1868, Caro joined BASF as deputy technical director and improved on the dyes he had discovered in Manchester, such as the blue indulin, and prepared new colorants.

In 1869, he began work on the commercialization of a recently patented process for the synthesis of artificial alizarin. This was the most remarkable and far reaching discovery in the nineteenth century dye industry because of the way in which new chemical theories based on Kekule's ring led to academic-industrial collaboration. It brought about substantial profits, and fostered the organization of industrial research.

Alizarin, like quinine and many potential novel dyes, was, from around 1850 considered to be related to coal tar compounds. Analysis indicated that the starting point for alizarin might

be naphthalene. Indeed, once the aniline colors appeared, synthesis of alizarin from naphthalene was investigated in Germany, France and Britain. However, no useful products appeared. The breakthrough occurred in 1867 at the Gewerbe Institute, a trade college in Berlin. There since 1860, Adolf Baeyer had undertaken research into natural products, and had shown a keen interest in indigo and alizarin. His assistant Carl Graebe established that alizarin was probably a quinone, and went on, with Carl Liebermann to show that it was a derivative of anthracene, and not naphthalene. Alizarin was, as they demonstrated in 1868, a dihydroxyanthraquinone. [21] Synthesis was achieved by bromination of anthraquinone, followed by hydrolysis.

The yield was low, but a patent was filed at the end of 1868. Several German and foreign firms were approached regarding licensing rights, and in May 1869 a deal was struck with BASF. In that month, Caro at BASF, as well as Perkin in London, and the Hoechst dyeworks, all independently discovered that sulfonation of anthraquinone could be achieved, with subsequent displacement of sulfonic acid groupings by hydroxyl at elevated temperature. The result was alizarin in high yield. This became the basis of commercial manufacture by Perkin and Hoechst from the end of 1869, and by BASF about one year later. [22]

William Perkin had patented his process in London on 26 June 1869, just one day later than Caro, Graebe and Liebermann. Once technical production had been achieved by Perkin, who also introduced an alternative dichloroanthracene route, BASF, which had been denied its Prussian sulfonation patent by the Berlin patent office, decided that the best way forward was to negotiate the market with Perkin. By March 1870, they had come to an agreement over cross licensing of the June 1869 patents. Perkin would monopolize the British supply of artificial alizarin, and BASF would control the mainland European and North American sectors. This was followed with transfer of technical information, mainly in the direction of Germany.

Synthetic alizarin soon began to replace the natural product, and was also manufactured in Switzerland. Once the various co-products had been isolated and characterized, greater control over the reaction became possible. The quality of alizarin also improved. The color was consistent and easier to apply than the vegetable product, the supply of which was subject to the vagaries of nature.

The Franco-Prussian War of 1870-71 had initially restrained this new phase of growth in the German dye industry, but afterwards there was no holding back. Marketing and customer service were improved, and British products were undercut. The French by this time had been pushed into a minor role by the collapse of La Fuchsine, which had stifled competitive activity until 1868. [23] Newly annexed Alsace, the leading printing region after Lancashire, became a captive market for German dyes.

## **Perkin's scale up of the Alizarin Synthesis**

*Anthracene becomes an important raw material. Laboratory and pilot plant development of process plant. High tonnage production of anthraquinones.*

William Perkin's firm was the first successful producer of alizarin and of a similar anthraquinone compound. His efforts, as much as those of Caro, Graebe and Lieberman, made the alizarin synthesis commercially viable. Subsequently, anthraquinone dyes were extended such that the full range of shades could be obtained, although the colors ranging from blue to green received the most attention. Their bright and fast dyes were found to be almost without equal. In particular, they were used in the synthesis of later generations of dyes, such as the indanthrenes, disperse dyes, acid wool dyes, and cationic dyes for polyacrylonitrile. They were also found to be applicable to cotton, which resists the simple non-reactive anthraquinone dyes, when converted into azoanthraquinone colorants. [24]

Perkin's principal contribution was in the design and manufacture of suitable process equipment, a considerable feat of chemical engineering based almost entirely on empirical studies. His work formed the basis of subsequent improvements carried out once knowledge about the chemical reactions became available during the 1870s. Fortunately, Perkin left a comprehensive record of the development of his alizarin manufacture from 1869 to the end of 1873, published in 1879, and complemented with information in his Hofmann Memorial

Lecture, published in 1896. [25] His processes made possible dye manufacture on a high tonnage scale, and encouraged moves towards unit operations. This became critical to the continued growth of the dye and, later, organic chemical industries.

In the development of the alizarin plant, William Perkin worked closely with his brother and partner Thomas Dix Perkin. They first investigated the supply of suitable quantities of the starting material, anthracene, a minor component of pitch, the non-volatile residue from the distillation of coal tar.

William Perkin recorded that in 1855 he had employed iron pots in order to distill coal tar pitch, from which anthracene had been obtained, for his research at the Royal College of Chemistry. In the factory there were a number of iron retorts, and with them several tons of pitch were also distilled. The solid crude anthracene was obtained from the distillate on standing, then placed in canvas bags so that residual oil could be pressed out and drained off. In July 1869, the first hydraulic press was introduced to make this work easier and more efficient.

The crude material was then washed with coal tar naphtha and redistilled from one retort into another via a hot connecting pipe. The resulting solid mass, a mixture of hard yellow crystals and powder, represented no more than one per cent of the starting pitch.

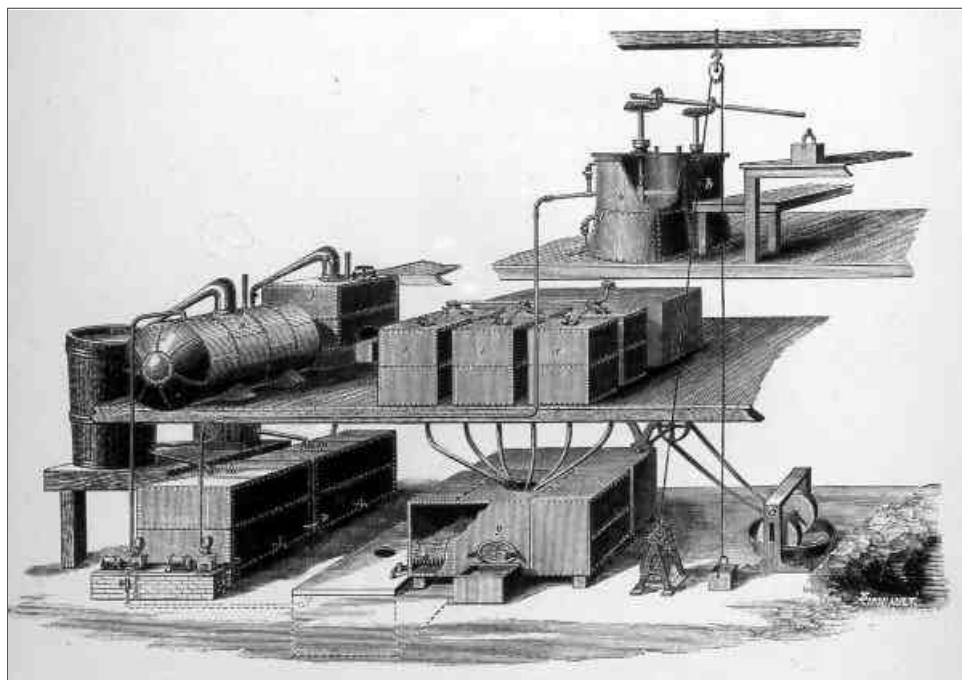
The Perkin brothers were aware that anthracene "could also be obtained from the last runnings of tar stills from which it crystallized on cooling." [26]

Having mastered the art of anthracene separation, Thomas then visited major coal tar distilleries to instruct the distillers in the art of anthracene extraction, "promising to take all they could make, and in this way a sufficient supply for our requirements was soon obtained of all sorts of qualities, some being not much thicker than pea soup, from the imperfect way in which it was drained "

Assessing the quality of the hydrocarbon required considerable ingenuity, and drew on the efforts of many chemists during the 1870s: "The value of the anthracene was estimated by washing with carbon disulphide, afterwards alcohol was used, but for our purposes we all along used an anthraquinone test. This method was worked out more perfectly afterwards on the Continent, and made a practical test for both buyer and seller; but at the time I am writing tar distillers were not sufficiently educated in such matters to use any but very simple tests." [27]

The anthracene which arrived from the distillers was in a thick pasty form packed in casks. This material was then placed between thick linen sheets and subjected to the hydraulic presses. However, as Perkin noted, once distillers began to extract all they could, the quality of the delivered material deteriorated rapidly, and "any article tested by alcohol, and showing a melting point of 190°C was sold as anthracene." [28] Oxidation to the quinone became excessively expensive since the reagents were also consumed by acting on other materials present with the anthracene. This was eventually overcome by a subsequent purification step in which the crude anthracene was distilled over caustic potash (potassium hydroxide), that removed unwanted constituents of the mixture. (These were not understood until the presence of carbazol was demonstrated by Graebe in 1880).

The fully developed anthracene production plant is shown in Figure 1, taken from Perkin's 1879 historical account. Operations commenced with grinding under edge rollers in a shallow tray, shown to the bottom right of the figure. The ground material was then carried to the top of the building by means of a hoist and deposited in the cylinders, bb, half filled with petroleum spirit (which was used instead of naphtha). Some 1,500 to 1,800 lbs. of crude anthracene were mixed with around 300 gallons of petroleum spirit at every charge.

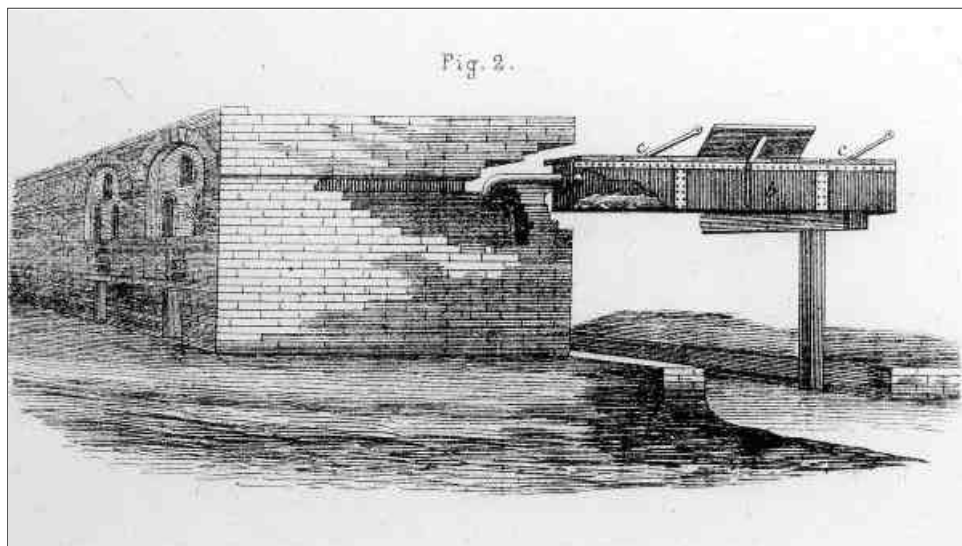


**Figure 1. Anthracene Production Plant. Edelstein Collection, Hebrew University.**

The mechanical agitator was then turned on, and the mixture was boiled with the aid of a steam jacket, d. The manhole cover was loosely held in place and this prevented evaporation of the nearly boiling petroleum spirit. After one or two hours the contents were run off into cooling tanks, spaced so that air could circulate freely between them. Cooled material was then transferred to the filter tank, where the petroleum was allowed to run off through the wooden perforated floor covered with coarse canvas, h, and into the underground tank, i. The contaminated solvent was afterwards steam distilled in the apparatus o and finally pumped back into the cylinders bb for further use. The anthracene was treated once more with petroleum spirit, and then transferred to the tank, j. Water was added, and steam was blown through the mixture to vaporize the petroleum spirit which was then carried away, condensed in the worm tube, l, and collected in the tank m. The water was then run out of the pot, followed by removal of the anthracene which was placed in dry casks to drain.

The first experiments with the caustic potash purification had been conducted in glass retorts, but they were less successful when scaled up. On 5 May 1870, in accord with the arrangement for a mutual exchange of technical ideas that accompanied the agreement between Perkin & Sons and BASF, William Perkin sent Heinrich Caro details of a newly designed cylindrical device. [29] This was an enlarged version of the first iron nitrator used at Greenford Green, and fitted with a hand operated horizontal stirrer, and two vertical outlet pipes. It was designed to take a mixture of 1,000 lbs. of anthracene and 250 lbs. of potash. In a later and somewhat more simplified retort, the distillation was carried out on a thoroughly ground mixture of dried anthracene, American or Montreal potash, and caustic lime. The purpose of the lime was to prevent the residue from caking into a hard mass, and thus enable working without the use of an agitator.

At first, outlet necks of the iron retorts were bolted into position, but this fixing arrangement was unable to withstand the repeated heatings, and the only solution was to have the necks cast on the retorts, as in Perkin's Figure 2.



**Figure 2. Retorts. Edelstein Collection, Hebrew University.**

Large tanks were used as condensers, with two or three retorts distilling into each one, until an explosion during cleaning out revealed the presence of excessive amounts of hydrogen. Thereafter, the operation became safer when specially designed raised iron troughs, b, smaller than the original receivers, were introduced. Distillate entered at one end of the trough and the other end was plugged with a loosely-fitting piece of wood that allowed slow diffusion of the hydrogen into the atmosphere. The tops of the troughs were covered with lids, bb, opened and closed with the aid of long handles. After accumulated hydrogen had been released by opening the lids, anthracene was removed, ground and dried. Potash was recovered from the retorts for re-use.

The manner in which the subsequent oxidation and sulfonation steps were carried out by Perkin & Sons are of special interest because they represent the basis of the first bulk manufacturing methods for artificial alizarin carried out by any company, and were used almost exclusively at Greenford Green until the middle of 1870. Perkin's graphic description fully conveys the atmosphere of large scale working in the early dye industry.

The oxidation of anthraquinone with potassium dichromate was carried out as follows:

The purified anthracene was ground very thoroughly with water under edge runners. It was then placed in a leaden-tank, with twice its weight of potassium bichromate dissolved in water. About three parts of sulphuric acid, previously diluted, were then added. After well stirring, a very energetic reaction set in, the mixture boiling up to near the top of the tank. When this had been moderated, steam was turned on, and the mixture well boiled for an hour or two. The yellow granular anthraquinone was then separated from the chrome alum solution, well washed, and after it had drained, though still wet, was purified by sublimation. At first we used two iron retorts, with openings at the top, and connected with a wide bent tube for this purpose, the one acting as a sublimer, the other as a receiver. Afterwards we employed retorts, with an outlet from the end connected with a large sheet-iron cylinder, having one end closed with canvas only.

The wet crude anthraquinone, when heated, gave off a considerable amount of steam which helped to carry the vapor of the anthraquinone forward, which condensed as an impalpable powder. As the sublimation proceeded, and less steam was given off, small crystals of anthraquinone deposited. On opening the retorts after the operation, magnificent hard yellow crystals were often found suspended from the roofs of them.

The sublimed anthraquinone was then dried, and finally purified by recrystallization from high-boiling coal-tar naphtha. The crystallized product was collected in canvas bags, drained, washed with a little clean naphtha, pressed and then dried.

The amount of pure anthraquinone we obtained from pitch anthracene was, speaking from memory, about twenty to twenty-five per cent. The yield from ordinary anthracene from the tar distillers, was, of course, much greater. The use of potash in the distillation of anthracene we did not adopt until after we had ceased using the anthracene from pitch, otherwise better results would have been obtained with this product. [30]

The sulfonation of the purified anthraquinone was carried out with fuming (Nordhausen) acid imported from Germany (concentrated sulfuric acid became available only in the mid 1870s):

In converting the anthraquinone into the sulpho acids, we at first used Nordhausen sulphuric acid, and heated the mixture in glass retorts, such as are used in the concentration of sulphuric acid, but, owing to the fragility of these vessels, we were induced to try cast iron pots. These were found to answer well, though not quite so well as glass.

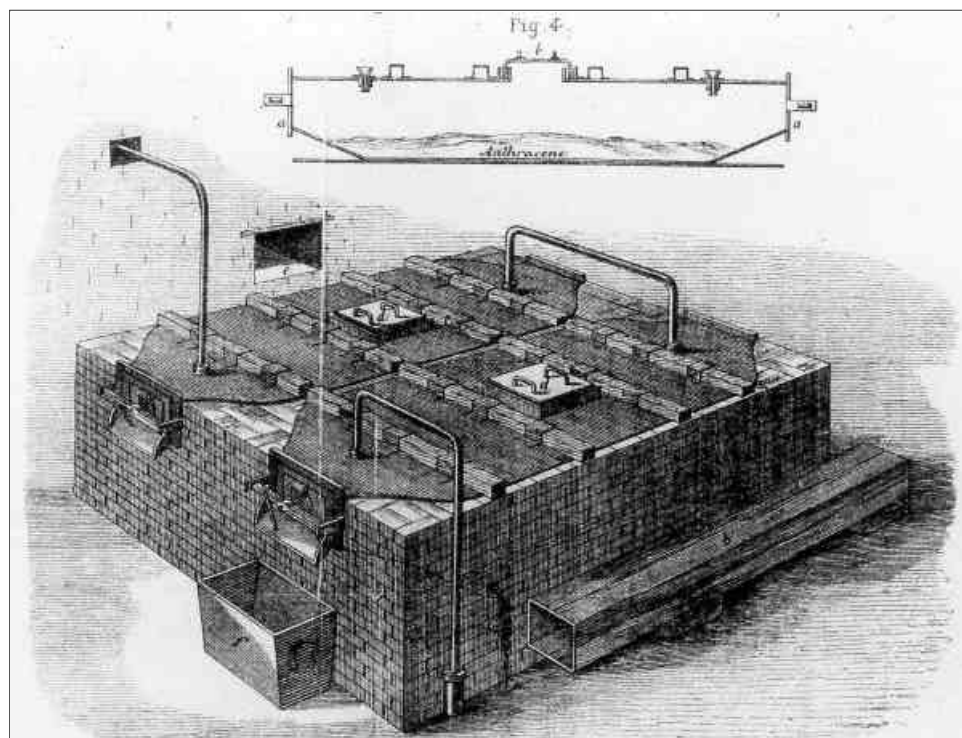
The Nordhausen acid was soon replaced by ordinary sulphuric acid. "We usually employed four or five parts of this to each part of anthraquinone, and heated the mixture up to 270-280° C." It was the increasing reliance on ordinary sulfuric acid (as well as on Perkin's anthracene, that was not well suited to the anthraquinone process) that encouraged greater use of the dichloroanthracene route:

I find we employed this process principally in our works until the middle of June, 1870. We then began to work on a larger scale than we had hitherto done with dichloroanthracene, and carried both processes on for a time; but, finding the latter the most economical, partially on account of the ease with which it yielded the sulpho acids with ordinary sulphuric acid, we employed it almost exclusively after a time, although frequently making coloring matters by the other method. [31]

The final stages, alkaline fusion of the sulfonic acids and acidification to afford products fit for the marketplace, were common to both anthraquinone and dichloroanthracene processes, and will be described after an outline of chlorination and subsequent sulfonation. This second method divides into preparation of chlorine, chlorination, sulfonation and lime treatment, prior to preparation of the potassium salts.

Chlorine was generated by the regulated addition of chloride of lime, mixed with water to form a creamy fluid, into hydrochloric acid in a well pitched wooden cask, and the gaseous product was collected in stoneware Woulfe's bottles. Perkin's method was simple and rapidly brought into operation, but the chlorine was expensive. Perkin noted: "I should imagine that this was the first instance of chlorine being prepared in large quantities in wooden tubs, and I have described it, as it might be useful to others who want a supply of this gas without loss of time."

An alternative method, cheaper to operate, but taking more time to set up, was based on Weldon's invention of 1866. This involved catalytic oxidation of the hydrogen chloride using manganese dioxide, followed by catalyst recovery. Perkin intended to install such plant, although this was never realized. Chlorination of anthracene was carried out in leaden chambers called chlorine ovens. These are shown in Perkin's Figure 4.



**Figure 4. Chlorine Ovens. Edelstein Collection, Hebrew University.**

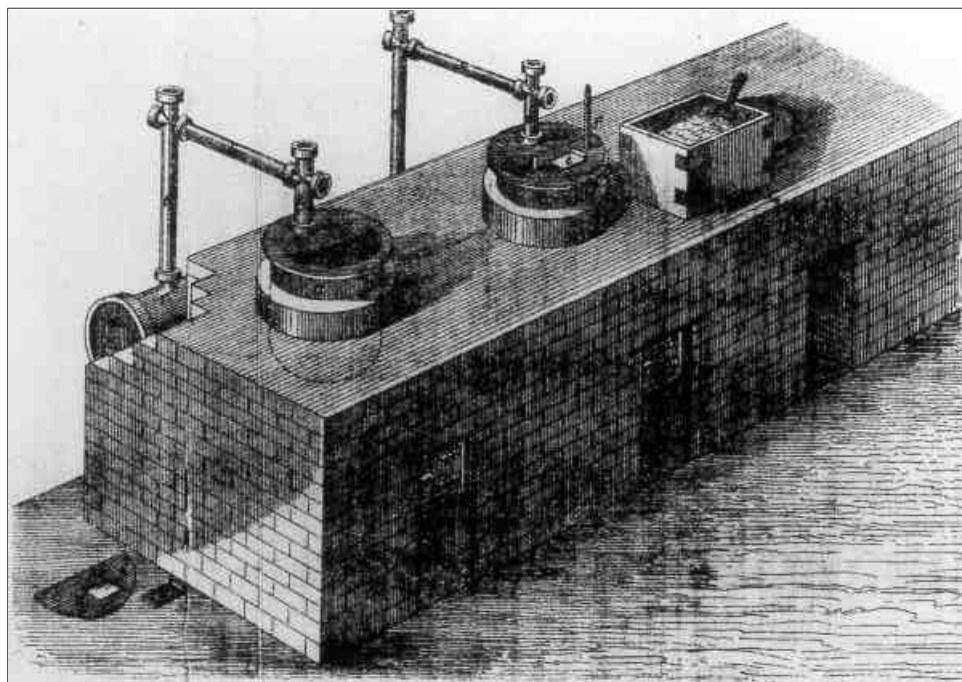
The end manholes were slabs of wood covered with lead. The ovens were charged through openings at dd (b in the cross section), and the lids to these were made airtight with a liquid seal of "chlorine oils," the residual oil from the reaction, which was placed in the door channels. Lead piping was used to deliver the chlorine and carry away hydrochloric acid and unreacted chlorine from the last stages of the chlorination. Since this caused loss of the valuable reagent, the ovens were then operated in pairs so that outgoing gas from the first oven was then passed into the second.

The next day a new charge of anthracene was placed in the first oven, the incoming gas was then directed into the second oven, to complete chlorination, and then passed through the fresh charge. By this continuous alternation in the supply of chlorine, losses were minimized.

A steam chamber was built into the surrounding brickwork to maintain the desired temperature. Hydrogen chloride gas was recovered for re-use by condensation in coke towers. Wooden tools were used to loosen the crystalline dichloroanthracene remaining in the oven, which was then transferred to tubs and broken up in the presence of caustic soda which neutralized the hydrochloric acid. The product was afterwards separated from the solution and hydraulically pressed between linen cloths to remove unwanted materials as the "chlorine oils."

The resulting crystalline cake then underwent further purification by repeated breaking up, soaking in coal tar naphtha, and pressing. Any residual naphtha was recovered by steam treatment. Finally, the product dichloroanthracene was dried on trays in a drying room and was found to be about 84 per cent pure.

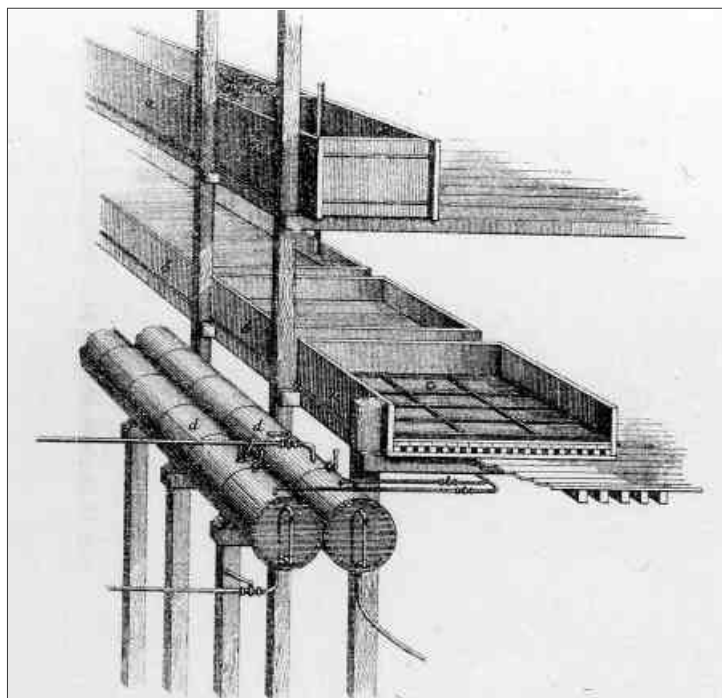
In the important sulfonation step, the dichloroanthracene was treated with sulfuric acid in iron pots, each capable of holding about 30 gallons of liquid, and fixed in place in rows above ovens. The whole arrangement was surrounded by brickwork to retain heat (Perkin's Figure 5).



**Figure 5. Iron Pots for Sulfonation. Edelstein Collection, Hebrew University.**

The pots were cast such that half the top was closed, and earthenware pipes led from this covered section to the main which carried away reaction gases to a condenser. The opening in the pot was covered with a lid made of lead, in which there was an open space for addition of the dichloroanthracene. This was added in small shovelfuls into the preheated sulfuric acid. Two small holes in the lid carried a thermometer and a wooden plug. The charge of acid in each pot was usually around 350 lbs., and when some 70 lbs. of dichloroanthracene had been added the temperature was raised to about 260° C, and held there until reaction was complete. This was determined by continuous monitoring. A glass rod was inserted through an unplugged opening into the reaction mixture to remove a small sample, which was then diluted with water, and the end of the reaction was indicated by "a nearly clear solution, devoid of fluorescence. The fire was then drawn, and the product left to cool down until the next morning. It was then found to be still warm, of a brown color, and the consistency of treacle. The lids being lifted off, it was ladled into copper pails, and carried away to be neutralized with lime."

Neutralization and separation of the solution containing the product from unwanted solid material were then carried out in the apparatus shown in Perkin's Figure 6 (below), and this had already reached an advanced stage of development when a description and drawing were sent to Caro in May 1870.



**Figure 6. Apparatus for Separation of Product. Edelstein Collection, Hebrew University.**

The crude product of the sulfonation was diluted in large wooden tanks, a, the solution was brought to boiling by blowing steam into it, and wet slaked lime was added to bring about neutralization. (This operation was later carried out in wooden tubs fitted with mechanical stirrers.) The neutral mixture was then run into the vacuum filters, b, connected to iron reservoirs, dd, that were evacuated by means of an air pump. The mixture was filtered through successive layers of sand, pebbles, and bricks, covered by a coarse canvas stretched out on a wooden frame, such as c. One reservoir was connected so as to receive the concentrated filtrate and first washings; further washings with boiling water were drawn into a second reservoir. Some product remained mixed with the calcium sulfate in the filters and was extracted by removing the solid, boiling it with water, and returning the mixture to the filters.

The salt solution in the first reservoir was concentrated "in iron pans heated either over a fire or by steam, until they contain about 15 per cent of lime salts. Soda crystals (sodic [sodium] carbonate) were then added in sufficient quantity to precipitate all the lime as carbonate, and thus to produce sodic salts of the sulpho acids. These were siphoned off from the carbonate of lime, and concentrated until they contained about 30 per cent of sodic salts."

These "sodic salts" were the sodium salts of the anthraquinonesulfonic acids, generally referred to as "soda salt," or "silver salts." At this stage in the alternative anthraquinone process, soda salts were prepared in a similar manner by the lime treatment. The salts were later found to be a mixture of two disulfonic acids and a monosulfonic acid, the proportions depending on which of the two methods was employed, and the amount of sulfuric acid added. Later, it was found possible to separate these salts from one another at this stage, "so that the different coloring matters they produce may be obtained in a more or less pure state." However, it is unlikely that Perkin ever carried out such separations in his factory.

The alkaline fusion was found troublesome to achieve on a large scale by both Perkin and Caro. The heating range had to be carefully maintained to prevent destruction of the product at high temperature. Laboratory experiments "were performed in an air bath, the products being heated in metallic dishes, a mixture of 'soda salt' [silver salt, the sodium salts of anthraquinonesulfonic acids] in a dry state with a saturated solution of the alkali being taken... and it was considered that caustic potash gave, on the small scale, the best

yield of coloring matter."

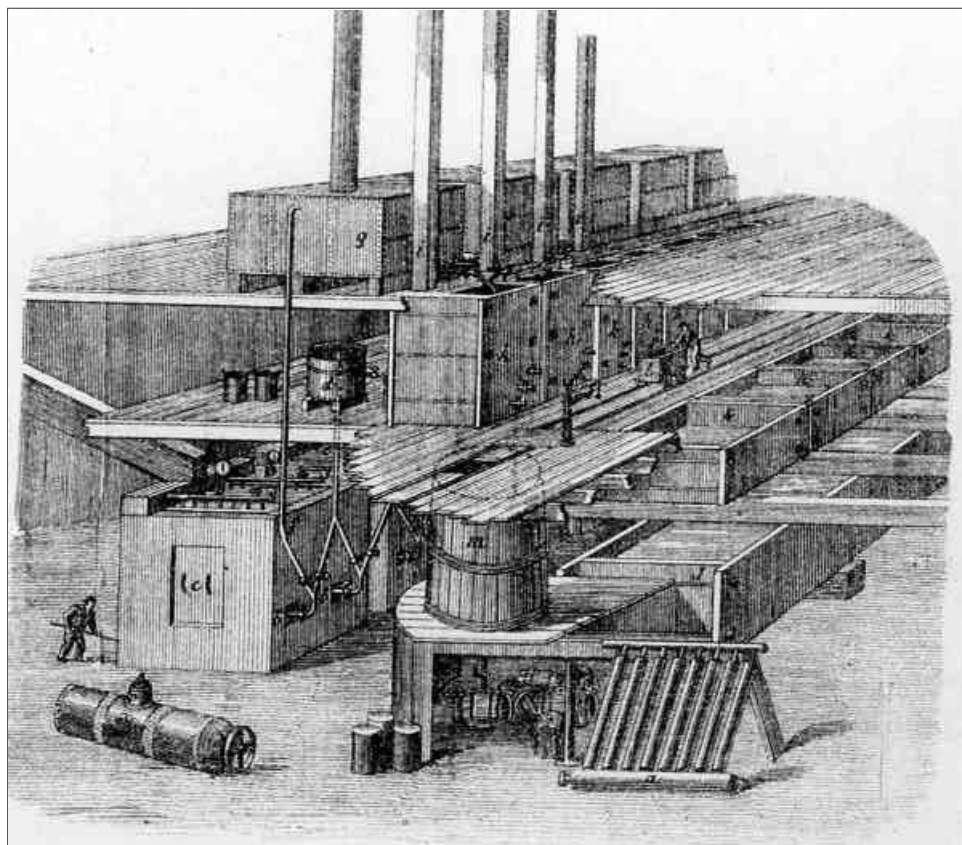
Experiments carried out at about 180° C indicated incomplete substitution of the sulfonic acid group by the hydroxyl. "One method we tried consisted in employing a long chamber, heated with flues to the requisite temperature, and arranged on the same principle as the ovens used for the continuous baking of fancy biscuits. It was hoped that by introducing shallow iron trays, with the usual mixture of soda salt and alkali in thin layers, and gradually working them forward to the other end of the oven, that by the time they had arrived there the decomposition would be complete, and thus a continuous method might be established." This was partially successful, but took too long, and temperature control was problematic.

Greater ingenuity was shown, and more success achieved, with an apparatus consisting of "a large wrought-iron cylinder, which was made to revolve inside a second, but fixed, cylinder of thick cast-iron, sufficiently large to allow of an air space of several inches between it and the interior cylinder. This was heated so as to form a hot-air chamber, the temperature being carefully regulated and observed with a thermometer. The axis of the revolving cylinder was hollow, and perforated with small holes, so that the steam, evolved from the mixture of caustic alkali and soda salt with which it was charged, could freely escape. In this arrangement, the heating was very satisfactory; but the operation took a considerable time, especially if the charge were large. Iron cannon balls were afterwards introduced, to keep the mass well mixed; but, curiously, they did not answer the desired purpose, as they became coated to such an extent with the alkaline mixture that, when the operation was over, they were found to be three or four times as large as when put in. Anthraquinone was found to sublime from this apparatus, and in a smaller one, which was overheated, anthracene was obtained."

This equipment actually saw service on a manufacturing scale during the earliest period of alizarin manufacture, but the reaction suffered from incomplete conversion, as well as the loss of product by reduction:

Experiments were then made in closed iron tubes, with the products mixed with water...and it was found that, if the caustic alkali and soda salt were in a considerably diluted condition, very little coloring matter was formed; the mixture, instead of becoming violet, was of a brown, or chocolate color, and contained, as we now know, chiefly intermediate products. On using less water, however, so that the mixture would contain about 2 per cent, or more, of caustic alkali, coloring matter was readily formed.

The final form of the plant that developed from these trials is shown in Perkin's Figure 7 (below). It was the result of a number of pilot experiments using closed wrought iron tubes of ten or fifteen gallons capacity. Sections of the newly invented Howard's safety patent boilers, made of 10 in. drawn iron tubes, were selected in order that the conversion could be carried out under pressure. The complete device is shown in the open at the bottom right and was installed in the brickwork structure being attended to on the left hand side of the figure. It was connected to the external pipes, bb, by a screw connection at one end, and stop valves fitted into the pipework enabled control of liquid to and from these "pressure tubes." These were heated in a hot air chamber, "in which flues passed underneath and at the sides. A thermometer was suspended through a hole in this chamber, and in case of the temperature rising too high, iron doors in the side were provided, which could be opened so as to quickly admit cold air, as seen at c."



**Figure 7. Final Form of Perkin's Alizarin Plant. Edelstein Collection, Hebrew University.**

When Perkin described the boiler to Caro early in May 1870, it was already assembled and awaiting the arrival of a valve, prior to trials. Caro was then experimenting with a steam treatment, presumably also in a pressurized vessel on a pilot scale. Subsequently, Perkin had a pressure tube made up for Caro, who appeared to have had less success with this equipment.

Initially, the caustic soda was added. This was of "70 per cent quality, dissolved; 700 lbs. weight was usually employed. 1,300 Lbs. of a concentrated solution of the soda salt was then added, and well mixed." [32] The mixture was contained in the iron pan fitted with a steam jacket shown at b. The valves were adjusted to permit the mixture to run into the pressure tubes by gravitation along pipe e. The valves were then closed and the chamber was heated to 180° C for one day. Portions were removed occasionally so that the progress of the reaction could be monitored. On cooling, the valves in the pipe f were carefully opened and the contents of the pressure tubes were forced to the top of the building into the tanks g, fitted with funnels to allow escape of steam through the roof.

The alkaline purple fluid was then slowly run into wooden precipitating tanks, h, containing dilute sulfuric acid. The color of the solution turned orange as the sodium was displaced from the salt to release the required hydroxyanthraquinones. Following overnight cooling, the supernatant liquid was run into the ground floor tanks j, and then water was poured onto the precipitate and the mixture was transferred to the "color filters" k, situated on the first floor, and fitted out in a manner similar to the filters used to separate the lime salts. The first drainings were collected into tanks on the ground floor from which any solid was occasionally collected.

The solid product from the filters was washed several times to remove salt, and until neutral to litmus paper. Dried material was delivered by the truck l to the stock tub m. The truck was weighed before and after each filling, so that the amount of dye (invariably of no more than ten percent purity) in the tub could be calculated. Finally, the coloring matter was thoroughly mixed to make homogenous. A sample was taken for analysis, and when

the strength had been established the solid was dissolved in water to the required strength. It was then available for distribution to the dyer and printer. Several stock tubs were available, according to the variety of shades manufactured. [33] The maximum annual capacity of Perkin's factory was about 450 tons of paste, although this was in fact mainly a hydroxyanthraquinone colorant that was closely related to alizarin.

## Why the British Share of the Alizarin Market Declined Rapidly

*Technical Improvements—The Alizarin Convention.*

Despite Perkin's massive achievement, the ultimate victors in the alizarin battle were the Germans. Their success derived from greater understanding of the fundamental science, improvements in the technology, and in the ability to control the world market through manufacture that was carried out by several firms on a large scale.

Typical of the scientific problems resolved was that concerning the sulfonation which, through use of excess sulfuric acid, afforded the disulfonic acid of anthraquinone.

Quite early on, however, it was noticed that both di- and monosulfonic acids were formed (Graebe and Liebermann, 1871), and this had considerable implications as to the nature of the product and its formation. Only the monosulfonic acid gave pure (violet shade) alizarin.

The Germans had a greater commitment to the anthraquinone route, the first one developed, and which gave alizarin as the major product from the monosulfonic acid, and they soon managed to control the reaction conditions to obtain the maximum yield. Perkin, however, continued to exploit the dichloroanthracene process, which afforded mainly a mixture of two disulfonic acids, and very little mono- acid. Red shade anthrapurpurin (or isopurpurin, a trihydroxy derivative), was the main product; alizarin was as a minor component.

The alizarin process plant also underwent considerable changes in Germany (as well as in Switzerland) during the 1870s and after. [34] Notably, the addition of potassium chlorate prevented the production of hydrogen in the fusion step, and this eliminated the reduction of products, as well as permitting the use of lower pressures. The neglect of such technical improvements and of the process that gave the product most in demand (the violet shade) foreshadowed the end of the innovative edge by British firms during the nineteenth century.

The Germans gained market control through the creation of the Alizarine Convention in 1881, which included the one British and several German manufacturers. The British firm, Burt, Boulton & Heywood, that had taken over Perkin's Greenford Green factory, and rights to his processes (and had many difficulties with the dichloroanthracene process), opened a new works at Silvertown in East London (where the violet shade alizarin was manufactured). In 1882-83, the British alizarin consumers freed themselves of German control by setting up the British Alizarine Company, which purchased the Silvertown alizarin factory. This, and a recession in Germany, caused collapse of the convention in 1885.

## Phthalein and Azo Dyes

*Contributions from theoretical chemistry. The structure of magenta. Patent law in Germany. A theory of color and constitution. Expansion in Germany and Switzerland. Britain falls behind. Congo red and benzopurpurine.*

During the 1870s academic chemistry in Germany became ever more related to the interests of the dye industry. The emphasis on aromatic compounds enabled the structural elucidation of alizarin by Baeyer (at the University of Strassburg [Strasbourg] from 1872 until 1875) and Caro in 1874. This industrial-academic collaboration led to other successes, such as the phthalein dyes, made by condensation of phthalic acid with phenols, another consequence of the partnership between Caro and Baeyer. [35] The first phthalein product was eosin, brominated fluorescein, introduced in 1874. Phthalic anhydride was made from the coal tar hydrocarbon naphthalene, which increased demand for this abundant compound.

Martius, co-founder of the Berlin-based AGFA, now changed the rules of the game for discovering new synthetic dyestuffs. He purchased some of the BASF eosine product, and placed it in the hands of his consultant, Hofmann at the University of Berlin. Hofmann rapidly published the formula, and details of the reaction, which made an important industrial secret public property.

Such advances also contributed to structural elucidation of magenta and its derivatives. The magenta type dyes were studied by Emil Fischer, an assistant of Baeyer at Munich, and his cousin Otto Fischer, partly with the help of Caro. [36] They were shown to be triphenylmethane derivatives, and from 1878 this led to new and improved products, like the immensely successful malachite green.

The late 1870s saw another dramatic change brought about by scientific developments. Otto N. Witt, a Swiss-trained chemist working at Williams Thomas & Dower, of Brentford, near London (on the site of Pelouze's former factory), was investigating the relationship between color and constitution using the diazo reaction developed by Peter Griess at the Royal College of Chemistry from 1858. Kekule had, in 1866, proposed the existence of the diazo radical, in which two nitrogens replaced one hydrogen of the benzene ring. Yellow and brown dyes in the series had been manufactured at Roberts, Dale & Co. during the 1860s, but at that time little was known about their constitutions. During the 1870s it was established that the former contained one and the latter three free amino groups. Witt speculated that between them lay an unknown compound containing two amino groups. He believed that it was of an orange color, and of moderate stability, judging by the properties of the other two members. In 1875, Baeyer and Jager proposed the coupling of groups of atoms in these reactions, which became the key to Witt's success.

Witt found the orange dye, with the predicted properties, and it was marketed as London yellow. Caro had come across a similar reaction, and he shared details with Witt at the "Special Loan Exhibition at the South Kensington Museum, London, in 1876. The BASF version was known as chrysoidine. This was the first successful azo dye based on starting with two different amino compounds. Francois Zacharie Roussin made other azo dyes using naphthalene intermediates, and these were manufactured by Poirrier in Paris (Poirrier had purchased rights to the Renards' patents following the collapse of La Fuchsine).

All of these processes were kept secret, as patent law was considered unreliable in both Germany and France (even in Britain a patent was not always the best course of protection).

Martius once again purchased a new BASF product and delivered it to Hofmann. Hofmann published the formulae of the three known azo dyes, as well as the reaction conditions, and the new process was now taken up by all the leading dye firms. In Germany, this encouraged moves towards a unified patent law, which was introduced in 1877. It had been set up with Hofmann's assistance, representing the newly formed German Society of Chemical Industry Interests (1876). [37] The monopolies on azo and other dyes could now be protected throughout the entire German empire, and the impact of scientific method encouraged the establishment of dedicated industrial research laboratories. [38] The new German inventions were also patented in other countries.

It was soon realized that in the diazo reaction different combinations of atomic groupings could be introduced. The combinations seemed infinite and many thousands of experiments were undertaken. Not many commercial azo dyes resulted, but those that were successful made massive contributions to the balance sheets and fueled the demand for more research. New intermediates were introduced, including aniline in which amino group hydrogens had been substituted, and hydroxy and amino derivatives of naphthalene. When the amino compounds of toluene were introduced redder dyes were created.

The azo work enabled Witt to put forward a theory of color and molecular constitution in 1876. This was the beginning of all modern theories of dyeing. Groupings of atoms that were essential for the specific properties of color and dyeing were defined. This made it possible to predict the type of compounds that might be both colored and capable of adhering to fibers, directing the course of industrial research in a way that had not been possible before. Later versions of the theory, like Henry E. Armstrong's quinonoid theory of 1888, led to further refinements. [39]

Azo dyes were manufactured in Britain on a considerable scale by Ivan Levinstein and Read Holliday & Sons. The Germans considered that many of these activities were infringements of their British patents, which led to lengthy and expensive litigation. From the early 1880s there were moves to reform the British patent law, with a clause that required the working of patents, thereby encouraging the Germans to consider setting up shop in Britain. The impact of German dyestuffs was spectacular; the dyes on the shelves of some Scottish consumers were invariably "Made in Germany."

From 1881, BASF fought a patent case over an important red azo dye (fast red AV) with Ivan Levinstein. The German firm was declared victor in 1887, after the affair had reached the House of Lords. The Dawson brothers of Huddersfield also came up against the might of the BASF in patent disputes.

In 1890, Bayer and AGFA joined to take control of Levinstein's Manchester factory, as well as to maintain a monopoly on direct azo dyes. These adhered to cotton without a mordant. The first one was Congo red, introduced by AGFA in 1884, and was followed by Bayer's version, known as benzopurpurine. This led to another cartel, the benzopurpurine convention. Through ownership of Levinstein, Bayer and AGFA battled in court to protect the monopoly against Read Holliday and others. Levinstein rid himself of his German partners in stages from 1895 and embarked on a campaign of patent reform and protectionism for British dye-makers. Patent reform took place in 1907, but it was too late to help the ailing British dye industry.

The direct azo dye primuline was invented by Arthur Green during 1887 at Brooke, Simpson & Spiller (successor to Simpson, Maule & Nicholson). Green joined Clayton Aniline Co. of Manchester in 1894, and worked on this and similar dyes. Clayton had been formed in 1876 by an immigrant from the Alsace, Charles Dreyfus, mainly to manufacture intermediates, especially aniline for printing aniline black.

In Britain, the need was felt for a professional body that would serve dye consumers and manufacturers. They were brought together through a common interest group, the Society of Dyers and Colourists, formed in 1884, and with a highly regarded technical journal. [40]

In the meantime the Swiss also expanded in the area of azo dyes. A newcomer was Kern & Sandoz, set up in 1886 by Alfred Kern, a former CIBA chemist, and Edouard Sandoz, previously with Durand & Huguenin (which had been formed in the early 1870s; Durand was previously with La Fuchsine in Lyon). They relied on the Germans for intermediates, as did CIBA, which undertook joint projects with BASF in the field of rhodamine dyes. [41]

From 1893 the partnership of Kern & Sandoz was known as Sandoz & Co., and two years later it became the Chemische Fabrik vorm. Sandoz. . In 1888, the chemist Traugott Sandmeyer joined Geigy. He had previously investigated Green's primuline, a colorant that was not protected by a patent. Sandmeyer established the constitution and the method of preparation, which was immediately scaled-up in the Geigy factory. Almost single-handed, Sandmeyer was responsible for a string of research successes, including the use of copper salts in the previously impossible diazotization of 1,2-aminonaphthols (1901). This was, in commercial terms, Sandmeyer's greatest success.

## **The United States Dyestuffs Industry**

### *Foreign interests and tariff walls—but little progress*

While Europe was experiencing the first impact of the aniline colors the United States was troubled by Civil War. However, this did not completely halt the transfer of new technologies from Europe, and one or two German immigrants did attempt to manufacture dyes in the early 1860s. The Renards had tried to dominate the market, but were thwarted by the efforts of Friedrich Hoffmann, a German chemist brought in by aspiring German entrepreneurs.

When Simpson, Maule & Nicholson in Britain gained a brief monopoly on the most important process for magenta, its competitors had cause to look elsewhere for new opportunities. . The Holliday family of Huddersfield opened an office in New York during 1864, and began to manufacture aniline and aniline dyes, and preparations from natural dyes. This greatly assisted the introduction of aniline black printing in the United States.

The Albany Aniline & Chemical Company of New York was another early factory opening in 1868. Its origins are uncertain, but appear to have resulted from visits by A. Bott to Hofmann's Berlin laboratory, and the efforts of Carl Rumpff who was to become associated with Bayer. Magenta was produced, but there were problems with other aniline colors at first. The Bayer company held an interest from the mid 1860s, and the dye range was increased from 1881 when the Bayer holding was bought out by a certain Hendrick, who was joined by W. Lesser. [42]

Oakes & Rathbone, a manufacturer of sulfuric acid, joined with J.A. Moffat to set up the American Aniline Works, probably during the 1870s. Aniline was prepared on a 7-8,000 lbs. scale in an old boiler, cooled on the outside with jets of water. The inventor F. Shuman assisted with the introduction of arsenic acid oxidation of aniline in the production of magenta. However, as at Albany Aniline, there was no success with other colors. Eventually, the entire plant was swept into the Ohio by a flood on the Kanawha River.

The United States textile lobby was powerful and wanted dyes as cheaply as possible which meant that tariff barriers were lowered, and this improved the competitive position of the German and Swiss firms. In the 1860s the tariff was \$1 per pound, plus 35 per cent ad valorem (a lower duty was in force for indigo and dyewoods).

In the 1870s the duty was reduced to 50 cents, plus 35 per cent ad valorem. Aniline oil, the important intermediate and the basis of aniline black printing, was admitted free of duty. [43] This was just as well since American gas and coke producers were reluctant to undertake the extraction of hydrocarbons from coal tar.

In a 1911 attempt to explain the absence of a strong United States dye-making industry, Jacob F. Schoellkopf (who opened the Schoellkopf Aniline & Chemical Co., at Buffalo, New York, in 1879), noted that there was a surplus of chemists in Germany after 1880, and this encouraged them to emigrate, including to the United States. He also stated that until the 1880s the reductions in tariffs did not prevent the creation of a United States synthetic dye industry. Accordingly, during 1880-83 nine plants were opened and prospects appeared bright. However, the Tariff Act of July 1883, which left only the 35 per cent ad valorem (with no duty on intermediates), enabled massive inroads by the Germans (and Swiss). Five existing factories were forced to close down, including Albany Aniline (1886), and subsidiaries of the British Dawson family of Huddersfield (Dan Dawson & Sons, of Philadelphia) and the Williams & Ekin firm of Brentford. [44] Schoellkopf survived by producing well-established intermediates and azo dyes, and emulating on a small scale the German style of research. Fast and direct blacks were much in demand, and a notable Schoellkopf product was Erie black GXOO, discovered by Oscar Muller in 1901. Six years later, Schoellkopf's first sulfur dye, sulfur brown, appeared.

Another survivor was Heller & Merz, formed in the 1860s to produce the popular mineral colorant ultramarine. Around 1880 the partnership began the manufacture of aniline dyes, notably the violet made from oxidation of alkylated aniline. The success of this branch of activity was probably due to the efforts of the newly arrived German chemist George Prochazka, who in 1897 left Heller & Merz to set up the Central Dyestuff & Chemical Co. in Newark.

Bayer was the most active German company in the early United States dye industry. In 1882, one year after selling its Albany Aniline holding, Bayer, through E. Sehlbach, assisted former Albany staff W. Lesser and H. Preiss to set up the Hudson River Aniline & Color Co. at Albany. Lesser and Preiss moved on in 1898 to join L. I. Waldman and form the American Color & Chemical Co., across the Hudson at Rensselaer. Early in 1903 Hudson River's works was destroyed by fire. This provided an opportunity for acquisition by Bayer, which at the same time bought out American Color (October 1903).

## **Table II**

Dyestuffs in the United States. Consumption of dyes, intermediates and raw materials, 1867-1914, in tons:

	Manufactured in USA	Imported
1867		27,000
1883		1,200,000
1890	700,000	1,900,000
1900	1,500,000	4,500,000
1910	4,300,000	7,000,000
1914	9,000,000	10,000,000

Note: in 1894 the ad valorem duty was reduced to 25 per cent; in 1897 it was increased to 30 per cent.

The 1883 tariff change was not the only reason for increased German imports. The alizarin market was at first dominated by BASF through the Graebe and Liebermann patents and their reissues. This was upheld by the Alizarine Convention when Bayer attempted to develop the business in the United States through its Glasgow sales outlet. There were several disputes and court battles. What concerned the consumers was that as long as BASF had the monopoly in the United States the prices of both the natural and synthetic products were kept high. The matter reached the Supreme Court, and judgment went against BASF in 1884. The ruling was that a patent could not be taken out for a natural product, even if it was made by chemical synthesis. This meant that all the German alizarin manufacturers could now reach United States consumers. The price fell and the natural product declined rapidly, as it had done in Europe.

In 1885, one year after the Supreme Court decision, the European Alizarine Convention collapsed, and until 1900 there were no controls on the production and marketing of alizarin. By this time the German companies were so powerful that it was mainly their alizarin, azo, and phthalein colors that reached American ports.

## Indigo

*The laboratory and factory campaigns to replicate a second natural product. BASF versus Hoechst. A threat to the British Empire. Decline of the natural product.*

From the late 1870s the English dye-makers had become incapable of sustaining their earlier lead in technical development, and were unable to develop markets outside the British Empire. They lacked the commitment to manufacturing adopted by the Germans, who placed great emphasis on production and quality, backed up with product testing and customer service. This was carried over to later generations of dyestuffs, whereby new discoveries suited to the needs of consumers worldwide reached the market place in the shortest possible time. The British commitment to natural indigo ensured that the factory-made blue colorant was to be another German triumph.

Information about the constitution of indigo had been obtained by Baeyer from the mid 1860s, and he patented a synthesis in 1880. The problem of commercialization was that, unlike in the case of alizarin and the other coal tar dyes there was no ready made carbon skeleton of coal tar hydrocarbon molecules to transform into the blue colorant. The framework had to be created first.

Initially this was via benzaldehyde made from toluene. Baeyer's research was backed by BASF and Hoechst, who were in competition to achieve artificial indigo. The laboratory work was assisted by Baeyer's 1860s constitutional formula for indigo. The structure became available in 1883, another triumph for Baeyer, then at the University of Munich. However, in the following years the scientific and technical leaders, Baeyer and Caro, became less involved in the indigo work.

Success in resolving the scientific puzzle came from Switzerland where routes from more abundant starting materials were found. In 1890, Karl Heumann at the Zurich Federal Polytechnic (ETH), found that aniline and naphthalene were possible starting materials. The aniline process used benzene; the naphthalene route was via its conversion to phthalic anhydride, and then into a derivative of phenylglycine. Rudolph Knietsch undertook research into indigo for CIBA in Basel and then joined the BASF effort. These events became critical to the success of BASF.

In July 1897, using the naphthalene process, BASF began to market synthetic indigo. This was based on the economical oxidation of naphthalene to phthalic anhydride with fuming sulfuric acid and mercury. Sulfur dioxide was evolved and recovered for conversion back into fuming acid by the contact process, developed on a large scale by Knietsch. BASF also undertook the then novel electrochemical production of chlorine and alkali, essential inorganic chemicals in the indigo synthesis.

The new product however, could only just compete with the natural colorant. BASF were confident that synthetic indigo would win out if the quality was good. They were proved right. The synthetic product began to make rapid headway once it was found to be easy to apply, and that, like synthetic alizarin in the 1870s, the color was consistent. From the turn of the century German indigo began to displace Indian indigo, much to the concern of the British planters and traders. BASF and Hoechst had set up manufacturing units in France at Villeneuve St. Georges and Creil, respectively and Hoechst opened an indigo factory in Britain at Ellesmere Port.

Swiss attempts to make synthetic indigo on a large scale were partially successful. Sandmeyer's process was revived in an improved form by Rathien of Hamburg during 1910, and in the same year von Heyden of Dresden commenced manufacture by the phenylglycine route.

## **1900-1914**

*The dye industry before the First World War. The strength of the German industry.*

The German influence over world markets became so great that practically every country imported German dyes, including major consumers in the Far East, like China and Japan. This was assisted by an increasing reliance on cartels and the introduction of new products. In 1900, under pressure from the Germans, the Alizarine Convention was revived. During 1901, Rene Bohn at BASF developed the fast yellow known as flavanthrone, followed by the blue indanthrone. These novel vat dyes, made from anthraquinone used in the alizarin process, were in demand worldwide, and were joined by Bayer and Hoechst versions (they became known as indanthren dyes).

The triumph of the indigo synthesis foreshadowed the end of natural dyestuffs as a major economic force. The remaining processors of indigo, dyewoods and vegetable colors were forced to merge in order to survive. In Britain the British Dyewood Chemical Company was formed in Glasgow in 1898 (in 1911 it was restructured as a limited company under the ownership of United Dye Corporation of New Jersey; it was acquired by British interests in 1927, and survived until 1980); the United Indigo & Chemical Co. in 1899; and the Yorkshire Dyeware & Chemical Co. in 1900. [45] United Indigo & Chemical Co. was a merger of Scottish, Lancashire and Yorkshire interests involved in the manufacture of natural indigo and dyewood products.

Until the 1920s and beyond, haematein from logwood was used on wool in large amounts, fustic was a popular yellow for mixed shades, and natural indigo was often preferred on wools for dark blues. Most of the logwoods exported from Haiti were bound for United States ports.

Shortly after the turn of the century the Germans formed communities of interests, powerful associations of firms that became more closely linked than in monopolies, but were not mergers. This helped maintain strength through agreements over prices and the amounts of various products individual members could produce. In 1904, Hoechst joined with Cassella of Frankfurt to form the double alliance, and Bayer, BASF and AGFA linked up to create the triple alliance, or Dreibund, also known as the Little IG. In the same year, the United States imported 20 per cent of German dyestuff production, more than any other

country; this included very little synthetic indigo.

During 1907, Kalle of Biebrich became associated with the Hoechst-Cassella group, thereafter known as the tripartite association. [46] In the same year the new British Patent Act included clauses making the working of patents compulsory. Although there were loopholes, it did force Hoechst and BASF to open factories in England, at Ellesmere Port (Hoechst, for indigo), and at New Ferry, Birkenhead (BASF's Mersey Chemical Works).

Whereas, in 1914 the British manufacturers British Alizarine, Ivan Levinstein, and Read Holliday produced 4,000 tons of dyes, the eight leading German manufacturers manufactured 140,000 tons in their factories, some in other countries. The Germans and Swiss exported a large part of their production, which led to joint discussions concerning control of markets.

### **Table III**

Major consumers of dyestuffs exported from Germany in 1913, in tons

United States	13,855
China	8,461
India	3,822
Japan	3,500

### **1914-1922**

*Impact of the First World War. Swiss dyes replace German products. Governments support the creation and renewal of dye industries: resurgence in Britain, France and the United States; Japan seeks independence.*

The First World War broke out in August 1914, and one month later the German government banned exports to Britain and its allies. The British naval blockade began to restrict German trade with non-belligerent nations, particularly the United States. Moreover, some British-made intermediates were no longer available in Germany. The German industries quickly integrated their activities to assist the Kaiser's war effort, especially self-sufficiency programs, and in 1916 the two communities of interests merged. Two years later the three largest Swiss firms, CIBA, Geigy and Sandoz, formed their own Interessengemeinschaft, the Baseler IG.

From 1914, the Swiss had stepped in to supply Britain and France, often with disguised German dyes or dyes made from German intermediates. Their businesses boomed, and Sandoz, for example, increased turnover eight-fold between 1914 and 1920. The Swiss replaced Germany as a source of many specialties, as well as indigo made from British intermediates. The British, after much soul searching as to why they had failed to develop a viable dye industry, [47] responded with massive efforts that led to the revival of their own industry. The manufacture of indanthrone vat dyes and synthetic indigo were notable successes.

James Morton of Carlisle, a complete newcomer to the manufacture of dyes, achieved the first British success in his textile and dyeing factory. In 1914, he engaged a few chemists to undertake the conversion of anthraquinone-2-sulfonic acid to yellow and blue vat dyes of the indanthrone type. Using a steel autoclave, and working at high temperatures and pressures, they achieved these objectives on a small scale. By the end of 1915 the dyes were being produced for in-house use, and the intermediates were also made at Carlisle. In 1916, Morton's team invented a replacement for the alizarin blue wool dye, which became known as Solway blue. Other consumers pressed Morton to place his products on the open market, including the powerful Bradford Dyers' Association, Ltd. Responding to these demands, Morton's Sundour Fabrics Ltd. set up The Solway Dyes Company (which in 1920 became Scottish Dyes Ltd.).

Herbert Levinstein, son of Ivan, acquired the sequestered Hoechst indigo factory at Ellesmere Port. There he manufactured phenylglycine from aniline, and indigo became available from 1916 in sufficient amounts to satisfy the Scottish and Lancashire printers and dyers. [48] The demand for military uniforms was met. (The BASF factory at Birkenhead was sold to Colonel E. A. Brotherton of Leeds.)

Dye-makers had other major strategic roles: they were leading suppliers of nitro compounds for explosives, and, from 1915, chemicals used in gas warfare. Consequently, consolidation was encouraged by the British government. Read Holliday had close links with the Bradford Dyers' Association, especially an important contract for supply of sulfur blacks. It did not take much government persuasion for Read Holliday to merge with the Bradford Dyers' Association and the Calico Printers' Association to form British Dyes Ltd. in 1914 (the prospectus was published in March 1915). However, immediately after the war considerable government persuasion, with help from the newly formed Colour Users Association (1919), was required to bring the rival Read Holliday and Levinstein interests together in May 1919. At that time the British Dyestuffs Corporation, Ltd. came into being, a merger of the Huddersfield-based British Dyes and the Manchester-based Levinstein Ltd. Another branch of the Holliday family, L.B. Holliday & Co. Ltd., was set up in 1916 in Huddersfield, and this remained independent.

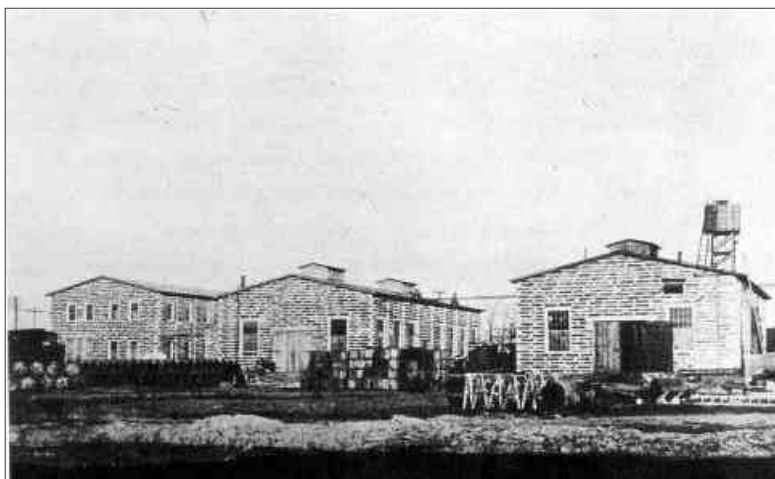
From the start of hostilities, the French government had supported moves for self-sufficiency. The major manufacturer in 1914 was Societe Colorantes et Produits Chimiques de Saint-Denis, Pointer's old firm. The important Hoechst and BASF factories were taken over by the government. In 1917, through the Service de Poudres, the government assisted in the creation of the Compagnie Nationale des Matieres Colorantes et Produits Chimiques, near Rouen, which employed 2,000 workers, and which produced synthetic indigo on a large scale from 1921.

The absence of German products encouraged manufacture in European countries that had previously not been involved in the dye industry. The first Italian factory, Industria Nazionale Colori di Anilina, was opened in Milan during 1915 with assistance from Manchester's Claus & Co. Ltd. (which was taken over by Levinstein in the following year), and specialized in sulfur, azo and triphenylmethane dyes. The Spanish industry was concentrated in Catalonia, where in Barcelona J. Pellicier and L. Sangier were joined by the Sociedad Espanola de Productos Quimicos.

In Russia, where in 1913 some ten firms, some foreign-owned, produced around 8,000 tons of dyes, and one-quarter of all imports arrived from Britain, there were severe shortages from 1914. This forced the dyers and printers to take action, producing sulfur, phenol and naphthalene dyes.

But it was across the Atlantic that the greatest transformation took place. In 1914 the United States dye manufacturers relied heavily on imported German intermediates, and the dyers and printers on German colorants, despite the 30 percent ad valorem duty. Schoellkopf (then known as the Schoellkopf, Hartford & Hanna Co., specializing in azo dyes and sulfur and direct blacks) and Heller & Merz together produced no more than 12 per cent of dyes consumed by the domestic market. With the outbreak of war, there were shortages and the price of dyes increased considerably. There was a surge in demand for natural dyes, notably Brazilwood (redwood), logwood and fustic. Bayer's interests alongside the Hudson were seized and sold to Sterling Products that was mainly interested in the pharmaceutical division. The dye-making facilities were purchased by the Grasselli Chemical Co., that operated a dye factory at Linden, New Jersey, in 1919.

Home based production was encouraged by the Revenue Act, of 18 September 1916, which provided a protective barrier for a period of five years. In 1915, Herbert Dow had started work on indigo, and by the end of 1916 the first American-made artificial indigo was available from the Dow factory at Midland, Michigan. Calco Chemical Company, at Bound Brook, NJ, was founded in 1915 and immediately began to produce intermediates. One year later the Federal Dyestuff Corporation of Kingsport, Tennessee was opened, and became a major producer of sulfur blacks.



**Calco Chemical Company, Bound Brook, New Jersey (ca. 1915).  
Edelstein Collection, Hebrew University.**

In May 1917, Schoellkopf, William Beckers Aniline & Chemicals Works (founded in Brooklyn during 1912), Century Colors Corporation of Nutley, New Jersey and the Benzol Products Company of Marcus Hook, formed the National Aniline & Chemical Company (NACCO). (Benzol formed in 1910, was jointly owned by the Barrett Manufacturing Co., largest distributor and distiller of tar products, the General Chemical Co., manufacturer of acids, and the Semet-Solvay Co., famed for its alkalis). Standard Aniline Products of Wappinger Falls, New York, was soon incorporated, as were facilities of Barrett, General Chemical, and Semet-Solvay. Together they formed a fully integrated network for coal tar products, intermediates, acids, alkalis and dyes, with a combined annual output of 16,000 tons. . . At Deepwater Point, New Jersey, E.I. Du Pont de Nemours & Co., with technical help from Levinstein, began production of indigo in 1917. [49] The United States entered the Great War, and the Trading with the Enemy Act was passed on 6 October 1917, which gave further impetus to the growth of an American dye industry. Thereafter the Federal Trade Commission began to issue licenses for German patents through the Chemical Foundation Incorporated. Indigo and sulfur blacks were the most important products manufactured in the United States.

By 1919 the United States had invested \$466m in its dye industry, in which Du Pont emerged as the leader. Over 2,600 chemists were employed in the industry, compared with 1,700 in 1917 (and a total of 214 employees in 1914). NACCO commenced the manufacture of artificial indigo in 1919. Success was measured by the value of exports, which in 1920 reached \$17m. In April alone some \$3m worth of dyes were exported, about one-third reaching China and Japan (prior to the anticipated introduction of a Japanese tariff on dye-imports).

Allied Chemical & Dye Corporation was formed in 1920, and this brought about greater integration of Barrett, General Chemical, Semet-Solvay, Solvay, and NACCO. Thereafter operations were based at the Buffalo site. [50] To protect the new United States dye industry, the Longworth Bill, introducing a protective tariff, was passed by the House of Representatives in September 1919, and the Dye and Chemical Control Act was passed on 27 May 1921. These moves restricted entry into the United States of German-made dyes. Over 200 intermediates were produced, but the shortage of coal tar anthracene created several problems, until this hydrocarbon was manufactured from phthalic anhydride and benzene in 1922.

However, in 1922 a depression set in that severely curtailed production in the United States. The situation was not helped by renewed attacks from the German manufacturers, although these were interrupted by the occupation of the Ruhr in 1923. There was a fierce battle with the Germans, Swiss and French for a slice of the Chinese synthetic indigo market, which took half the world supply. The Chinese were the largest dye-users, consuming some 70 million pounds annually, compared with the 55 million pounds used by the second largest consumer, the United States.

Japan, previously totally dependent on Germany for synthetic dyestuffs (6,000 tons alone in 1913), also began their manufacture during the war. Several firms set up in business, and the largest company, Japanese Dyestuffs Manufacturing Co. (Nippon Senryo Seizo Kabushiki Kaisha), of Osaka, received considerable government assistance. Mitsui Mining and Tokyo Gas extracted coal tar hydrocarbons in 1914. Sulfur blacks and azo dyes were produced, as well as triphenylmethane dyes, and Mitsui (at Omuda, Oushu) and the Japanese Dyestuffs Manufacturing Co. attempted the production of indigo. After the war, Japanese Dyestuffs specialized in basic colors, direct cotton dyes, acid and sulfur colorants, and mordants. Mitsui continued with indigo and alizarin production. By 1920 Japanese dye exports to China were competing effectively against the products of Switzerland, Germany and the United States. The government-owned iron works and the Manchurian Railway coke works set about increasing the availability of coal tar products.

The British Dyestuff Corporation (BDC) opened an agency in Japan during the time that German imports were interrupted after the war, and United States-made dyes were not well received. BDC also created the Dyestuffs Corporation of America by absorbing Levinstein's transatlantic sales outfit and the Read Holliday interests in America. It became an important sales outlet, and also offered dyes from Du Pont.

The revival of confidence in Britain was demonstrated in 1922 at the British Industries Fair, held at the White City, London, where new and old dye-makers displayed their colorful wares. The major participants were: BDC, British Alizarine Co. Ltd., L.B. Holliday & Co. Ltd., Scottish Dyes, John W. Leitch & Co. Ltd., Hickson & Partners, Ltd., John C. Oxley's Dyes & Chemicals Ltd., James Robinson & Co. Ltd., Gray's Dyes & Chemicals Ltd., J.B. & W.R. Sharp Ltd., Williams Bros. & Co., Alliance Colour & Chemical Co. Ltd., and the Ajax Aniline Dye Manufacturing Co. Within a decade the number was to fall, mainly as the result of mergers within the chemical industry that were associated with the formation of a major national producer.

#### **Table IV**

Production of the new dye-making nations, in millions of pounds

1918		1919	
Italy	2	France	6-7
United States	58.5	Japan	16 (85 percent sulfide)
1923		1925	
United States	93.5	Italy	10 (80 percent sulfide)

#### **Post-war Innovations and Anxieties**

*Dyes for synthetic fibers. Disperse and phthalocyanine dyes.*

The 1920s saw several technical innovations, mainly in the areas of increased color fastness and dyestuffs for synthetic fibers. In that year chemists at Scottish Dyes discovered the first bright green vat dye, called Caledon Jade Green, which was popular for the next fifty years. With the introduction of cellulose acetate on a large scale immediately after the war, dye chemists had to adopt completely new approaches. (Cellulose acetate was also known as acetate silk, one of the forms of artificial silk, and was called Celanese in Britain, and Lustron in the United States; the term "Rayon" was introduced in 1924). Previously, dyeing had been carried out in aqueous media and fibers from natural materials (cotton, silk, wool and linen) absorbed the dye. Ionic groupings polarized the dye molecules and this favored solubility. However, these groupings resisted attachment to cellulose acetate, which did not absorb water.

Disperse dyes provided an answer to the awesome challenge presented by novel textile materials, and were associated with discoveries in Britain. They were applied as a dispersion of particles in water and relied on new advances in theoretical chemistry. Arthur Green and William Perkin junior (son of the discoverer of mauve), had undertaken research on these and other new dyes for British Alizarine, Levinstein, and Morton.

The results were products that held fast on synthetic fibers, notably the ionamines, discovered by Green and K.H. Saunders in the laboratory of BDC in 1922, and that were applied to cellulose acetate. Once attached to the fiber they were diazotized and developed in a manner similar to Green's primuline. They offered possibilities for new yellow, orange, red, maroon, purple, black and blue shades.

These were rapidly followed by a range of insoluble azo dyes and novel anthraquinone colorants that would become known as "acetate" dyes. The Ionamines showed that water-soluble dyes for acetate were possible, but ICI had little success with this research, which was also taken up in Germany. The first experiments were also conducted on what were later known as fiber reactive dyes. However, they were not fully understood, or exploited, until the 1950s. Progress was invariably hindered by misconceptions. **[51]** Direct dyes for viscose rayon also appeared in the 1920s, and were copied by Swiss and German manufacturers.

The vast range of dyes called for a new system of classification. Previously this was based on the Farbstofftabellen (Tabellarische Übersicht der Kunstlichen Organischen Farbstoffe) of G. Schultz and P. Julius, first published in 1888 on the occasion of A.W. Hermann's seventieth birthday. By 1914, five editions had appeared. They contained details of some 1,000 dyestuffs that were known by 10,000 trade names! This was a most unsatisfactory situation, and since an English language guide was in demand the British Society of Dyers and Colourists undertook the task of indexing dyestuffs.

The first edition of their Colour Index, edited by F.M. Rowe, appeared in 1924, and the long-term aim of introducing systematic nomenclature was finally achieved in 1956 (with participation from the American Association of Textile Chemists and Colorists after 1945). **[52]**

Business, as well as dyestuffs, was reorganized. The trend in Europe (outside of Germany), North America and Japan had been toward the introduction of protective tariffs that might assist the growth of national industries, and further mergers to create powerful trading corporations capable of exerting economic muscle in the international arena.

From 1924, the French Compagnie Nationale des Matieres Colorantes et Produits Chimiques came under the controlling interest of Etablissements Kuhlmann, which had a minority interest in the Paris-based firms of Societe des Matieres Colorantes et Produits Chimiques de Saint-Denis, and a majority holding in the Compagnie Francaise de Produits Chimiques et Matieres Colorantes de Saint- Clair-du-Rhone. The only rival was the CIBA factory at St. Fons, near Lyon.

The major event in Britain was the formation of Imperial Chemical Industries (ICI) in 1925 by the merging of the four largest British chemicals firms, one of which was British Dyestuffs Corporation. Through prior share purchases, Scottish Dyes was absorbed in 1928, and its associated Soledon Ltd. (set up in 1920) in 1934. The Scottish connection proved particularly valuable.



**Imperial Chemical Industries Ltd., Dye Label. Edelstein Collection, Hebrew University.**

In 1928, chemists working at the Grangemouth works of Scottish Dyes observed a blue color in the steel reactor in which phthalimide was prepared from phthalic anhydride and ammonia. This was an iron-containing compound similar to natural pigments like chlorophyll and blood, and the copper analogue became Monastral fast blue (1934). [53] This prototype phthalocyanine dye has been described as the most important colorant discovered in the twentieth century. [54]

In 1934, the IG Farben Corporation (see next section) introduced its version, Heliogen Blue B, made by an improved method, much to the amazement of ICI's dyestuffs group, which mused that it was "a revelation of the resources they [IG Farben] are able to throw into any opening for research, whether provided by their own initiative or by that of their competitors." [55] ICI later acquired a license to use the German process.

### **Business Trends, 1920-1939 ( [56] )**

*Protectionism, the rise of major corporations and international cartels. Stalemate and the cartel breakers.*

The massive chemical corporation IG Farben was set up in Germany at the end of 1925. There were 67,000 workers, including 1,000 chemists. About 36 per cent of sales were represented by dyes. Bayer's Uerdingen factory specialized in intermediates, and Leverkusen, also in the Bayer sector, in azo dyes. The creation of IG Farben heralded and forced many changes elsewhere. Thus, although ICI was similar in size to Du Pont, and both had the largest ranges in their respective countries, they were no match for the giant IG Farben.

ICI and its forerunners may have introduced the most novel dyes in the interwar period, but it did not have the international marketing experience of IG Farben. Also, German dyes were included among the reparations, and despite the lack of income they promoted a return to confidence in German products in ways that no sales effort could have equaled. (Considerable amounts of German dyes were seized after the war, and for a period of five years the Germans were forced to provide a quarter of their output at prices dictated by the Allies).

Before the First World War, the German hold on the world market meant that there was no need for the creation of international cartels, although discussions were conducted with the Swiss. With the entry of several nations into the dye industry, and the competing international export efforts by 1920, the Germans were forced to seek out new strategies, as were their competitors.

Although the Germans found it difficult to regain their former positions in North America and Europe, because of the revival of dye industries and the introduction of tariff walls, they were able to make massive inroads into the important and expanding markets for synthetic dyes in the East. This created a dependence on German supplies not unlike that experienced in Europe and North America before 1914. The result was that the exports of

other European nations were threatened. Consequently, by the mid 1920s the Germans were in a strong position to exert considerable influence on other dye-makers in Europe. Sometimes this came about as the result of new government measures aimed at restricting the entry of German products into European countries.

In the United States access to German colorants, particularly the indanthrene vat dyes, was still needed in the 1920s, and the German firms wished to regain dye markets lost during the war. This led to the formation of the predecessor of the German-owned General Aniline & Film (GAF), a leading manufacturer of vat and azo dyes at Rensselaer, New York, and Linden, New Jersey.

In Britain, the Dyestuffs (Import Regulation) Act of 1920 had come into force on 15 January 1921. This cut off many German products in an attempt to promote their production in Britain. However, British dye-makers needed German assistance to control several important markets. The British Dyestuffs Corporation and the Germans immediately began discussions over cooperation in dyestuffs and other sectors, and market division. Despite opposition from British professional chemists, many industrialists, and members of Parliament, negotiations were revived in 1927. ICI was anxious to retain the Empire market, and also to acquire control of Clayton Aniline, then in Swiss hands. The link up did not materialize, partially as a result of government pressure. In 1927, also, the British government introduced a tariff of 33 1/3 on imported synthetic organic products. [57]

### Table V

Capacities of leading producer nations, in millions of pounds

Germany (1913)	280	Italy (1922)	10
Japan (1919)	10	France (1923)	24
Britain (1920)	43	United States (1923)	94
Switzerland (1920)	24		

Source: "The American Dye Industry," Journal of the Society of Dyers and Colourists, 40 (December 1924): 428-429.

### Table VI

Coal tar dyes in 1926, at a time of major mergers, production in tons

Germany	63-75,000
United States	36-43,000
France	11-17,000
Great Britain	13.5-18,000
Switzerland	8.7-10,000
Italy	7,000
Japan	7,000

### Table VII

Export of dyes, as a percentage of the world market 1926

Germany	64.8
Switzerland	16.4
United States	8.3
Great Britain	4.1
France	3.3
Czechoslovakia	1.0
The Netherlands	0.9
Italy	0.6
Belgium	0.4
Poland	0.2

Source for Tables VI and VII: Harm G. Schroter, "Cartels as a Form of Concentration in Industry: The Example of the International Dyestuffs Cartel from 1927 to 1939," *German Yearbook on Business History* 1988 (Springer Verlag: Berlin, 1990), pp. 113-144. . Within a year, however, cartel arrangements were initiated by the two largest exporting nations, Germany and Switzerland. These were favored by new and existing national corporations and partnerships. The Germans, Swiss, and French (whose industry was controlled by Kuhlmann), linked up in 1928, and in 1932 they were joined by ICI. The British firm was, throughout the discussions, under pressure to take over its smaller British rivals. It did, in fact, acquire the British Alizarine Company in 1931, and exerted influence on most other firms. However, L.B. Holliday, which was responsible for a quarter of British exports, had rejected all advances. By increasing the production of certain dyes, Holliday was able to bring about the withdrawal of the import license on those specific colorants. ICI and IG Farben were infuriated, and in response jointly set up the Trafford Chemical Co. in 1938 so that IG Farben's colors could be manufactured in Britain.

Antitrust legislation prevented penetration of the United States market by the European cartel. The European answer was the setting up of German and Swiss factories in North America, where the tariff wall was also a serious obstacle to imports. However, the Great Depression held back progress for all participants. The turnover of Du Pont, for example, fell from \$214m in 1929, to \$127m in 1932.

It is interesting to note that the Soviet Union, despite a shortage of raw materials, was producing 10,000 tons of dyes each year for the home market in newly opened and former Swiss and German factories near Moscow. After the Revolution of 1918 the Bureau for Aniline Manufacture was established, and two years later it controlled seven factories specializing mainly in sulfur and azo dyes. By this time, German dyes were imported in considerable amounts.

The second half of the 1930s saw considerable improvement in growth. In 1938, ICI had around 60 percent of British sales, the CIBA- owned Clayton Aniline around 25 percent, and L.B. Holliday just under 15 percent. The Swiss, almost completely export oriented, had retained their positions, and their community of interests. CIBA was the major dye-maker; combined turnovers of Chemische Fabrik vorm. Sandoz (Sandoz AG from 1939) and J.R. Geigy AG did not equal that of CIBA. The latter specialized in vat dyes, and Sandoz in anthraquinone derivatives.

Minor Swiss firms were Chemische Fabrik Rohner AG, a family business formed in 1906 at Pratein, and Durand & Huguenin AG, which reprocessed IG Farben dyes. Geigy had interests at Grenzach and Rouen, while CIBA, which from 1919 totally owned Clayton Aniline, retained its St. Fons factory. IG Farben held half the share capital in Durand &

Huguenin, and in 1928 acquired Rohner. In the United States, the Swiss IG had purchased the Ault & Wiborg dyestuffs factory (Cincinnati Chemical Works) in 1920. Through the international cartel and their foreign interests the Swiss controlled almost 20 per cent of world dyestuffs sales.

Most French sales in 1938 came from Kuhlmann's Compagnie Nationale des Matieres Colorantes et Manufactures de Produits Chimiques du Nord Reunies, of Paris. A quarter was accounted for by the Saint-Denis factory and the Kuhlmann-controlled Saint-Clair-du-Rhone unit. They were all members of the Centrale des Matieres Colorantes, and party to the cartel agreement with IG Farben and the Swiss. Kuhlmann held shares in other French firms, including minor producers.

The Italians specialized in sulfur dyes for cotton. These had been developed commercially in the 1890s, required low technology and were, accordingly, cheap to produce. In 1931, Montecatani took over Aziende Colori Nazionali Affini (ACNA), of Milan, a merger of six firms. Cassella had bought out the second largest firm, Soc. Chimica Lombarda A.E. Bianchi & Co., of Rho, in the 1920s, and the share holding was used to bring Bianchi into the international cartel. In 1925 the Swiss IG acquired the Italian Soc. Begamasca per l'Industrial Chimica, of Seriate. ACNA was responsible for just over 50 percent of sales, Bianchi for about 16 percent, Begamasca, 15 percent, Industria Chimica Dot. Saronno, of Melegnano, 13 percent, and Industria Piemontese Colori Anilina, of Cirie, 5 percent.

The 1938 lineup in the United States was headed by Du Pont, National Aniline & Chemical Co. (NACCO; part of Allied), and American Cyanamid, which had taken over Calco in February 1929. In 1930, Cyanamid's Calco division absorbed Heller & Merz. The IG Farben-owned General Aniline & Film Corporation (GAF), Dow Chemical Co., and the Swiss-owned Cincinnati Chemical Works, accounted for a further 20 percent of sales. Du Pont and NACCO could boast of considerable export achievements, and Du Pont was the most innovative of the American firms.

In Japan, only Japanese Dyestuffs and Mitsui were operating in 1923, despite the introduction of a 35 percent tariff on imports. The decline in the number of producers was caused by a severe recession and growing imports from Germany and the United States. The industry was revived during the 1930s, and at the end of the decade the following firms were operating: Japanese Dyestuffs, which controlled about two-thirds of the local market, Mitsui Bussan Kaisha Ltd., of Tokyo, Mitsui Kozan Kabushki Kaisha, of Tokyo and Miike, and Mitsubishi Dye Co., also of Tokyo. There were arrangements for control of the indigo market with the international cartel.

Much of the remainder of the worldwide dye industry before the Second World War was controlled, directly or otherwise, by the cartel, sometimes because of Swiss, French, British or German holdings. In Poland, Pabjanicer AG, founded in 1899 by CIBA, was owned by the Swiss IG, and Winnica was formed in 1929 by IG Farben and Kuhlmann. The Czech Aussiger Verein joined the cartel in 1934, along with the IG Farben concern Tofa, set up in 1925, with factories at Reichenberg and Brunn. Other firms brought into agreements were: in The Netherlands, N.V. van Chemische Producten Vondelingenplaat, of Schiedam, and Nederlandse Farben- und Chemikalienfabrik, of Delft; in Spain, the Fabricacion Nacional de Colorantes y Explosivos, of Barcelona, and Chimica Industrial Espanola SA Quiesa; in Romania, Colorom Chimische Fabrik R.A.O., of Zeiden, Codlea; in Bulgaria, Coloriska S.A., of Sofia; in Greece, SA Oeconomides & Co., of Piraeus; and in Brazil, Cia de Productos Industriales M. Hamers S.A., of Rio de Janeiro. **[58]** Brazilian production had started in 1922, with two factories in Sao Paulo and one in Rio de Janeiro. Sulfur blacks were produced on a considerable scale and intermediates were imported.

With the outbreak of war in August 1939, the international cartel collapsed. The Swiss IG was dismantled a few years later, and Geigy, Sandoz and CIBA acquired the majority of shares in Durand & Huguenin.

German occupation of mainland Europe brought new changes to the structure of the dye industry, although in reality the effect was to perpetuate earlier cartel arrangements. In March 1941, the French government agreed to the formation of the Franco-German corporation to be known as Francolor. In this way, IG Farben absorbed the main French dye manufacturers. Freed of German control after the war, Francolor continued to trade and,

following acquisitions of French interests, the name has been retained by Britain's ICI. IG Farben's statement to the French concerning common interests during the Francolor negotiations half a century ago is not without irony in 1992:

Note that, set in the framework of our programme of European re-organization, these proposals are economically very advantageous to you. They are in your interests. They are in the interests of IG Farben. They are, above all, in the interests of Europe. [59]

German hegemony was particularly strong in Eastern Europe, where, for example, Czechoslovakia's leading dye-maker, Spolek, came under the control of IG Farben. After the Soviet Union entered the war in 1941 its aniline production was increased, but dye production declined. [60]

## **International Dye-making from the 1950s**

*The break-up of IG Farben. New manufacturing nations. Expansion in Japan and India. Reorganization in Europe after 1960. Decline in the United States.*

In 1945, the Allied Control Council took charge of the assets of IG Farben, and teams of Allied scientific and technical investigators delved into the secrets of all aspects of German industry. Their findings, the US FIAT (Field Intelligence Agency Technical) and British BIOS (British Intelligence Objective Subcommittee) reports, were made widely available, and textbooks on dyemaking began to cite German advances from the 1930s (notably Krishnasamy Venkataraman's two volume Chemistry of Synthetic Dyes, based on his visit to post-war Germany). These included water soluble dyes for cellulose acetate, metallized azo dyes for nylon 6, direct cotton dyes, and benzo fast chrome dyes for wool and cellulose.

Soon it was agreed that the German factories that had once made up IG Farben would be released from allied control. The successors to Hoechst and Bayer were formed in 1951, and BASF in 1952; the BASF plant in French hands was released in March 1953. Bayer, formerly in the British zone, continued with dyes alongside other synthetic products, medicinals, plastics, etc., and absorbed AGFA. Hoechst, formerly in the American zone, took over Cassella in 1969.

During the 1940s and early 1950s research was aimed at fast dyes for cellulose, colorants for the increasingly popular nylon and other new synthetics, and chemical theory as it related to color, constitution and dye fastness. Progress was made with new azo, basic, anthraquinone, indigoid, sulfur, and phthalocyanine dyes. Pre-war developments were followed up. For example, ICI had introduced its Solacet range of water soluble dyes for cellulose acetate as early as 1933; L. B. Holliday had launched the Supracet disperse dyes for acetate and, later, nylon.

Around 1950, most dyes were applied to cotton and viscose rayon, and some sixty new direct cotton dyes appeared, mainly from Bayer, CIBA, Geigy and Sandoz.

The companies that IG Farben had controlled in Europe reverted to their original, or state, ownership. These included Spolek in Czechoslovakia. During the early 1950s, new nations began the manufacture of synthetic dyestuffs, including Argentina, India, and Mexico. [61] Subsequently, European firms opened up manufacturing units in developing countries, participated in joint ventures, and took over established business. The growth of textile industries outside of Western Europe and the United States, where they were in decline, and restrictions over the use of many traditional dye-making chemicals, encouraged the expansion of dye-making elsewhere.

Selective duties on imports have also assisted new producing nations. When restrictions were partially lifted in Mexico around 1980 much damage was done to the home industry as foreign dyes flooded the market. Recovery followed a rise in duties which suggested that, as after the First World War, a country "can only build up an industry with good tariff protection, since it will be many years before economy of scale can be reached. After all, the US dyestuff industry for many years enjoyed a comfortable duty protection." [62] However, as elsewhere, tariff walls, licenses and duties encouraged foreign firms to open up manufacturing operations. The result was that in Mexico during the early 1980s there were seven foreign-owned factories, and only four national companies, led by Pigmentos Y

Oxidos (now Pyosa), of Monterrey, which also exported. The first Mexican firm, Argo SA, which began production in 1952, became closely linked with Bayer, as did Colorquim (originally set up by Sun Chemical, and taken over by Du Pont). Anyl Mex, opened in 1968, relied on plant designed in Czechoslovakia, and was later sold to Britain's ICI.

The Mexican government subsidizes the manufacture of intermediates by providing benzene, toluene, xylene and naphthalene from state owned petrochemical plants at 10-20 percent below world market prices.

Technology transfer agreements involving West European corporations and developing nations were also encouraged by the increasingly stringent regulations and environmental controls in Europe and North America and the geographical shift in the centers of textile production. Many plants in Argentina and Brazil, for example, are owned by German or Swiss nationals.

From the 1950s the cotton industry of Hong Kong that once satisfied the needs of Thailand, Indonesia and the Far East began to make massive inroads into European and American markets. Growing production of textiles meant growing consumption of dyes and textile chemicals, and new opportunities for Asian manufacturers of these products. The dye industries of Indonesia, Pakistan, South Korea, Taiwan, Thailand, and the People's Republic of China, like that of Mexico and a number of developing countries, began with low technology products that satisfied local markets. Today Korea manufactures important intermediates; and China has considerable production capacity, including intermediates such as beta naphthol. In Pakistan, Pak Dyes, set up in collaboration with Bayer and Hoechst, produces large amounts of azo dyes (200 tons per annum) and sulfur black (300 tons each year). The industry in Pakistan is partially state owned, but in August 1992 a privatization commission invited bids for shareholdings.

In Japan, Sumitomo had taken over the major producer, Japanese Dyestuffs Manufacturing Co., in 1944. Mitsui Chemical Industries, established in 1941, and Mitsubishi Chemical Industries, created in 1944 from Japan Tar Industries (formed in 1934), became formidable rivals. In many ways this marked the emergence of Japan as one of the world leaders in dye manufacture. By 1966, Japan was already the fourth largest dye producer, and each of its five major corporations (Sumitomo, Nippon Kayaku, Mitsui Toatsu Chemicals, Mitsubishi, and Hodogaya Chemical) had established joint ventures with foreign companies. In 1968, Mitsui Toatsu Chemicals merged with Toyo Koatsu and Mitsui. Japan soon became a leading exporter of dyes, and was mainly responsible for the remarkable increase in new products worldwide, totaling no less than 964, during 1974. **[63]**

Japanese production at the end of the 1970s reached 132 million pounds, 50 percent more than in 1975. In 1980, the Japanese government permitted the creation of a cartel to resolve questions of oversupply, and to assist research and development strategies. When Mitsubishi contracted with Atlantic Chemical Corporation in the United States over the marketing of each other's dyes, there was considerable concern in the American dye industry. **[64]**

Government assistance also became available in India, where, as a result of competitive pricing policies, one-third of production was exported in 1979. The Indian dye industry had grown rapidly following that country's independence. Atul Products Ltd., situated at Gujarat, some 200km from Bombay, was formed in 1949, and created joint enterprises with ICI (Atic Industries, 1955), and CIBA (Cibatui, 1960). Agencies were opened in Europe, the United States, and in Asia and the Far East. Indian Dyestuffs Industries, situated in Bombay and the second major producer, was formed in the 1950s. Among the other notable firms is Amar, some 50km from Bombay, and set up in 1954, Rathi/Chemiequip, and Exim.

In the Soviet Union dyestuffs production continued to grow after the Second World War, in line with the 4th Five-Year Plan (1946-1950), reaching over 95,000 tons in the early 1970s. Since then, however, the output has declined to around 75,000 to 80,000 tons at the end of the 1980s. Sandoz collaborated in a new dye-making venture in the Ukraine, where, it was planned, 6,000 tons of sulfide dyes were to be produced each year. **[65]** The merger of CIBA and Geigy, which became the world's leading dye producer, took place in 1970. Italy's Montecatani and Edison merged in 1966 and the new corporation was renamed Montedison Group in 1970; it continues to produce dyes and intermediates. In 1980, ACNA, a member

of the group expanded production of intermediates considerably. Montedison signed a five year contract with the Polish Chemical Authority in 1981 for exchange of products; Poland would supply intermediates for dyestuffs.

There were several upheavals in France, characterized by not always successful mergers and diversification. Over half the French chemical industry fell into state control and there was considerable reorganization in 1982-83 and during the early 1990s. Kuhlmann became part of the Pechiney-Ugine-Kuhlmann group in 1972 and dyestuffs and other chemicals were generally run down or sold off. By 1989 some 40 per cent of the private sector was in the hands of foreign-owned companies.

There were also upheavals in Britain. In 1981, the British Economic Development Committee for the Chemical Industry predicted the decline of production in Western Europe (mainly Britain, Germany, and Switzerland) due to the emergence of manufacturers in Eastern Europe and the Far East. This led to considerable reorganization. Thus the former Yorkshire Dyeware & Chemical Co., known as Yorkshire Chemicals Limited from 1971 (by which time natural dye preparations had been replaced by the manufacture of synthetics), was particularly vigorous in promotion of its products. New outlets were established in Europe (especially Italy), the Far East, and in the United States as Yorkshire Pat-Chem, Inc. Today the color division of Yorkshire Chemicals plc is based in Leeds, while specialty products are manufactured at Selby, North Yorkshire

L.B. Holliday was less fortunate. Although the firm had received the Queen's award for exports in 1978, the recession during the following years led to receivership in 1981. A.T. Bray bought out the assets in 1982 and set up Holliday Dyes & Chemicals Ltd., in 1992 a thriving enterprise. This company is currently expanding its efforts in the United States and in other foreign markets

ICI's response was to "strengthen its position as a world supplier of dyes, pigments and auxiliaries through the proposed acquisition of the French chemicals company PCUK-Produits Chimiques Ugine Kuhlmann." [66] The acquisition of PCUK, whose dyes were sold under the Francolor trademark, took place late in 1982, and included manufacturing units at Oissel (south of Rouen specializing in azo dyes and pigments). Saint Clair du Rhone (midway between Lyon and Grenoble; azo leather and triphenylmethane dyes), and Villers Saint Paul (north of Paris; phthalocyanine blues and Solanthrene vat dyes).

The PCUK subsidiary Societe des Produits Chimiques et des Matieres Colorantes de Mulhouse was also taken over by ICI, as were the British subsidiaries Alliance Dye & Chemical Co., and Catco Chemicals of Bolton, Lancashire, and the Fosfanil factory in Brazil. This increased ICI's color sales by 50 percent, with an annual turnover exceeding £250m.

The conditions of sale had been agreed on 1 October 1982, and early in the following year ICI Francolor SA was created, a wholly owned subsidiary of ICI incorporating its former sales agency, ICI France. [67] ICI had thus inherited not only the interests of the successors to Perkin, Simpson, Maule & Nicholson, Levinstein, the Hollidays, and Morton, but also the innovative tradition established by Poirrier at Saint Denis, Paris, where in the 1860s the new alkylation of aniline process was first conducted. Not far away, at Villers Saint Paul dye making was fully computerized in 1982, while at Oissel, "red and yellow azo dyes are synthesized by a continuous process. This is believed to be the first and only one of its kind in the world."

Many factors would contribute to changes in the United States dye industry. The boom years were the 1950s and 60s. In March 1950, seventy percent of Arnold Hoffman & Co., Inc. of Providence, Rhode Island, and Dighton, Mass. was purchased by Britain's ICI. Soledon and Caledon dyes were made at Dighton, and there were additional facilities at Charlotte, North Carolina. The takeover by ICI was soon complete, and the title ICI Organics was adopted in July 1963 (ICI America, Inc., from October 1958). This was the formative period of the present ICI Americas. In 1954, the Althouse Chemical Company, of Reading, Pennsylvania, was purchased by Crompton & Knowles, a long established firm of textile machinery manufacturers. They opened a Belgian subsidiary, Althouse Tertre SA, 1969. A completely new dye-maker, Fabricolor, was founded in 1961, with a works at Paterson, New Jersey.

The 1970s saw the beginning of a series of cutbacks that would reduce the size of the national industry by almost half. This was initially caused by the creation of over-capacity in anticipation of the growth of synthetic fibers, the oil crises, then by concern over pollution (especially US government health and safety regulations), and finally by worldwide recession. In particular, environmental factors began to favor the manufacture of the important anthraquinone vat dyes outside the United States.

During the 1970s, Allied Chemical & Dye's National Aniline Division, General Aniline & Film (GAP), and American Cyanamid decided to withdraw from this sector. Allied sold out its indigo business to the newly formed Buffalo Color Corporation, of Buffalo, New York. GAF sold its dye-making business to BASF (1978), and Harshaw Chemical Co. (which had manufactured dyes since taking over Zinsser & Co.) became part of the new leader, Crompton & Knowles (1979). Crompton & Knowles also purchased Belle Chemical Co., of Lowell, North Carolina, Otto B. May, of Newark, New Jersey, and Atlantic Industries, of Nutley, New Jersey. The United States lost some 40 per cent of its manufacturing capacity, and Du Pont, after some remarkable technical successes that were not matched by sales successes, pulled out of dye-making in 1980 (the dye-making division was sold to Crompton & Knowles). [68] CIBA-GEIGY acquired American Color & Chemical, and the Sandoz share of a jointly-owned factory at Toms River, New Jersey. [69] Toms River had opened in 1950 to manufacture CIBA's vat dyes. Later azo dye manufacture was commenced by the partnership. By 1988 exactly half the twenty-two producers active in 1976 had disappeared. Imports had risen more than threefold, and accounted for over one-quarter of colorants consumed (compared with eight percent in 1976).

Today, Crompton & Knowles Corporation's Dyes and Chemicals Division is the largest United States-owned dye-maker, with plants and offices in Reading and Gibraltar, Pennsylvania, and offices and laboratories in Charlotte, North Carolina, and elsewhere. [70] The Crompton & Knowles Atlantic Industries Division operates from Nutley, New Jersey, and Greenville, South Carolina. In 1990 a new plant was installed at Greenville that boosted production of liquid dyes by 300 per cent, and in 1992, C&K purchased ICI's Oissel plant in France.

The demise of the major United States dye manufacturers has been accompanied by an increase in new plant investment by Swiss and German corporations, especially Sandoz and CIBA-GEIGY. Sandoz introduced novel colors whose methods of manufacture overcome pollution problems. Considerable activity had developed in the processing of imported presscake, and a number of firms such as Carey Industries, Inc., Sunbelt, Organic Chemical and others have achieved considerable growth in this area.

Links with eastern Europe are found in the United States, where Fabricolor has close connections with Synthesia and Spolek of Czechoslovakia. Spolek, founded in 1856, had been absorbed by IG Farben in the early 1930s. At this writing Spolek employs some 800 people and produces 4,000 metric tons annually. Synthesia, in Pardubice, employs 1,800 people, with an annual production of 12,000 metric tons. The dyestuff division of Synthesia was formed in 1939, the company having previously been involved primarily in the manufacture of explosives. Both companies market their dyes through Ostacolor, in Pardubice.

## **New—and Old—Products**

*Widespread availability of fiber reactive dyes. The introduction of bifunctional groups. Disperse dyes. New demand for Indigo.*

March 1956 was the centenary of the discovery of Perkin's mauve, and the event was celebrated, like the fiftieth anniversary, by international gatherings in London and New York. Appropriately, the ICI Dyestuffs Division marked the event with the announcement of the first successful fiber reactive dye, reacting chemically with the fiber to form covalent bonds. These exceptionally fast dyes became the first members of the Procion range, ideal for cotton dyeing (Procion Yellow R, Procion Brilliant Red 2B, and Procion Blue 3G). In 1957, they were supplemented by CIBA's Cibacron, and imitated by Hoechst's Remazol, which used a different reactive principle. The CIBA colors were actually the result of technical agreements with ICI over use of cyanuric chloride as intermediate and CIBA's pioneering work with monochlorotriazine groups.

In 1959, Bayer introduced its Permafrix range of reactive dyes that were extended, and renamed Levafix, in 1961. During 1959, ICI introduced Procynyl chlorine-containing reactive disperse dyes suitable for nylon, followed in 1961 by Procynyl dyes with metal complex structures possessing a fiber-reactive group that attaches to cotton.

ACNA of Italy introduced its Reacna range of reactive dyes in 1965, and two years later ICI brought out the Procion Supra dyes for cotton and viscose rayon. All these colorants contain reactive groups of the same chemical structure, and are called homobifunctional reactive dyes.

In 1959 and 1961, respectively, ICI and Hoechst filed patents for reactive dyes containing two different functional groups (heterobifunctional dyes), but the first dye of this type was not manufactured until 1975 when Hoechst made available Remazol Brilliant Red SBB, which contained three reactive groups. The first series of multifunctional dyes, the Sumifix Supra range, was introduced by Sumitomo of Japan in 1979, and thirteen of these colorants are now available. They all contain a monochlorotriazine and a vinylsulfone group. Hoechst, Nippon Kayaku, Bayer and CIBA-GEIGY brought out similar colorants in the 1980s, and the number of patent applications for this group has now reached well over one hundred. [71] Reactive dyes are a principal product of the German-Japanese partnership of Hoechst with Mitsubishi Kasei Co. Ltd.

Today, the fiber reactive dyes are available in a wide range of shades, are extremely brilliant, are wetfast, and can be applied economically. They were originally applied to wool, but the dyeing performance does not match that on cellulose. In Japan, for example, fiber reactive dyes account for over half of the colorants used for cellulosic fibers.

Disperse dyes continue to offer novel approaches to dyeing, and are another ICI success story. They are used to dye polyester fibers, which do not contain the functional groups that enable chemical bonding, nor permit coloration in aqueous solutions. They are applied as fine dispersions, and can be used with other synthetic fibers, including nylon. These and other new dyes permitted the introduction of a wide range of synthetic materials as fashion fabrics.

During the late 1970s, ICI developed a continuous dyeing system for polyester-cellulose blended fabrics, and this was introduced in 1980 for use with disperse-reactive dyes (Dispersol-Procion T). The current range of Dispersol C dyes are recommended for the rapid processing of polyester and polyester-cellulose fabrics; Dispersol D dyes where high levels of heat fastness are required; and Procion MX dyes for maximum versatility. Caledon SF liquid dyes, used in conjunction with a multi-functional auxiliary and a resin, are suitable for one pass continuous dyeing and finishing of cellulose and polyester-cellulose fabrics.

Fiber-reactive and other special dyes for synthetic materials appeared in the Soviet Union from the 1960s. Disperse dyes production reached 3,000 tons in 1987. Taiwan's Everlight Chemical Industrial Corporation has added fiber reactive dyes to its disperse, direct, acid and leather colorants, and in Korea, Kyung-In Synthetic produces reactives as well as disperse dyes. Crompton & Knowles Dyes and Chemicals Division's reactive colors appear under the Intracron trade mark; the vinyl sulfones in this class have recently been extended.

ICI's strategy in the '70s and '80s followed growth forecasts that suggested reactive, disperse, Nylomine, and phthalocyanine greens showed best potential, so many traditional lines were phased out. By purchasing Kuhlmann in 1982, ICI overcame having too narrow a product range and enabled a complete range along with ongoing research for completely novel colorants.

Benzodifuranone colorants for dyeing and printing ladies' clothing on polyester and poly-cotton blends were developed in the early '80s and sold to users in the form of a red colorant to overcome bleeding problems. For these benzodifuranones (Red CBN, Scarlet SF, Red BNPC) ICI received the Queen's award for Technological Achievement in June, 1990.

In the '60s the faded look took hold. Ever since, increased manufacture of indigo in the U.S. (Buffalo Color Corp.), in Britain (ICI Specialties), Germany (BASF), Japan (Mitsui Toatsu Chemicals) and elsewhere as well, including India and Mexico (Pyosa). In 1988 world demand reached 14,000 tons.

In 1988, at the Ellesmere Port indigo factory Hugo Levinstein acquired during World War I, ICI spent £3m introducing a spray drying technique to achieve a cleaner form of the dye previously sold as a paste or powder. The product, "pearls of dye", sold under the Microperle label, inherited from Kuhlmann, includes other vat dyes based mainly on anthraquinone.

The methods of indigo manufacture today are similar to those introduced at the beginning of the twentieth century, but the raw material, as in the case of all dyes based on aromatic hydrocarbons, is now oil, rather than coal.

## Diversification

The availability of commercial dyestuffs has led to considerable diversification. From the 1890s, dyes were used to investigate chemotherapy, and in the 1930s a bright red azo dye became the first of the sulfonamide drugs. Many dye firms soon turned to pharmaceuticals. Today the electronics and communications industries have become consumers of dyes that absorb light at the semiconductor wavelengths, including metal phthalocyanines. These have received the name functional dyes. New molecules are being designed for both the fashion world and the high technology industries; with the introduction of novelties like heat-sensitive liquid crystal dyes for textiles, the traffic is two way.

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