

## Sir William Henry Perkin: The Man and his 'Mauve'

*G Nagendrappa*

Today we cannot imagine our lives without a variety of colours. Every colour we see, consume, enjoy, apply and use wherever we need has a dye associated with it. More than 90% of the thousands of dyes used now are synthetic. A little more than 150 years ago a handful of dyes of only natural origin were available. In 1856 the era of synthetic dyes was ushered in by a spirited young chemist, William Henry Perkin, when he was trying to synthesize quinine, but obtained a coloured substance instead. It was a much desired colour and therefore became an instant hit. The following is an account of Perkin's life as a chemist and an industrialist par excellence.

Eighteen hundred and fifty six was the year when one of the most celebrated accidental discoveries in chemistry was made. It impacted not just chemistry or science in general, but many other areas of human activity. It provided stimulus to the economy, and became an instrument of social, cultural and political change. Textiles and printing became more colourful and cheaper; artists had more choices of shades to paint with; staining of biological specimens revolutionized biology and medicine. The discovery kindled a rapid growth in research activity that went directly into industrial manufacturing.

It was not only the momentous happening, but the vigorous pursuit to exploit it by an enthusiastic teenage youth that led to the developments that followed. The young man was William Henry Perkin, who is credited with the preparation of the first synthetic dye called mauve or mauveine or aniline purple. It became the basis on which a new chemical industry was built, which became a model for others to follow.

### Early Life

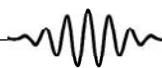
William Henry Perkin was born in London on 2nd March 1838,



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### Keywords

Perkin, mauve, mauveine, quinine, dye.



The changes in forms and colours, appearance and disappearance of the crystals in solution had a magical effect on the young Perkin's mind.

three months before Queen Victoria was crowned (28th June 1838). He was the seventh child and second son of George Fowler Perkin (1802–1862) and Sarah Perkin. George Perkin was a builder and carpenter. The Perkin's family was one of the wealthiest in Shadwell, the locality where they were living in London. William's first schooling was at Private Arbour Terrace School situated a few hundred yards from his home. He was an intelligent student endowed with musical talent, and skills in drawing, painting and photography. His first photograph was a self-portrait taken when he was 14 years. He was proficient in playing several musical instruments, and music was a part of his regular activity throughout his life.

Senior Perkin used to get copies of building plans made by William with the intention, in addition to using his drawing skill, to influence William to take up architecture as career. But destiny's design was different. Just before he turned thirteen, William observed a friend performing some chemistry experiments with crystals and crystallization. The changes in forms and colours, appearance and disappearance of the crystals in solution had a magical effect on the young mind. He thought that the magnificence of chemistry was far greater than any other subject he knew. So he wanted to study chemistry. However, chemistry was not a popular subject in those days and it was taught in very few schools. But destiny was in Perkin's favour, for he at 13 was sent to the City of London School by Cheapside near St. Paul's Cathedral, as it was closer to his house; the school had chemistry as a subject of study, and Thomas Hall taught it. Hall, who had learnt chemistry from A W Hofmann, was an inspiring teacher and encouraged Perkin to do safe experiments at home and to attend Letheby's (a well-known analytical chemist) chemistry lectures at the London Hospital. This deepened Perkin's interest in chemistry further. At 14, he obtained permission from Faraday to attend his lectures at the Royal Institution, during his spare time. The exposure to the great master of experimental science was a thrilling experience to the young boy. By now Perkin's interest in chemistry was unshakable. But in his father's view the



subject had no good future and he wanted William to become an architect. Hall who was aware of William's passionate love for chemistry stepped in and convinced the reluctant father to allow William to pursue a career in chemistry. William, at 15, joined the Royal College of Chemistry, London, where AW Hofmann, one of the great organic chemists of the time, was Professor of Chemistry.

Perkin took some analytical courses and worked on the reactions of anthracene. He oxidized anthracene to anthraquinone by nitric acid and carried out chlorination and bromination of anthracene. Impressed by his work, Hofmann made him an honorary assistant. Further, Perkin conducted experiments on the reaction of anthracene with cyanogen chloride. The work was published in the *Journal of Chemical Society* in 1856, which helped him get a promotion as staff assistant.

### Quinine Inspires, Mauveine Arrives

Starting from Wöhler's accidental synthesis of urea in 1828, synthesizing organic compounds had gained much favour with chemists of the day. Quinine, the only important medicine for malaria, was high in the mind of Hofmann as a synthetic target, because the medicine obtained from the bark of cinchona tree, grown mainly in South America, was in short supply. Hofmann had suggested that it would be nice if someone could synthesize quinine. The challenge was taken by Perkin in 1856, and he started the work on quinine in the laboratory he set up at home.

The most basic requirement for synthesizing a compound is the knowledge of its molecular structure, i.e., how its atoms are connected. In 1856, knowledge of chemical structures was just then emerging, though fairly correct molecular formulae could be determined. The structures of only small molecules could be written. The ring structures were still unknown. Perkin was therefore completely ignorant of the quinine structure (*Box 1*). It was indeed presumptuous on the part of Perkin to have undertaken quinine synthesis, which must be attributed to his irrepressible enthusiasm and confidence. It seems that he had no doubt

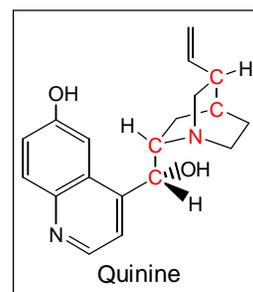
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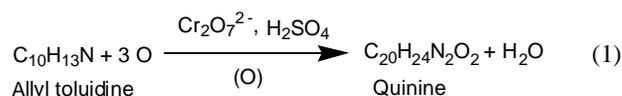
**Box 1.**

Quinine was identified as the active constituent of cinchona in 1820 by Pelletier and Coventou. Pasteur determined its optical activity as *leavo*-rotatory and carried out some reactions in 1852. The molecular formula was found to be  $C_{20}H_{24}N_2O_2$  by Liebig in 1831 and later in 1854 by Strecker. The correct molecular structure was established in 1907 by Rabe. A partial synthesis of quinine was announced by Rabe and Kindler in 1918. The correct stereochemistry was settled by the early 1940s. In 1944, Woodward and Doering published a formal synthesis of quinine with the required stereochemistry, which is considered to be a milestone in organic synthesis, but also a subject of criticism and controversy. A fully stereocontrolled total synthesis was achieved only in 2001 by Stork and his coworkers. Between 1944 and 2001 and thereafter also, several other notable papers on quinine synthesis have appeared.

Quinine has four stereogenic centres (marked with red C, Bridgehead red N is also chiral, but its chirality merges with bridgehead red C). As a result, there are sixteen stereoisomers, of which the natural quinine is just one. So, one can imagine the formidable problem ahead of a synthetic chemist who ventures into quinine synthesis.



about the outcome. His reasoning was simple. The empirical formula of quinine was known to be  $C_{20}H_{24}N_2O_2$ . Therefore it is quite logical to assume that one can combine two molecules of a compound with molecular formula  $C_{10}H_{13}N$  to get  $C_{20}H_{26}N_2$ , at the same time adding two oxygen atoms and removing two hydrogen atoms. And it would be perfectly understandable if one thought, in 1856, of oxidizing a compound with formula  $C_{10}H_{13}N$  to get a compound of formula  $C_{20}H_{24}N_2O_2$ :

**Marvellous Mauve from Muck**

Perkin chose allyltoluidine, which has the formula  $C_{10}H_{13}N$ , as the reactant and heated it with potassium dichromate and sulphuric acid as oxidizing agent. Of course, only a miracle would have produced quinine from such a concoction, and indeed what Perkin got was a reddish brown precipitate. However, he did not give up, but decided to investigate the reaction with aniline, a



simpler compound. He treated aniline sulphate with potassium dichromate. Now he obtained a black precipitate. When he added methanol, probably to wash it, he noticed that methanol became purple coloured. As the colour was attractive, young Perkin thought of using it as a dye. He dyed a silk fabric with the colour and sent it to a well-known dye house Pullar & Son who approved it with admiration for its much desired attractive purple colour and its fastness on the fabric. The dye was called Aniline Purple, Mauve or Mauveine. He applied for a patent<sup>1</sup> for it on 26th August 1856, with the intention of manufacturing it. The patent was granted on 20th February 1857. At 18, William Perkin was on his way to become one of the most celebrated figures of chemistry and chemical industry. Hofmann was unhappy that Perkin was leaving the Royal College of Chemistry to take up manufacturing, as it was considered not a desirable activity for people of refined social rank.

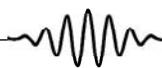
For Perkin, the situation to start an industry to manufacture Aniline Purple was not quite favourable. He had no industrial experience or business skill. He had to mobilize funds, get assured supply of raw materials, find buyers of the finished products, acquire land and take care of other related matters. He could overcome every hurdle with his abundant enthusiasm, patience and resoluteness.

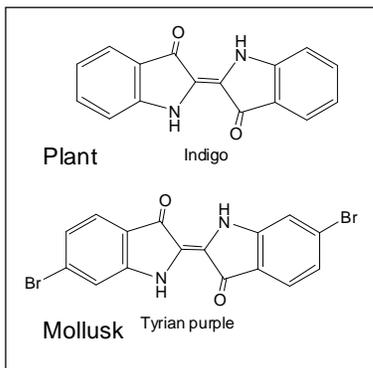
Perkin's father, who had changed his stance by now, put all the required money, and his brother Thomas Dix Perkin provided building and business support. The modern dye industry was born with the establishment of Perkin & Sons at Greenford Green, England, to manufacture mauve in 1856.

The dye was called mauveine in France. It became very popular there, as Empress Eugenie, wife of Napoleon III, took pleasure in wearing dresses made of fabrics dyed in mauveine, which the fashionable ladies emulated. Queen Victoria of England did not fall behind – she wore mauve dyed dress to her daughter's wedding in 1858. The popularity of mauve colour and the market with it for the dye soared making the business of Perkin & Sons

<sup>1</sup> In the Classics Section (p.856), the details of the patent application including the procedure for the preparation of the dye, submitted by Perkin, are reproduced in full. Some comments on the patent are to be found in the Reflections article by A Filarowski (p.850).

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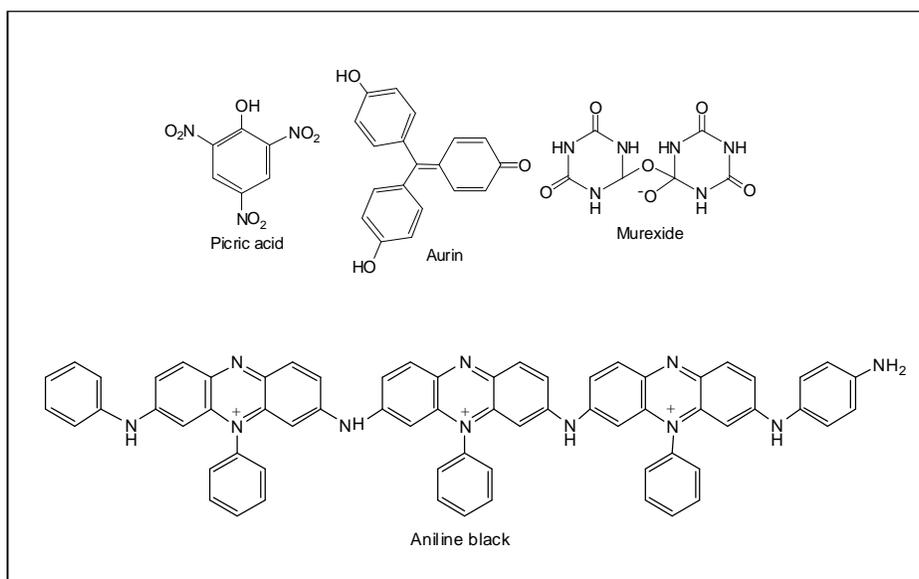


grow fast. The era of synthetic dyes was ushered in, and soon most of the natural dyes were dislodged.

### The Scene Before

The dyes which were in use prior to the introduction of the synthetic ones were those that were extracted from natural sources, like insects, plants (madder, indigo), animals (lichens, mollusks, snails), bat guano, minerals, etc. Using these dyes posed problems of variable supply and quality, inconsistent dyeing, and their fast fading property. As the synthetic dyes became largely successful in overcoming these disadvantages, the use of natural dyes soon receded; within 20–25 years, 90% of dyes in use were synthetic.

Though a few synthetic dyes were used before, yet mauve is credited to be the first synthetic dye. The previously used dyes, picric acid, aurin, murexide and aniline black, and some blue, violet and red dyes prepared by Friedrich Runge (1795–1867) had no good dyeing properties. On the other hand the appearance of mauve in the arena of dyes introduced the new regime of synthetic dyes, justifying its position as the first synthetic dye.



### The Luck Hid in the Impurities

When Perkin started the work on the oxidation of aniline, it was not his adroitness alone that led to mauve, but also a providential coincidence. The aniline sample that he was using was not pure; it contained toluidines in considerable quantities. Had there been no toluidine, there would still be some kind of a dye, but the result would not have been so spectacular. The purple shade of mauve was the most desired colour by the high society. The need for a purple dye was earlier met by the expensive Tyrian Purple extracted from mollusks. Discovery of mauve, which Perkin had initially called Tyrian Purple, changed the scenario as it was available to common people at affordable prices.

Perkin inferred the presence of toluidine in mauve from its elemental analysis. Later he found that toluidines and other aniline derivatives (e.g., xyloidines) also formed similar dyes. He made a dye from pure aniline and called it pseudo-mauveine, though its colour was not much attractive. Of all these new dyes the best was still the mauve. So Perkin's luck lay in impure aniline mixed with toluidines.

Mauve itself is not a pure compound. It is a mixture of two major components A and B, and small amounts of other purple dyes. The components A and B were isolated and their structural identity determined only in 1994<sup>2</sup>. They are phenazene derivatives. The component A contains two aniline, one *o*-toluidine and one *p*-toluidine molecules, while the component B contains one aniline, two *o*-toluidine and one *p*-toluidine molecules.

Within a short time Perkin & Sons experienced good success. However, Perkin did not become complacent. He worked with greater vigour on the preparation of newer dyes and developing better dyeing techniques. He prepared more dyes by modifying the mauveine structure. For example, he ethylated it and produced a dye of redder shade and called it Dahlia; by oxidizing it with lead oxide, he obtained Aniline Pink or Parasafranine. He prepared aminoazonaphthalene of scarlet colour by oxidizing

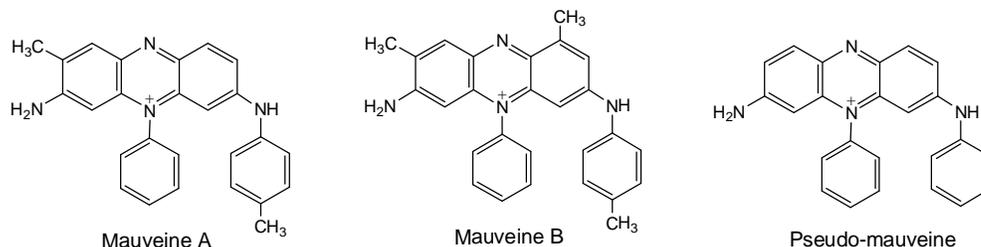
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<sup>2</sup> O Meth-Cohn and M Smith, *J. Chem. Soc., Perkin Trans.*, Vol.1, pp.5-7, 1994.



**Box 2.**

By 1896 Perkin had concluded that the mauveine dye was a mixture containing a compound derived from aniline alone, which he called pseudo-mauveine, and compounds derived from aniline and toluidine(s) was the actual mauveine. The mauveine itself is a mixture and was shown to contain two major compounds Mauveine A and Mauveine B by Meth-Cohn and Smith in 1996.



diaminonaphthalene with mercuric nitrate, in addition to Magenta, also called Aniline Red or Rosaniline or Fuchsine or Perkin's Green, and several other dyes.

The most important dyes made by Perkin & Sons were Mauve, Britannia Violet (methylated Rosaniline), and Perkin's Green (acetylation product of blue Britannia Violet).

### A Model of Emerging Chemical Industry

The Perkin brothers together designed novel equipment and machinery for purification of raw materials, synthesis of dyes and starting compounds, dyeing textiles, fabric printing, etc. As Perkin & Sons was a unique company at that time, all the required materials were not available on order; they had to devise them on their own. Perkin & Sons became a well-established chemical industry and a leader not only in making dyes and their application, but also in chemical engineering.

### A Rival Appears

A significant advancement in the dyes industry happened when BASF was founded in Germany in 1865. (It is the biggest producer of dyes in the world today). Graebe in association with Caro

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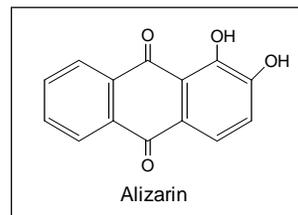


started work in BASF on alizarin, a popular red dye obtained from the roots of madder plants, and used for thousands of years. He found the dye to be a quinone. In 1868 Graebe and Libermann converted alizarin into anthracene, a chemical isolated by Dumas in 1833 from coal tar. Based on these results they synthesized alizarin in 1869. It turned out to be the first natural product synthesis.

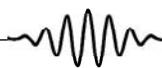
With his rich experience in anthracene chemistry he had acquired while working with Hofmann, Perkin was also able to independently formulate a similar synthesis for alizarin at the same time. He applied for a patent, but one day after Graebe, Libermann and Caro did. The patent was granted to the BASF group. Perkin was disappointed, but got the rights to sell alizarin in Britain, while the BASF to the rest of the world. He started manufacturing the dye in 1870, a year before the BASF could in 1871.

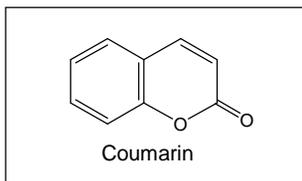
### The Curtain on the Company

The more resourceful BASF rapidly increased its capacity and from 1872 steadily exceeded that of Perkin & Sons. In addition, BASF sold the dye at a cheaper rate. This reduced the profits of Perkin's company who found it difficult to sell the dye at their price. Alizarin, in the early years of its production, had become a significant part of Perkin & Sons' business. Therefore, the declining profits meant that they had to increase the production capacity as well as cut the production cost in order for the company to make enough profit and sustain growth. Faced with the challenge, the brothers (their father had died in 1865) thought that the situation was critical enough to decide either to expand by further investment or sell the company when the going was still good. They chose the second option and sold it in 1874. One of the other compelling reasons for this decision seems to be Perkin's irresistible urge to do more research, for which he had little time while working full time for the company. It should be noted that he had continued to do research even while running the industry and published thirty papers during 1857–1874.



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<sup>3</sup> G Nagendrappa, 'Chemistry triggered the first civil disobedience movement in India; Indigo in Indian independence – Role of a broken thermometer', *Resonance*, Vol.8, No.3, pp.42–48, 2003.

### Box 3. Faraday Rotation

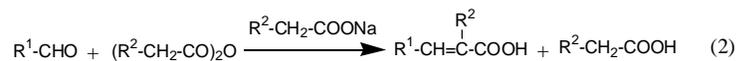
The plane of polarization of an electromagnetic wave is rotated under the influence of a magnetic field parallel to the direction of propagation. Amount of rotation =  $R_m \lambda^2$ , where  $\lambda$  = wavelength and  $R_m$  = rotation measure. The effect occurs in most optically transparent dielectric materials including liquids when they are subject to strong magnetic fields. It has many applications in astronomy to study pulsars.

### The Scene After

The sales proceeds from the company were substantial. Perkin retired wealthy and famous from an industry, the first of its kind in the world, which he had founded and nurtured. He was just thirty five years of age at that time, but had the vast experience from being a “scientific advisor, research director, works chemist, chief engineer and colourist,” (Ian Holme). He had built an industry which was a model for others to emulate.

Perkin was still very young and full of energy. The considerable wealth and worldwide fame did not make him inactive, nor did he spend his time in enjoyment and luxury. He now devoted all his time to research, his first love. Even during his industrial period, he had accomplished the synthesis of several compounds, e.g., glycine, coumarin (the first natural perfume to be synthesized), glycolic acid, tartaric acid (showed relationship among tartaric, maleic and fumaric acids), and a number of dyes.

Perkin's post-industrial work continued to be in the area of synthesis and characterization of organic compounds including dyes. His earlier work on coumarin eventually led to the general method of synthesis of unsaturated acids, such as cinnamic acid from aldehydes and acetic anhydride (or other fatty acid anhydrides) in the presence of sodium acetate (or salt of the acid). This is now the well-known Perkin reaction:



Baeyer used Perkin reaction in 1899 to synthesize indigo<sup>3</sup>. From 1881 Perkin focused attention on finding the relation between the constitution of organic compounds (of homologous series) and their Faraday rotation (*Box 3*) or magnetic rotating power and published 58 papers on this subject. In 1889, he was awarded the Davy Medal of Royal Society for this.

Perkin published more than 180 papers on synthetic and analytical work, most of them in the *Journal of Chemical Society*. The first paper was published in 1856 and the last was in 1907, the

year of his death. His speeches, addresses at ceremonies and presentations formed some 15 publications.

Perkin's industrial model and practices influenced in shaping the emerging contemporary chemical industry. Coal tar, an environment-polluting waste product of coal gas and coke industry, became a good source of raw materials for making dyes, drugs, pharmaceutical products, solvents, perfumes, flavours, cosmetics, disinfectants, agricultural chemicals, surfactants, detergents, explosives, motor spirit, tar for road laying and many other chemicals. Though modern chemical industries have largely replaced coal tar by petroleum for raw materials, we should not forget its crucial role in founding the industry.

### Personal Life

One would think that, because he was so immersed in his industrial activity and scientific research, Perkin had no time for any social activities or personal life. But one would be surprised to know that he led a normal family life and pursued several hobbies.

In 1859 Perkin married Jemima Harriet Lisset, his first cousin. She gave birth to two sons. The elder one, born in 1860, was given the same name as his father's, William Henry Perkin Junior and the younger one (born in 1861) was called Arthur George Perkin. Jemima died of tuberculosis in 1861. Perkin had a second marriage (1866) with Alexandria Caroline Mollwo, who bore him one son, Frederick Mollwo Perkin and four daughters, Sascha, Lucy, Annie and Helen Mary. All three sons, following the footsteps of their father, studied chemistry. Perkin Jr. occupied the chair of Organic Chemistry at Manchester University and then at Oxford University. A G Perkin became Professor and Head of the Department of Colour Chemistry and Dyeing at the University of Leeds. Frederick Perkin worked in his father's laboratory, became Head of the Chemistry Department of the Borough Polytechnic Institute and later a chemical consultant. He developed low-temperature carbonization process, worked in the

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area of fuel oils, smokeless fuels and electrochemistry. The four daughters helped Perkin in his social work and expanded the aviary with exotic birds, a hobby started by their father.

The entire Perkin family was oriented towards music. William was a proficient player of piano, violin and double bass. His brother Thomas was an accomplished violinist whose hobby was collecting stringed instruments. The family used to get-together on Saturdays in Thomas Perkin's house and together with the sisters, they made music. Perhaps, if Perkin had not succeeded in chemistry, the Perkins would have become professional musicians. William relaxed by cycling and gardening. He liked travelling.

Perkin was not only a great scientist, but also a wonderful human being. He has been variously praised by virtually everyone with whom he interacted. Prof. Meldola, one of Perkin's friends and President of the Society of Dyers and Colourists, in 1908, said, "...The example which he has set us as a man will for all time serve to point the moral that all these qualities which make for success in industrial pursuit...may be conjoined with the highest and best attributes of humanity...His life was noble in simplicity, single-minded devotion to his work...a character known to be religious in the highest and best sense of the term...an enduring example of humanity in the face of success which would have marred many men of smaller moral caliber."

Perkin was not only a great scientist, but also a wonderful human being.

His obituary mentions, "...His neighbours at Sudbury loved him for his quiet philanthropy...his generous courtesy and kindness of heart..." He was deeply religious, a strict vegetarian and teetotaler. In fact this ethos of Perkin motivated him to stop the manufacture of Magenta, which needed mercuric nitrate for synthesis. Perkin knew the harmful effect of mercury and he did not want his workers to be harmed. This concern for the well-being of the workmen shows the highest humanitarian morals of the Perkin brothers. Perkin was a humble and unassuming person. He used to avoid his own part while lecturing on the development of dyes industry.



### Activities in Professional Societies

Perkin did not confine himself only to family and hobbies, research and industrial activities. He actively participated in the activities of professional societies. William Henry Perkin's grandfather Thomas Perkin had connection with Leathersellers' Company, which influenced him to join that organization in 1861, and he served it as office bearer from 1881 to 1897 at various levels from Steward to Master. He represented the company on the governing body of the city and Guild of London Institute.

Perkin served as a secretary of the Chemical Society (1869–1883) and as their President (1883–1885). He was also the President of the Society of Chemical Industry during the same period (1884–1885). Later in 1907 he became President of the Society of Dyers and Colourists (SDC) and President-elect of the Faraday Society. He served on the Council of Royal Society (1879–81 and 1892–94) and as Vice President of the Society (1893–94).

### Honours and Awards

Perkin's scientific research and its application was so useful to chemical knowledge and society of the day that many awards and honours were conferred on him. He received a silver and later a gold medal in the same year 1859, when he was just 21 years, from La Societe Industrielle de Mulhouse, in recognition of mauve's importance.

He was elected Fellow of the Royal Society (London) in 1866 when he was 28 years old.

He was awarded the Royal Medal (1879), the Davy Medal (1889), the Chemical Society's Longstaff Medal (1888), the Albert Medal (1890) of the Society of Arts, the Birmingham Medal (1898) of the Institution of Gas Engineers, a gold medal of the Society of Chemical Industry. He accepted with some reluctance a knighthood and became Sir William in 1906.



Great historical importance attaches to this, the first coal-tar dye, and universal interest has been aroused in it not only amongst dyers and colourists, but amongst the public generally. At the same time there appears to be much confusion as to the exact hue of the original mauve. It therefore seemed of interest to insert a dyed pattern in the Journal illustrating this dye, and Dr Perkin has very kindly supplied a small quantity of mauve manufactured in 1863 or 1864 for that purpose. The pattern has been dyed in the Bradford Technical College dye-house.

Reproduced with permission from Society of Dyers and Colourists, UK.



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The Coal Tar Colour Jubilee and the 50th anniversary of the discovery of mauve was celebrated on 27th July 1906 at the Royal Institute in London. At the meeting Perkin was presented with the Lavoisier Medal of La Societe de Chimique de Paris by Prof. Haller and the Hofmann Medal of the Deutsche Chemische Gesellschaft by their President Prof. Emil Fischer (Nobel Laureate). At the meeting, lectures by eminent scientists were presented praising the work of Perkin.

Perkin visited USA during the 50th anniversary year. He was elected an Honorary Fellow of the American Chemical Society. At the same time the ACS instituted Perkin Medal to be awarded every year to an American in Applied Chemistry and he was presented with the first impression of the Medal. The SDC paid him their highest honour by electing him an honorary member before they elected him their President in 1907. The *Journal of Chemical Society* had titled its two organic chemistry parts as Perkin Transaction 1 and Perkin Transaction 2 from 1972 to 2002.

### The Inevitable

Continuous travelling in 1906 to participate in the 50th anniversary celebrations took its toll on the health of Perkin. He had an attack of double pneumonia and appendicitis and he passed away on 14 July 1907.

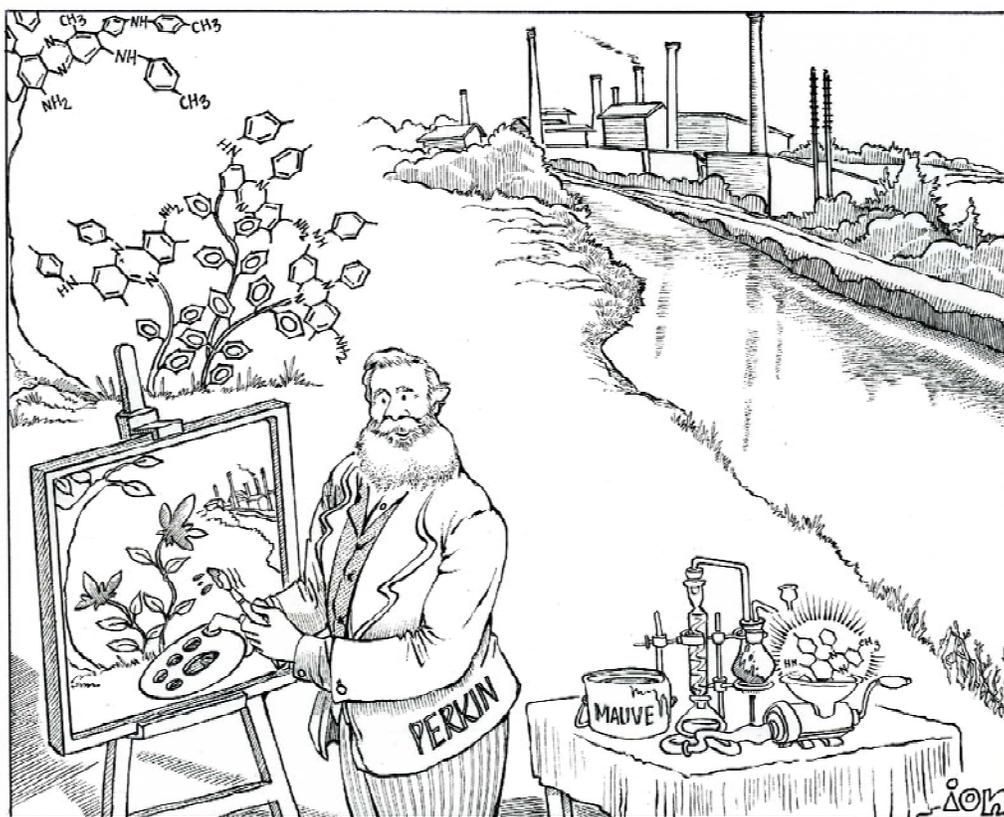


## Suggested Reading

Substantial amount of material is available on the internet. Interested person may use the keywords and get the information. For biographical particulars see,

- [1] I Holme, Sir William Henry Perkin: a review of his life, work and legacy, *Color. Tehmol.*, Vol.122, pp.235-251, 2006.
- [2] For a historical perspective on quinine synthesis see, J I Seeman, The Woodward–Doering/Rabe–Kindler total synthesis of quinine: setting the record straight, *Angew. Chem. Int. Ed.*, Vol.46, pp.1378-1413, 2007.
- [3] For the analytical composition of mauve see, M M Sousa, M J Melo, A J Parola, P J T Morris, H S Rzepa and J S S de Melo, A study in mauve: Unveiling Perkin's dye in historic samples, *Chem. Eur. J.*, Vol.14, pp.8507-8513, 2008.

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I painted this picture with colours you would dye for...