
Perkin's Mauve: The History of the Chemistry

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Those of us who owe our living in part to the global dyestuff and chemical industry should pause today and remember the beginnings of this giant industry which started 150 years ago today with William Perkins' discovery of mauveine whilst working in his home laboratory during the Easter holiday on April 28, 1856. Prior to this discovery, all textiles were dyed with natural dyestuffs and pigments.

What did Perkin's Reaction Entail?

William Henry Perkin carried out his experiments at his home laboratory in the Easter break of 1856. He was trying to produce quinine ($C_{20}H_{24}N_2O_2$). This formula was known but not the structural formula.

Because chemistry was in such an early stage of development Perkin thought that by simply balancing the masses (simple additive and subtractive chemistry) in an equation he would obtain the required compound. He therefore believed that if he took two allyltoluidine molecules, $C_{10}H_{13}N$, and oxidised them with three oxygen atoms (using potassium dichromate) he would get quinine ($C_{20}H_{24}N_2O_2$) and water.



It is unsurprising to us now but Perkin reported "that no quinine was formed, but only a dirty reddish brown precipitate."

However, he continued in his trials and decided to use aniline ($C_6H_5NH_2$) and its sulphate, and to oxidise them using potassium dichromate. This produced a black precipitate that Perkin at first took to be a failed experiment, but he noticed on cleaning his equipment with alcohol that a coloured solution was obtained.

Perkin's Patent

W H Perkin filed his patent on the 26th August 1856 for "Producing a new colouring matter for the dyeing with a lilac or purple color stuffs of silk, cotton, wool, or other materials." (sic) Patent No. 1984, AD 1856. The nature of the invention for this purpose is stated in the patent (see Classics section, p.854).

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It is obvious that this is a long drawn out process of manufacture and it has to be taken into account that little large scale chemical production was taking place, so the decision to make this product was indeed a monumental one. Perkin would have to undertake the manufacture of aniline on a large scale as well, as no such facility existed.

Perkin's Laboratory

Perkin, between filing his patent on the 26th August 1856 and its sealing on the 20th February 1857, spent much time (as mentioned in his contribution to the Hofmann memorial lecture) in his laboratory at home with the help of his brother (T D Perkin) to get to this detailed method of production and this is highlighted further in the patent in the full specification. This lists a number of starting materials that Perkin must have experimented with.

“I take a cold solution of sulphate of aniline, or a cold solution of sulphate of toluidine, or a cold solution of sulphate of xylydene, or a cold solution of sulphate of cumidene, or a mixture of any one of such solution with any others or other of them, and as much of a cold solution of a soluble bichromate as contains base enough to convert the sulphuric acid in any of the above mentioned solutions into a neutral sulphate.”

Perkin also mentions the method of dyeing the material with extra information on how to dye wool.

In his Hofmann memorial lecture [1] Perkin highlights the problems he had.

1. Neither he nor his friends or family had seen the inside of a chemical works and the knowledge they had was obtained from books.
2. Benzene was only produced in small quantities and was of such a poor quality that Perkin found he had to purify it before use.
3. No nitric acid strong enough to prepare nitrobenzene was available and rather than complicate their works they experimented and decided on the following route. They took the benzene and using mixtures of sodium nitrate and sulphuric acid to produce an acid sodium sulphate they could, having manufactured specialist equipment, produce large quantities of nitrobenzene. This was the first manufacture of nitrobenzene in these quantities in iron vessels.
4. Had Béchamp not discovered three years previously that finely divided iron filings and acetic acid could be used to convert nitrobenzene into aniline, Perkin states that the coal tar industry could not have been started.



So the discovery of a colouring matter in the Easter of 1856 and the work and experimentation that went into the manufacture of the first commercial batch of what was then called Aniline Purple or Tyrian Purple in December 1857 shows us a man with a knowledge of chemistry as it was held at the time; a man who overcame problems of supply of raw materials, equipment and scale-up from laboratory to bulk in a very short space of time.

Mauveine

The name mauveine derives from the French manufacturers' name for this colour, produced in France because Perkin's Patent was invalid in France as he filed it too late.

Perkin supplied the acetate of the base into the market because it was remarkable for its stability and tinctorial strength. But did he understand anything about the chemical structure, formula or the actual reaction he had carried out? There is a section in Report, International Exhibition, 1862, Class II, sec. A, 130 on the production of the second aniline dye, rosaniline, that states that Hofmann had showed that the production of this dye was dependent on the impurity contained in aniline at the time, toluidine, and that to produce the dye in quantity a mixture of the two, aniline and toluidine, was necessary. There was not yet an understanding of the different positions the methyl group could take.

However, at the time of the Hofmann memorial lecture [1] Perkin states that in 1862, referring to the above paper, he said, "In the case of Mauveine, this discovery was not of so great importance as in the case of rosaniline, because pure aniline yields a purple colouring matter (pseudomauveine), as well as mixtures of aniline and toluidine". Perkin also said he was investigating mauveine in his own laboratory at this time and discussed this with Hofmann who left him to his investigations.

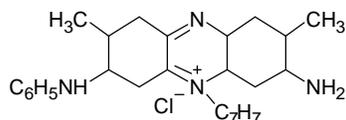
These investigations led to the formula being reported as $C_{27}H_{24}N_4$ [2].

Further investigations [3] showed that the commercial product contained two colouring matters, one forming a very soluble and apparently uncrystallisable salt called pseudomauveine ($C_{24}H_{20}N_4$) produced from pure aniline, and as it was uncrystallisable could not be commercial as a solid dyestuff, and another, less soluble, crystalline salt ($C_{27}H_{24}N_4$) derived from para-toluidine and aniline. In this paper he also wrote "by using aniline containing much larger quantities of toluidine a redder colouring matter was obtained". He states that the structure of the crystalline salt could not be investigated at the time because of its stability and because they "do not freely undergo changes with reagents" and that at the time of the Hofmann memorial lecture (1896) the structure was unknown. Therefore Perkin understood that two components, aniline and *para*-toluidine, were necessary for the production of mauveine.



Chemical Structure

The structure of mauveine reported for many years was produced from pure aniline, i.e. it was pseudomauveine. This is surprising as it had been established by 1896 that pseudomauveine was of no commercial value and that the dye available commercially was derived from a mixture of toluidine and aniline. This structure is sometimes attributed to Fischer and Hepp (1888).



This is the structure of mauveine given by G Shultz and P Julius in their *Table of organic dyes* [4], and is sometimes attributed to Gustav Shultz from his investigations of this dye. The same structure appears in the *Colour Index* first edition of 1924 [5]. This same structure also appears in the *Colour Index* third edition [6]. This structure is described as the “idealised structure” in the book *Dye Makers of Great Britain* published in 1987 [7].

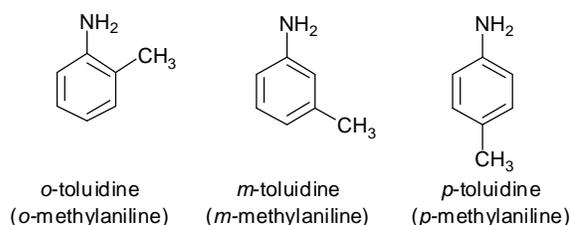
In 1956, for the celebration of the centenary of the discovery, W H Cliffe wrote about his attempts, and failure, to produce a worthwhile sample of mauveine using the patent as a starting point as so little evidence of the actual process remained [8].

We can only summarise why no investigations into the structure of commercially available mauveine were not conducted but perhaps it was because the dye only had a short existence, very quickly becoming obsolete and expensive to produce in comparison to the new dyes discovered and brought to market as the industry poured money and well trained chemists into the field of dye research. It was more important to understand the structure of other dyes which could provide a better insight into the chemistry involved.

After a time investigations into mauveine would have had no commercial significance and as has been shown the investigation that finally established the structure of commercial mauveine was only undertaken for historical reasons.

However, there appears to be no attempt to discover the true structure of mauveine until the paper by Otto Meth-Cohn and Mandy Smith in 1994 [9]. Their search of the literature indicates that the above structure is the most common one used but others that are erroneous also appear.





This piece of experimental work used a sample of dye produced in the Greenford Green works of Perkin and Sons Ltd. They argued that the structure could not be correct as *m*-toluidine was a key requirement which they say would not be possible by the oxidation of crude aniline derived by nitration and reduction of a benzene/toluidine mixture. They established that two components exist in the sample they investigated – major component A and minor component B, (see p.786).

What Does this Tell us about Perkin's Discovery of Mauveine?

A number of points in fact:

1. Perkin was fortunate that he used aniline from coal tar as this contained more toluidine than the usual source of aniline at the time, which was from the destructive distillation of indigo with sodium hydroxide. This produces no toluidines. He was probably using coal tar aniline because of his work with Hofmann.
2. He had the ability to view his experiments with a critical eye and find a use for the reaction, which shows that he could combine the theoretical with the practical. This was not an attribute associated with scientists of the day. Of the reaction of Hofmann to the young Perkin's decision to leave the Royal College of Chemistry, Perkin wrote, "At this he appeared much annoyed, and spoke in a very discouraging manner, making me feel that perhaps I might be taking a false step which might ruin my future prospects". Hofmann soon followed Perkin into the field of dye research.
3. He was lucky to have dyed a piece of silk as it appears that the colour on wool is not as bright and on cotton can look almost grey, whereas on silk it produces a deep bright shade.
4. The subsequent commercialisation of the product proved the ability of the man as a chemist having to undertake the manufacture of raw materials for the first lots and scale up a laboratory process that appears to have given low yields to a viable large scale chemical manufacturing process, the first of its kind. There is some evidence that not all was rosy at



the works as it was reported by Morris that recent excavations at the Greenford Green site for redevelopment in 1956 had uncovered masses of mauve coloured jelly. Either these were failed large scale experiments or early production was hit and miss.

5. We cannot judge Perkin by our knowledge today and put his discovery down to luck. Many things have been invented and discovered but forgotten because nobody could find a use for them and the saying “the harder you work the more luck seems to come your way” may be apt for Perkin who was fortuitous because of his persistence with chemistry experiments to the extent of having his laboratory at home for use after college and during the holidays.

Suggested Reading

- [1] W H Perkin, *J. Chem. Soc.*, p.596, 1896.
- [2] *Proc. Royal Soc.*, Vol.12, p.713, 1864.
- [3] *J. Chem. Soc.* p.717, 1879.
- [4] G Schultz and P Julius, *Tabellarische Übersicht der kunstlichen Organischen Farbstoffe* (Berlin: Hermann Heyfelder, p.250, 1902.
- [5] F M Rowe (Ed), *Colour Index*, 1st Edition, Bradford, SDC, 1924.
- [6] *Colour Index*, 3rd Edition, Bradford, SDC, 1982.
- [7] M R Fox, *Dyemakers of Great Britain 1856–1976*, Manchester: Imperial Chemical Industries, Vol. 101, 1987.
- [8] W H Cliffe, *J.S.D.C.*, Vol.72, p.356, 1956.
- [9] O Meth-Cohn and M Smith, *J. Chem. Soc., Perkin Trans.*, Vol.1, No.5, 1994.
- [10] L E Morris, *The Dyer*, Vol.115, p.770, 1956.



Andrew Filarowski is currently Technical Director of the Society of Dyers and Colorists, UK. He has extensive knowledge of chemistry and application of chemicals and dyes in the textile industry. In his current role he is responsible for various SDC programmes: education, training, consultancy, standard test methods and the Colour Index. The Society is an educational charity and membership body whose aim is to communicate the science of colour in a changing world.

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