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From process to plant: innovation in the early artificial dye industry

WILLEM J. HORNIX*†

The rise of the synthetic dye industry was based on exciting discoveries of nineteenth-century chemists. They prepared in their laboratories, from components of coal tar, coloured substances with potentially promising dyeing properties.[1] However, this was only part of the story.

The development of a laboratory recipe for a synthetic dyestuff into an efficient and profitable industrial process calls for knowledge and skills other than those obtained by chemical training, and for facilities rather different from those present in a chemical laboratory. Throughout the nineteenth century scale-up could only be carried out in the factory itself, by people who contributed technical, chemical, or management skills. The products of this development are the chemical appliances, organized in chemical plants. Around 1860, at the beginning of the synthetic dye industry, such appliances were primitive and their use was labour-intensive. Thirty years later process plant was already sophisticated and the industry had become capital-intensive. These developments are the subject of this paper.

Information about the industrial processes and the chemical plants of the nineteenth-century synthetic dye industry is scattered and invariably incomplete. There are a number of important printed sources, especially contemporary handbooks, monographs, dictionaries and encyclopedias, patents, articles in chemical and technical journals, and

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† Smaller type is used to distinguish technical information from the general story.

This research was suggested by Tony Travis of the Sydney M. Edelstein Center of the Hebrew University, Jerusalem, and initiated during my stay there as Senior Research Fellow, March–June 1990. Parts of this paper were presented at the International Workshop on the History of Chemical Technology, Jerusalem, May 1990, at the Conference of Technological Development and Science in the 19th and 20th Centuries, Eindhoven, November 1990, and at the 'First Mineralkontor', Veszprem, August 1991.

I would like to thank Tony Travis, Elisabeth Vaupel and Ernst Homberg for their help and criticism, and the archivists of BASF AG (Ludwigshafen) and the Deutsches Museum (Munich) for allowing me to make use of the resources under their care.

[1] The history of dyestuffs chemistry was recently treated by R. Stoltz, *Schriftreihe f.Geschichte der Naturwissenschaften, Technik und Medizin* (1980), **17**, (2), 84–101; (1981), **18**, (1), 62–83; (2), 29–48, and by W. J. Hornix, 'De ontwikkeling van de kleurstofchemie van 1850 tot 1887' (The development of dyestuffs chemistry 1850–1887), in H. van den Belt, B. Gremmen, E. Homburg and W. Hornix, *De ontwikkeling van de kleurstofindustrie* (*The development of the dye industry*), final report of a Science and Society project, Nijmegen, 1984, 49–104.

reports of the international exhibitions.[2] There is, in addition, archival material available which supplements and corroborates the results of historical analysis of published sources.

The information available from the foregoing gives a sufficient basis for answering a few interesting questions. The first is whether the appliances for the preparation of artificial dyestuffs can be characterized as scaled-up laboratory apparatus, and whether the industrial preparation of synthetic dyestuffs can be characterized as 'applied chemistry'. Also it is pertinent to ask whether the relationship between science and technology in this case can be expressed in terms other than those which the term 'application' suggests. Other questions concern the role of the patent system, and the patterns of communication. However, before I attempt to answer these questions a story with many technical details has to be told.

THE FIRST COAL-TAR DYES: PICRIC ACID, MAUVE. THE INTERMEDIATES: NITROBENZENE AND ANILINE

William Perkin's famous aniline purple or mauve, the preparation of which was patented in 1856, was not the first coal-tar dye. The yellow picric acid had been produced by Guinon in Lyon since 1845. The heavy distillation fraction of coal tar, containing 'phenic acid' (phenol), was treated with nitric acid, and the dye was extracted from the resulting mixture. Guinon's apparatus (Figure 1), taken from Girardin (1861), can be recognized as scaled-up laboratory equipment. In 1856 Boboeuf took out a patent in Paris protecting the

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[2] The handbooks of dyeing and printing and those of chemical technology of the period aimed to be up-to-date with respect to the preparation and use of coal-tar dyes. There are monographs dealing with certain well-defined classes of dyes, which sometimes give much technological information. The dictionaries of chemistry and chemical technology of the period contain highly relevant articles by experts in the field.

British patents on synthetic dyes are found in class 2 (acids and salts, organic and other carbon compounds, including dyes), French patents in class XIV, 2 (Arts chimiques, Matières colorantes), and, after 1877, German patents in class 22 (Farbstoffe, Firnisse, Lacke). These patents on synthetic dyes are about processes leading to colouring matters, not about apparatus. Only extraction processes for natural dyes were protected by patents in which special appliances were described. However, there are patents about apparatus relevant to artificial dyestuff production in quite different classes. Of great help are: for British patents the *Abridgments of Specifications*, published at the Patent Office; for French patents the compilation *Tables des Volumes ...*, and the *Subject-Matter Index, Patents for Inventions (Brevets d'invention) Granted in France from 1795 to 1876, inclusive*, translated, compiled and published under authority of the Commissioner of Patents, Washington, 1883; and for German dyestuffs patents the critically and systematically analysed compilation of P. Friedländer, *Fortschritte der Theerfarbenfabrikation und verwandter Industriezweige, 1877–1887*, Berlin, 1888, *Bis idem., 1887–1890*, Berlin, 1891, etc.

Technological source material on dyes can be found in the technical journals with, after 1855, an invaluable entrance provided by Wagner's *Jahresbericht der chemischen Technologie*. The main difficulty with the technological literature is that references are not abundant, and consequently much effort has to be invested in deciding what is original and what is derived.

An important source for industrial information consists of the reports on the international exhibitions, generally written by experts in the field since they were often members of the jury of exhibitions. The reporters had excellent personal contacts and were free and generous in the communication of their knowledge. The reports of exhibitions held in 1862 (London), 1867 (Paris), 1873 (Vienna) and 1878 (Paris) play a crucial role in this story.

These publications will be cited in so far as they give new information. Handbooks, monographs, dictionaries and encyclopedias are also indispensable as guideposts to new technological information.

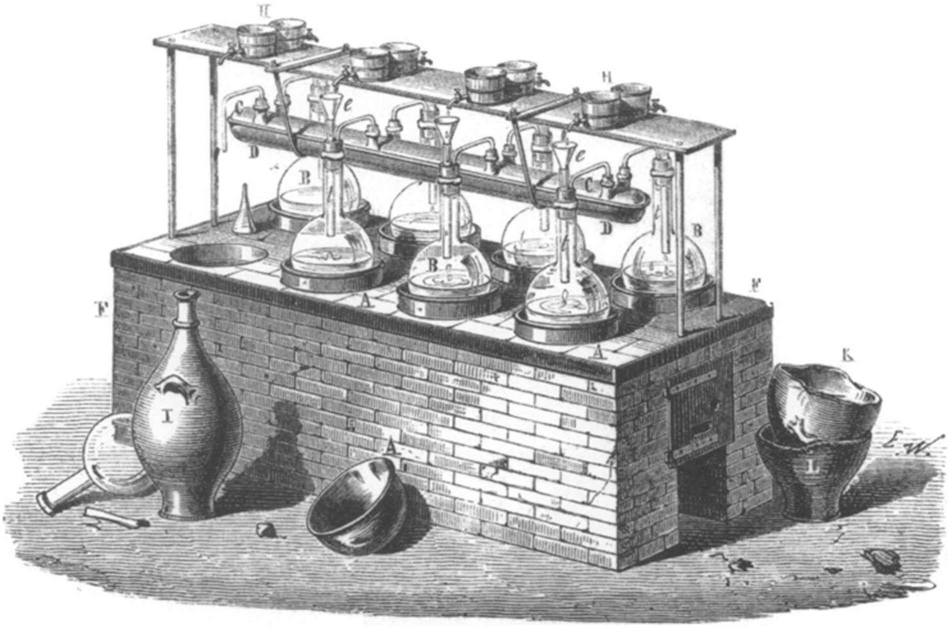

Figure 1.

isolation of phenol from coal tar, which made its nitration much more economical, and this enabled widespread use of picric acid as a dye.[3]

Perkin's patent described a purple dye, resulting from the oxidation of aniline with potassium dichromate and subsequent extraction with methanol.[4] Its successful introduction on the market in 1858–59 made the industrial and scientific world even more aware of the new potential for coal tar, since it was the source of benzene, from which aniline was obtained. The development of Perkin's discovery into an industrial process was not an easy task for the still inexperienced teenaged student of August Wilhelm Hofmann.

Nitrobenzene, the intermediate between benzene and aniline, was already an industrial product, made by nitration of 'technical benzene', the fraction of light oils distilling below 100 °C. It was made on a small scale by Mansfield in London around 1847 and by Collas in Paris since 1848. They used glass or earthenware ('*grès*') appliances.[5] Perkin later

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[3] See W. F. Farrar, *Endeavour* (1974) **23**, 149–55, who refers to N. Guinon, *Revue scientifique* (1849), **5**, 233 (not seen); and J. Girardin, *Leçons de Chimie Élémentaire appliquée aux Arts industriels*, 4th edn, Paris, 1861, ii, 599, fig. 515. Boboeuf, French patent no. 15271 of 17 March 1856.

[4] W. Perkin, British patent no. 1984, 26 August 1856; French patent no. 20326, 8 April 1858.

[5] The earliest appliances for the nitration of benzene are described in C. Girard and G. de Laire, *Traité des dérivés de la houille applicables à la production des matières colorantes*, Paris, 1873, 251–5. Mansfield's British patent no. 11960 of 11 November 1847 is a 50-page illustrated treatise on manufacturing 'spirituous substances and oils' and 'applications to the purposes of artificial light'. The nitration of benzene is only a minor aspect of his patent. An illustration of an earthenware version of an apparatus for the nitration of benzene is given by M. Reimann, *Technologie des Anilins*, Berlin, 1866, 13. See also T. (A. S.) Travis, 'Early intermediates for the synthetic dyestuffs industry', *Chemistry & Industry*, 15 August 1988, 508–14; and A. S. Travis, 'Perkin's mauve: ancestor of the organic chemical industry', *Technology and Culture* (1990), **31**, 51–82.

claimed that he had been the first to use iron reactors for the nitration process.[6] This permitted scaling up.

> His nitration reactor was a 30–40 gallon cylinder, fitted with a hand-driven stirrer and provided with a siphon tube for introducing the reactants. The reactor was fitted with an earthenware worm to condense vaporized benzene, and to dispose of noxious fumes.[7] The reduction of nitrobenzene into aniline by acetic acid and iron filings was carried out in a similar reactor, set in a brickwork furnace. These very primitive appliances were soon replaced by more sophisticated and larger versions.[8]
>
> The oxidation of aniline (sulphate) with potassium dichromate called only for a large vat. The precipitate of the reaction was, after filtration, extracted with naphtha and then with methanol. The alcoholic extract was distilled off, leaving the mauve dye as a bronze-coloured mass. Perkin explained that the extraction 'had to be performed in a closed vessel under pressure, or in connection with a condensing arrangement', without giving detailed descriptions.[9] The appliances mentioned were at the time certainly not new. Extraction of logwood with hot water under pressure had already been described in 1855.[10]

Information on the improvement of Perkin's industrial preparation of mauve is practically non-existent. In any case, the dye itself lost importance from 1864 because of competing products of better quality.

The improvements on the preparation of the intermediates between benzene and mauve, nitrobenzene and aniline, are much better documented, especially as they were essential to the whole branch of aniline dyes. These preparations were exploited on a large scale by the London firm Simpson, Maule & Nicholson after 1859. Presumably, it is their apparatus that is described by Hofmann, Girard and de Laire in their contribution to the report on the international exhibition of 1867 in Paris. The detailed description fits certain illustrations in Girard and de Laire's *Traité des dérivés de la houille* of 1873 so well that we can conclude that the latter show the appliances described in 1868.[11]

> The nitration apparatus (Figure 2) consists of a 1000–1500-litre cylindrical iron vessel *a*, fitted with a power-driven agitator *b*. Temperature regulation was achieved by a serpentine pipe, *k*, wrapped around the vessel in a jacket *m′* and through which steam or water was circulated. The mixture of nitric and sulphuric acid was introduced via an S-shaped tube. Another tube, *f*, functioned as a chimney for the escaping nitrous vapours. Along *f* water trickled down the sides of the water seal *h*. There is a manhole, *d*, and the apparatus could be emptied via the cock *l*. The apparatus could also be used for washing the product.
>
> The reduction of nitrobenzene with iron filings and acetic acid was carried out in an iron reactor of similar capacity which could be connected with a condensor either for refluxing or for distilling. The axis of the agitator was a tube through which steam could be injected, whether for heating or for steam distillation after the reduction was completed.

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[6] W. H. Perkin, *J. Chem. Soc.* (1896), **69**, 609.

[7] W. H. Perkin, *J. Soc. Arts* (1869), **17**, 99–105, 109–14, 121–6. The apparatus is shown in fig. 1, p. 101. Girard and de Laire (1873), op. cit. (5), plate II, fig. 1, is more detailed than Perkin's figure.

[8] The earliest evidence consists of drawings of a reactor of about 50 gallons capacity, fitted with a power-driven stirrer, and delivered in 1861 by a London firm to Roberts, Dale & Co. W. Pillmer to Roberts, Dale & Co., Caro Nachlass, Special Collection, Deutsches Museum (uncatalogued item).

[9] Perkin, op. cit. (7), 104.

[10] A pressure boiler for dye extraction of Bohra is reproduced in Wedding, *Verhandlungen des Vereins zur Beförderung des Gewerbenfleisses in Preuszen* (1855), 113–14, plate XVI.

[11] A. W. Hofmann, G. de Laire and C. Girard, *Report on the colouring matters derived from coal tar*, Appendix of M. Reimann, *On Aniline and its Derivatives*, revised and edited by W. Crookes, London, 1868, and Girard and de Laire, op. cit. (5), 251–8, plate II, figs. 1, 3, 4, 5 (legends pp. 630–1) for the preparation of nitrobenzene, and pp. 330–50, plate II, fig. 2 (legends p. 630) for the preparation of aniline.

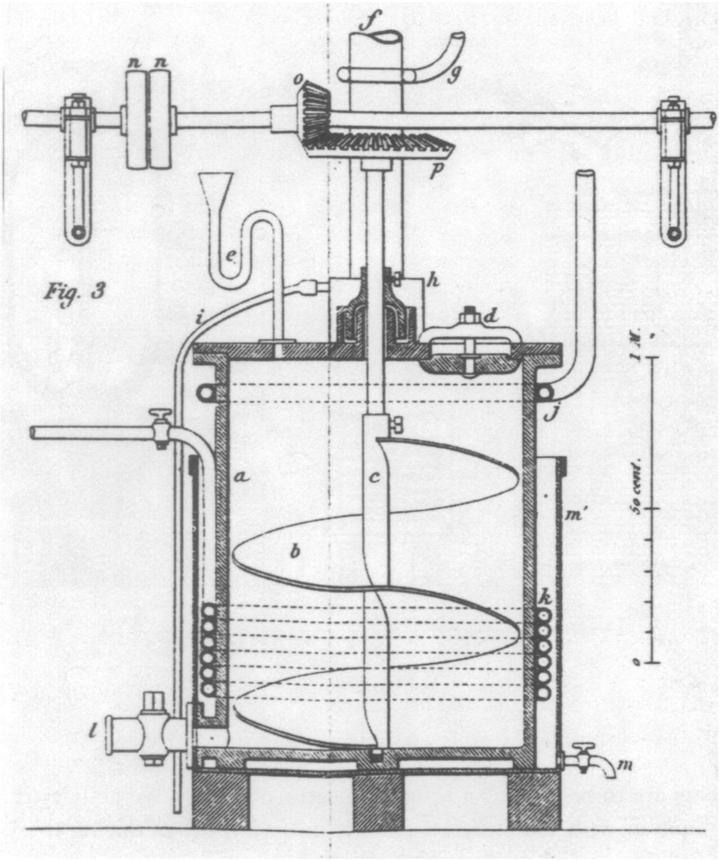

Figure 2.

The apparatus used at Simpson, Maule & Nicholson was considered efficient, safe and adequate for several decades. Presumably, it was not considered innovative: there are no patents protecting the apparatus, and there is no indication that the firm tried to keep its construction secret.[12]

MAGENTA

Perkin's mauve triggered a vast amount of chemical research for alternative methods of preparing dyes from aniline resulting in a long series of patents. In the three-year period commencing 1859 there were twenty-nine British patents on colouring matters from

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[12] The situation is different with respect to the raw material for the preparation of aniline: benzene. The separation of coal-tar components by distillation is the subject of a long series of patents, forming a continuous tradition during the entire period under investigation. The development of coal-tar distillation is closely connected with that of the dyestuffs industry and is a worthwhile subject of a separate chapter of the history of chemical technology.

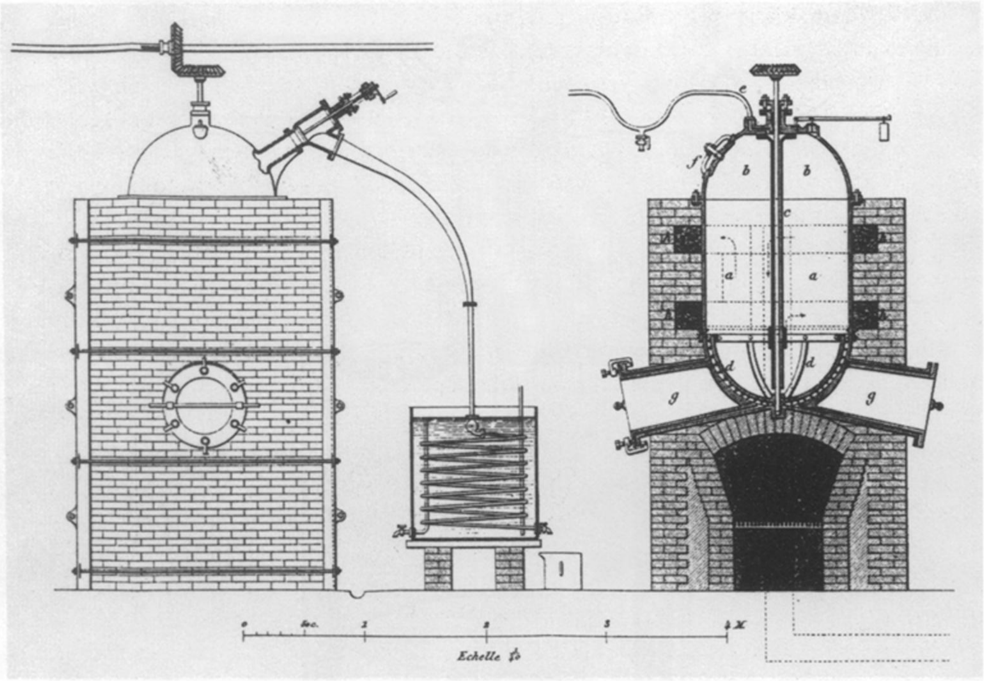

Figure 3.

aniline. If patents are to be used as a rough indicator of innovative activity this number is impressive, compared with the eighteen patents on natural dyes during the same period. However, few ever protected marketed products.[13]

The aniline dye with the greatest impact on the dyeing and printing industry, and which provided the main incentive for improvement and scaling up of aniline production was magenta, fuchsine or aniline red. The first patent on this dye was taken by Renard frères on 8 April 1859 in Paris and in their name by Brooman on 12 April 1859 in London.[14] Renard's fuchsine appeared to be an immediate and lasting success. It remains an important commodity.

Renard's first industrial process of 1859 was very primitive:

> according to the description of Girard and de Laire in the *Traité* of 1873, it consisted only in the heating of aniline with anhydrous tin bichloride ($SnCl_4$) in enamelled iron pots without any subsequent purification of the product.[15] In the patent specification the product is dissolved in water and the dye precipitated by adding salt.

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[13] Patent statistics derived from the *Abridgments of Specifications* (1905) op. cit. (2). Marketed products are listed in G. Schultz and P. Julius, *Tabellarisches Uebersicht der künstlichen organischen Farbstoffe*, Berlin, 1888, and in Theodore Chateau, *Nouveau manuel complet, théorique et pratique, de la fabrication et de l'emploi des couleurs d'aniline, d'acide phénique, de naphthaline et des homologues de ces substances, etc.*, Paris, 1868.

[14] French patent no. 22706, 8 April 1859; British patent no. 921, 12 April 1859.

[15] Girard and de Laire, op. cit. (5), 551–2.

Renard's fuchsine was a sensation. It set off a series of trials to find other processes leading to an identical or comparable colour. In the three-year period 1859–61 some twenty patents were taken out on red dyes prepared from aniline. These brilliant red dyes were marketed under different names. The Renard frères firm sued their competitors before the French courts in cases of patent infringement. The competing dyes and the different methods of preparation were judged to be identical, and consequently a monopoly was established for the proprietors of the first patent.[16]

Renard's original industrial process was soon replaced by a preparation using arsenic acid as the reactant upon aniline. This process was patented by Henry Medlock in London on 18 January 1860 and by Girard and de Laire on 1 May 1860 in Paris and on 26 May 1860 in London.[17] However, Medlock's patent was declared void after lengthy patent litigation in Britain.[18] From the outset, the process was recognized as very effective, and for many years it proved to be the most profitable way to prepare magenta. Consequently we have the opportunity to follow the industrial development of this process over a considerable period.

Detailed descriptions are given by Wurtz (1863), Reimann (1866), Hofmann, de Laire and Girard (1868), Reimann (1868), Perkin (1869), Girard and de Laire (1873), Schoop (1885) and Mühlhäuser (1887, 1889).[19] Here, I shall concentrate on Wurtz (1863), Girard and de Laire (1873) and Mühlhaüser (1889).

The earliest description of the industrial use of the arsenic acid process is given in Wurtz's report of the 1862 International Exhibition:

> At Renard frères & Franc the red colorant was produced by heating 15 kg aniline and 25 kg arsenic acid solution (76 per cent solid acid) in capacious cast-iron retorts placed over the vault of a furnace in an air bath at 150–170 °C. The hot melt was poured onto cast-iron plates, and, after cooling, broken into fragments. These were digested in large iron tanks with twice the weight of hydrochloric acid; the liquid was heated continuously by injecting a current of steam. After filtration the hot solution was allowed to fall into a large cast-iron tank containing excess soda solution through which steam was bubbled. Flakes or granules separated out, and were collected by perforated ladles. Recrystallization took place in iron tanks containing water, again heated by passage of a stream of steam. This afforded a deposit of green magenta crystals.[20]

Girard and de Laire's (1873) description of the oxidation process of aniline is accompanied by detailed drawings of the reactor (Figure 3).[21] These drawings fit the earlier

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[16] H. van den Belt, 'Action at a distance. A. W. Hofmann and the French patent disputes about aniline red (1860–1863), etc.', in *Expert Evidence: Interpreting Science in the Law* (ed. R. Smith and B. Wynne), London, 1988, 184–209, 263–8; A. S. Travis, *The Rainbow Makers. The Origins of the Synthetic Dyestuffs Industry in Western Europe*, Bethlehem, Pennsylvania, 1992, chapter 5.

[17] British patent no. 126, 18 January 1860.

[18] Travis, op. cit. (16), chapter 5.

[19] A. Wurtz, 'Matières colorantes dérivées du goudron de houille', in *Exposition universelle de Londres de 1862* (ed. M. Chevalier), Paris, 1863, i, 277–308; Reimann, op. cit. (5); Hofmann, de Laire and Girard, op. cit. (11); Reimann, op. cit. (11); Perkin, op. cit. (7); Girard and de Laire, op. cit. (5); P. Schoop, *Dinglers polytechnisches Journal* (1885), **258**, 276–84; O. Mühlhäuser, *Dingl. pol. J.* (1887), **266**, 455–67, 503–17, 547–63; Otto Mühlhäuser, *Die Technik der Rosanilinfarbstoffe*, Stuttgart, 1889.

[20] Wurtz, op. cit. (19), 295–6.

[21] Girard and de Laire, op. cit. (5), plate VI, fig. 1, 2 (legends p. 631), description pp. 568–70.

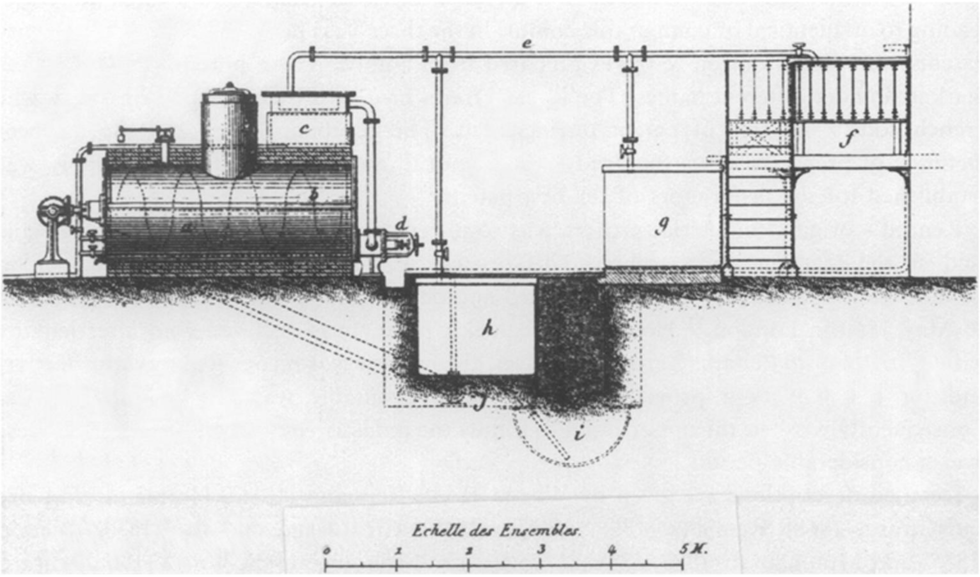

Figure 4.

description in the report on the 1867 Exhibition, and consequently the reactor shown can be dated before 1868:

> The retort, of a capacity of about 2,500 litres, is furnished with an agitator [*d*] moved by steam. A large tube [*c*] parallel to the axis of the agitator descends to the bottom of the apparatus, and serves to conduct steam into it [via *e*]. At the upper part there is a man-hole [*f*], a valve, and a cock which places the apparatus in connection with a reservoir of warm water; at the lower part are two taps [*g*?] for drawing off. The neck of the retort communicates with a large serpentine tube, serving to condense the aniline which volatilises in the course of the reaction.[22]

In the apparatus 800 kg of commercial aniline was treated with 1370 kg arsenic acid solution (72 per cent anhydride). The mixture was heated for 8–10 hours at 190–200 °C. The temperature was regulated by circulation of hot air from the furnace below, through the channels *h*, *k*. The aniline still present was then drawn off by steam introduced via *c*. Boiling water was introduced till a homogeneous mass was obtained which was drawn off through the pipes g.

Girard and de Laire describe three different methods for the isolation of pure magenta from the hot fluid mass containing mainly the arsenate of the colour base. The so-called neutral process is, historically, the most interesting: the crude magenta solution is treated with boiling water at 130 °C under increased pressure.

The relevant drawing (Figure 4) shows cylindrical vessels of about 6000 l capacity fitted with steam jackets, a manhole in the dome and a safety valve. A steam engine drove the helical agitator. Piping introduced water and high pressure steam at round 2 atmospheres into the vessel, and into its jacket,

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[22] Hofmann, de Laire and Girard, op. cit. (11), 114–15. The indications between brackets are not in the original text.

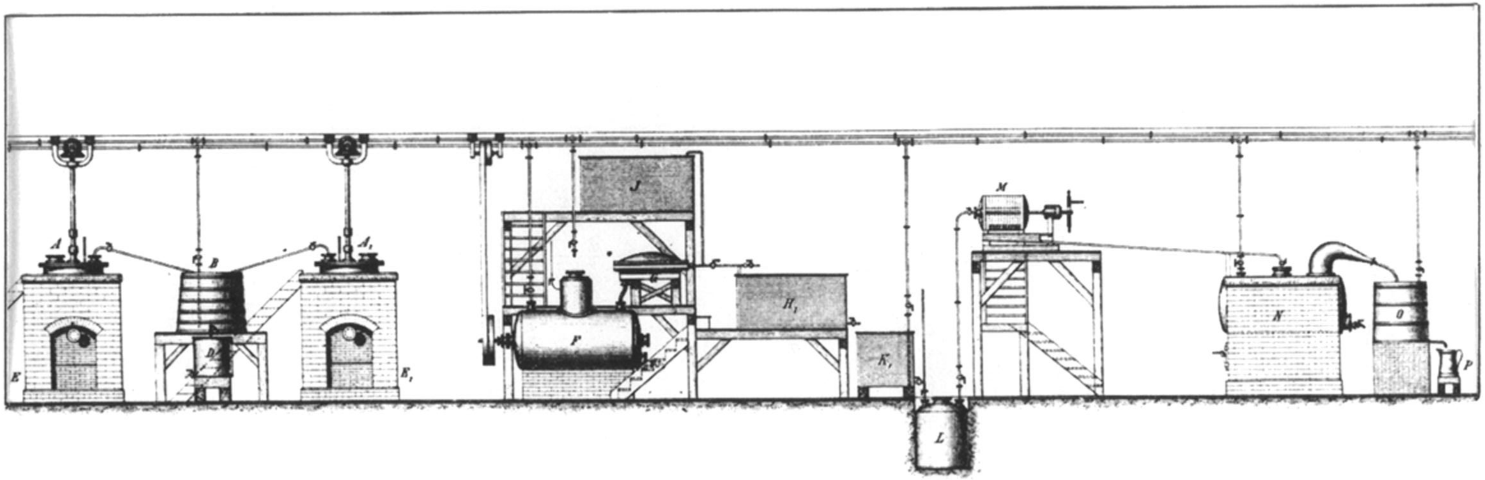

Figure 5.

which enabled filling, emptying and heating of the boiler. After the extraction in the boiler was completed, the hot contents were pressed by steam through the pressure filter *c* to the vat *f*, where the chloride of the colour base was precipitated by adding salt. After cooling and filtration in the succeeding crystallization vats *f*, *g*, *h* (the description is very short at this point) crystalline magenta was obtained. The filtrate from *h* was returned via *i* to the extraction boiler by the pump *j*, to be used in a new cycle.[23]

We know about prototypes of the extraction boiler and pressure filter from Reimann (1868): a simple drawing of Crookes shows a striking resemblance to Girard and de Laire's appliances.[24] The origin of this type of extraction boiler can be sought in the technology of stearic acid production for candles. Delapchier's apparatus (1854) for fat hydrolysis was a horizontal cylindrical boiler, fitted with an agitator, which worked at 1.25–1.5 atm. and 106–112 °C.[25] It belongs to a long tradition recorded in many British and French patents. Of special interest are the contributions of Léon Droux, patentee of many patents on fat hydrolysis under pressure between 1865 and 1874.[26] The last of this series protects horizontal cylindrical appliances provided with mechanical stirrers with helical blades. Pressure filters were also the subject of patents, such as Radloff's British patent of 15 September 1862.

During the 1870s an alternative route to magenta was developed industrially via the oxidation of 'technical' aniline with nitrobenzene. Nevertheless the arsenic acid process, with its obvious health hazards inside the factory and its conspicuous environmental risks, remained the most important route, also during the 1880s. The immediate health risks could be reduced by minimizing contact of the workers with the poisonous substances, and the environmental risks by regeneration of the arsenic acid, which cut back on industrial waste.

New developments in the technology of magenta production with arsenic acid are not reported before 1885. An illustrated article by Schoop in *Dinglers polytechnisches Journal* (1885) was soon followed by publications by Mühlhäuser in the same journal (1887) and by the latter's monograph *Die Technik der Rosanilinfarbstoffe* (1889), which showed detailed drawings of a magenta production plant.

Figure 5 shows Mühlhäuser's drawing of the plant for preparing crude magenta (Rohfuchsin) and crude cerise (Rohcerise) from a mixture of aniline and toluidine, already recognized during the 1860s as the essential components of 'anilin for red'.[27]

The two identical reactors *A* and A_1 connected with the serpentine (not seen) in *B* each handled the oxidation of 340 kg 'aniline' (i.e. aniline + toluidine) with 570 kg arsenic acid (74 °B). The aniline volatilizing during the reaction was condensed in *B*. The reactor was emptied into the flat open container *E* and the solidified product was broken into fragments and then put into the extractor *F* (capacity 4000 l) to be boiled under pressure (1.5 atm.) with water. After filtering through the pressure

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[23] Girard and de Laire, op. cit. (5), plate VIII (legends on p. 632).

[24] Reimann, op. cit. (11), 43–4, fig. 7, p. 43.

[25] Delapchier, *Le Génie industriel* (1854), 323–4, plate 128, fig. 9.

[26] French patent no. 66635, 20 March 1865 (and several additions), no. 79126, 9 January 1868, no. 93643, 26 December 1871, no. 102197, 12 February 1874. R. von Wagner, *Handbuch der chemischen Technologie*, 11th edn, 1880, 933–4, fig. 275, gives a description and illustration of Droux's pressure boiler, taken from Léon Droux, *Appareil pour la saponification des matières grasses sous pression et avec agitation mécanique*, Paris, 1876.

[27] Mühlhäuser (1889), op. cit. (19), plate IX. The same plate shows the two plants for the separation and purification of the components of crude magenta and cerise (not reproduced here).

filter *G*, salt and hydrochloric acid were added to the filtrate in H_1 and the mixture was left to cool to about 70 °C: crude magenta crystallized out. The solid was separated by filtering through the filter box (not seen) above K_1. Addition of soda to the filtrate in K_1 led to precipitation of 'Rohcerise' which again was separated by filtration. The filtrate was pressed via the pressure tank *L*, through the filter press *M*, and was collected in the distillation tank *N* to recover aniline by steam distillation. The filtrate of a second extraction of the contents of *F* was stored in *J*, and used for extraction of a new charge.

The subsequent separation of the crude magenta and cerise in purer products was carried out in two other plants, consisting of extraction boilers, pressure filters, filter presses, filter boxes, crystallization tanks, and pressure tanks, identical with those already described.

The similarity between Mühlhäuser's drawings and those of Girard and de Laire (1873) is remarkable. The extraction appliances and the pressure filters are practically identical. By comparing Girard and de Laire (1873), Schoop (1885) and Mühlhäuser (1887, 1889) it can be concluded that the improvements on the magenta technology of 1873 were not of the apparatus but mainly of the processes, the purification methods in particular. These innovations resulted from the analysis of the mixtures formed by the oxidation process and from research into the best process conditions. From Mühlhäuser's (1887) article it appears that these conditions were found through factory floor experiments.

SUBSTITUTED ROSANILINE DYES

The importance of magenta was derived not only from its characteristics as a dye. It turned out to be an important intermediate for making other dyes. In 1861 Girard and de Laire had prepared a blue dye by heating aniline red with aniline.[28] A number of other reactants were claimed as capable of transforming aniline red into new dyes. Before 1868 some forty-seven patents which gave aniline red as their starting material had been filed at the Patent Office in London. Again, only a few proved to be of practical value.

The commercial successes of mauve, magenta (aniline red) and aniline blue, and the chemical expertise sought in the court cases between 1860 and 1863 around the supposed infringement of Renard's fuchsine patents brought about the interest of contemporary chemists. The chemistry of coal-tar dyes remained uncertain until Hofmann analysed purified aniline red and aniline blue. It was Hofmann who concluded in 1862–63 that the red was formed from one molecule of aniline and two molecules of toluidine, and that the mix of aniline and toluidine in 'technical aniline' determined the yield of aniline red. Hofmann also discovered that aniline blue originated from a substitution reaction in which three hydrogen atoms of aniline red are replaced by three phenyl groups derived from aniline.[29] These results directed dyestuffs research towards other substitutions, for instance of alkyl groups and aldehyde groups. The expectations in this field are reflected in twenty-three patents before 1867.

The first in this series was filed by Hofmann during May 1863. It described alkylation of aniline red which gave the brilliant dyes Hofmann violets,[30] which displaced mauve from 1864 on. In Hofmann's patent the reaction between rosaniline and ethyl-iodide in

[28] French patent no. 48033, 2 January 1861; British patent no. 97, 12 January 1861.

[29] A. W. Hofmann, *Proc. Roy. Soc. Lond.* (1863), **12**, 645–7, 647–8; **13**, 6–9, 9–14, 341–7, 485–91.

[30] British patent no. 1291, 22 May 1863; French patent no. 59309, 11 July 1863.

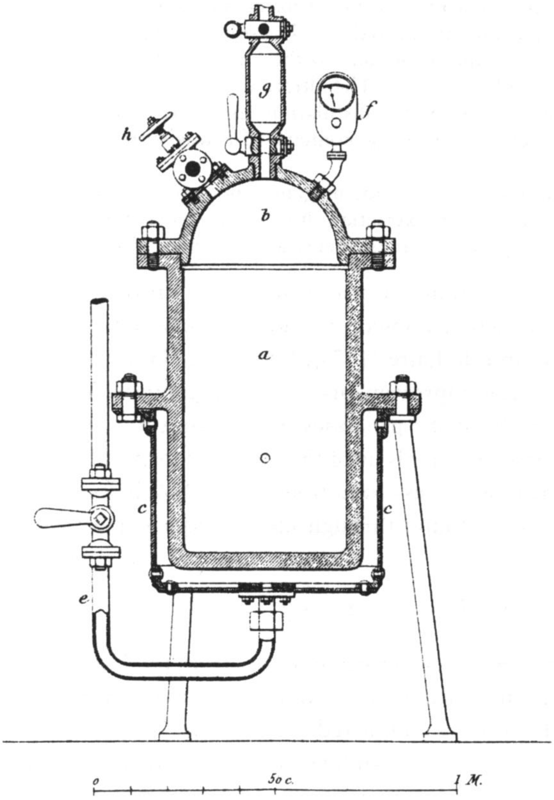

Figure 6.

alcoholic solution is described as taking place in a tightly closed iron vessel at a temperature of 100–150 °C.

Hofmann's report of the 1867 Exhibition gives details of the same process carried out in an open copper alembic at ordinary pressure. Girard and de Laire's *Traité* (1873) presents detailed drawings of the open appliances used originally, as well as the more modern closed ones (Figure 6).[31] These must have been used from the end of the 1860s, since Turgan's *Les grandes Usines*, vol. 9 (1870) shows engravings of photographs of identical appliances in use at the factory of Poirrier in Saint-Denis.[32]

Hofmann's views on the constitution of aniline blue and of his new violets as phenylated and alkylated rosanilines, respectively, induced the search for alternative pathways to these dyes. The breakthroughs in this field are patents of Girard and de Laire and of Poirrier and Chappat in 1866. Girard and de Laire claimed the preparation of diphenylamine or phenylated aniline (and homologues) by heating a mixture of aniline chloride and aniline

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[31] Hofmann, de Laire and Girard, op. cit. (11), 130–1; Girard and de Laire, op. cit. (5), plate X (figs. 1, 2), plate XI (figs. 3, 4), legends pp. 633–4, descriptions p. 599. The closed vessels were charged with 10 kg rosaniline, 5–20 kg alkyliodide, and 10 kg potassium hydroxide, in 100 l alcohol.

[32] Turgan, *Les Grandes Usines. Études industrielles en France et à l'étranger*, Paris, 1870, ix, 304, 305.

(or its homologues) at a temperature of about 250 °C in closed vessels, held at 5 atm. pressure. The subsequent transformation into colouring matters with dyeing properties was achieved with 'sesquichlorure de carbone' (C_2Cl_6).[33] Poirrier and Chappat patented the preparation of alkylated aniline, toluidine etc. by the action of alcohols upon chloride of aniline (or its homologues). The temperature was stated to be 250–300 °C which implied that the process was performed in closed vessels withstanding about 50 atm. pressure.[34]

A detailed description of the industrial processes and the appliances used can be found in Girard and de Laire's *Traité* of 1873. The preparation of diphenylamine took place in an enamelled cast-iron digester of 200–250 l capacity. A tube, fitted with cock, connected the digester with the outside via a condenser. According to the authors the yield could be increased from 20–30 to 60–75 per cent if the ammonia gas produced was released from time to time. The reaction was recognized to be an equilibrium reaction. A similar 'autoclave' (shown in a drawing not corresponding with the text), is used for the preparation of dimethylaniline by the method of Poirrier and his chemist Charles Bardy. Control of the temperature was critical because the pressure (of methanol) could lead to explosions.

The increasing importance of dimethylaniline in the 1870s stimulated improvements in its industrial preparation.

The enamelled surface of the original digesters did not withstand the corrosive action of the reactants very long, and the replacement or restoration of the scaled-up vessels was very expensive. C.E. in *Dinglers polytechnisches Journal* of 1878 recommends 5 cm thick cast-iron or 2 cm thick copper vessels withstanding 50 atm., gilded on the inside, or provided with an interchangeable, closely fitting, thin-walled, enamelled copper vessel, tightly fixed with molten lead.[35]

These high pressure digesters fit neatly into a tradition that was quite distinct from the pressure boilers used for the extraction of magenta or the hydrolysis of fats. The digesters described by Hofmann, Girard and de Laire and designed by Bardy are scaled up and adapted laboratory appliances, not related at all to steam-boiler technology.

ALIZARIN[36]

A new chapter in artificial dyestuffs production was opened in 1869 with the synthesis of one of the most important natural dyes, alizarin. The persistent trials to find a synthetic pathway from naphthalene to alizarin, supposed to be a naphthalene derivative, came to a dead end in 1868. Graebe then scrutinized this supposition via reduction of the dye. The reduction product was recognized as anthracene, a previously useless component of coal tar. Graebe proposed a structural formula for anthracene, $C_{14}H_{10}$, consisting of

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[33] French patent no. 70876, 21 March 1866; British patent no. 1093, 12 April 1866.

[34] French patent no. 71970, 16 June 1866; British patent no. 1912, 23 July 1866.

[35] C.E., *Dingl. pol. J.* (1878), **230**, 245–51, 351–5; An illustration of such a digester is given in A. Wurtz (ed.), *Dictionnaire de Chimie pure et appliquée* (first) Supplement 1880 (no date indicated, however, the relevant 'fascicules' are announced in *La Revue Scientifique*, 2nd series, (1880) **19**, 384). Early illustrations of digesters are reproduced in *Das Laboratorium* (1835), Heft 36, plate CXLII.

[36] For a recent discussion of the alizarin synthesis and the early development of the industrial production of synthetic alizarin see Elisabeth Vaupel, *Carl Graebe (1841–1927) – Leben, Werk und Wirken im Spiegel seines Brieflichen Nachlasses*, Ph.D. dissertation, Ludwig-Maximilians-Universität, Munich, 1987. Apart from the interesting historical analysis presented, the publication of Graebe's scientific correspondence and of correspondence between Caro and Perkin, and Caro and Liebermann in the second volume is an important feature of Vaupel's thesis.

three condensed benzene rings and reformulated alizarin as dihydroxy-anthraquinone $C_{14}H_6O_2(OH)_2$. The newly proposed formula was soon confirmed by the discovery of a synthetic pathway from anthracene to a dihydroxy-anthraquinone identical with alizarin.[37] However, this first synthesis, carried out by Graebe and Liebermann in 1868 and immediately patented, was of no use for industrial scale-up.[38]

The scientific and industrial world, alerted by the patent and the concise publications of the discoverers, sought out a profitable pathway. Within four months of the filing of the first patent a promising pathway from anthracene via anthraquinone and anthraquinone-sulphonic acids was found by Heinrich Caro of the Badische Anilin und Soda-Fabrik (BASF), jointly with Graebe and Liebermann. A new patent was filed at the London patent office on 25 June 1869. One day later Perkin delivered an almost identical patent.[39] The pathway via anthraquinone was found independently by the Hoechst firm but kept secret.[40] The Prussian patent of Graebe, Liebermann and Caro was rejected, and consequently the new route was protected only in Britain, France, and eventually also in the United States. In November 1869 Perkin patented another pathway via dichloro-anthracene and anthraquinone-disulphonic acid.[41]

The development of the laboratory recipes for alizarin into feasible industrial processes appeared to be highly problematic. It is possible to give a good picture of industrial alizarin production in 1870, around 1874 and around 1878, and consequently to reconstruct the development of alizarin technology during these formative years.

ALIZARIN PRODUCTION IN 1870

The 1870 picture results from the analysis of Perkin's retrospective paper on alizarin in the *Journal of the Society of Arts* of 1879 on 'The history of alizarin and allied colouring matters and their production from coal tar',[42] and the correspondence between William Perkin and his brother Thomas with Caro in 1870.[43] In Perkin's 1879 paper we find a description of the first industrial preparation of alizarin in his factory at Greenford Green. This used the anthraquinone route and can be summarized as follows:

> Crude anthracene ('green grease'), extracted from pitch, was purified by extraction with naphtha, filtration, and sublimation of the residue mixed with caustic soda. The purified anthracene was placed together with a potassium dichromate solution in lead-lined tanks. Dilute sulphuric acid was added, the energetic reaction was moderated, and then the mixture was boiled for 1–2 hours. The anthraquinone precipitate formed was separated by filtration and purified by sublimation from iron

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[37] See Vaupel, op. cit. (36), i, 122–41, and W. J. Hornix, 'The synthesis of alizarin', paper presented at the XVIIth Congress of the History of Science, Berkeley, 1985.

[38] British patent no. 3850, 18 December 1868.

[39] H. Caro, C. Graebe, C. Liebermann, British patent no. 1936, 25 June 1869, and French patent no. 88621, 18 January 1870; W. Perkin, British patent no. 1948, 26 June 1869.

[40] See *Dokumente aus Hoechster Archiven*, **42** *Beginn der Alizarin-Aera*, Hoechst AG, 1970: manuscript Dr Riese, 'Geschichte der Alizarinfabrik' (12 May–26 June), 46–8; Dr E. Lucius, 'Diarium', July 1874, 61–3.

[41] W. H. Perkin, British patent no. 3318, 17 November 1869, and French patent no. 90007, 16 May 1870.

[42] W. H. Perkin, *J. Soc. Arts* (1879), **27**, 572–602.

[43] Transcriptions of correspondence between Caro and Perkin (i.e. W. H. Perkin, T. D. Perkin, and Perkin & Sons) appear in Vaupel, op. cit. (36). The relevant letters are those dated 21 January till 3 June 1870 (SSDM 2170–2176, 2135–2143).

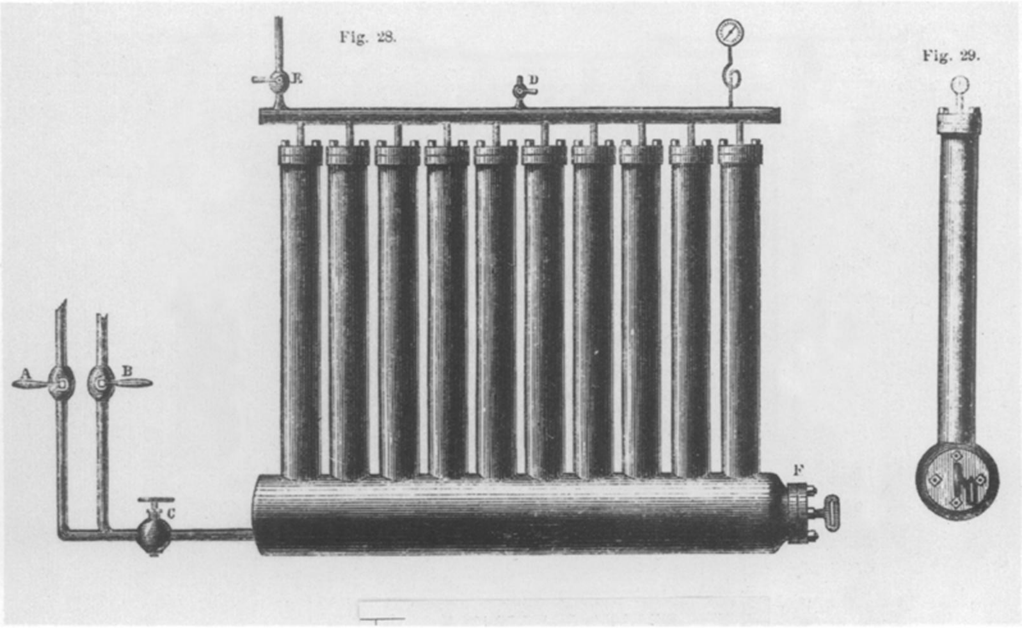

Figure 7.

retorts in large sheet iron cylinders. After further purification by crystallization from high boiling coal-tar naphtha, the dry anthraquinone was acted upon with Nordhausen (fuming) sulphuric acid, initially in glass retorts, but soon after in iron pots. Because of difficulties in supply, fuming sulphuric acid was replaced by concentrated sulphuric acid, but this required a higher temperature (270–280 °C). The anthraquinone (di-)sulphonic acid formed was treated with lime and soda solution to obtain the sodium salt. The sodium salt was mixed with a concentrated solution of caustic soda and heated in closed 'pressure tubes'. By treatment of the product of the alkaline melting process with dilute mineral acids the alizarin precipitated and could be separated by filtration.[44]

In the letters of the Perkin brothers to Caro we find sketches of the apparatus for anthracene sublimation, for anthraquinone sulphonation, for the transformation of the sulphonic acid into the sodium salt and its subsequent isolation, and for the alkaline melting process. These sketches are so similar to the detailed illustrations of the alizarin plant in the 1879 paper, which pretends to be up-to-date, that we might presume that in May 1870 the design of the definitive plant in many respects was completed. However, the plant described in the 1879 paper operated the dichloro-anthracene route. According to this paper Perkin started alizarin production along this route in June 1870. We must conclude that the results of the technical development along the anthraquinone route could be used in the construction of the plant operating the dichloro-anthracene route, and that part of the information about this plant is relevant for the industrial processes operated before June 1870.

The illustrations of the 1879 paper make the 1870 sketches of the sodium salt preparation plant and the alkaline melting and alizarin separation plant particularly

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[44] Perkin, op. cit. (42), 594.

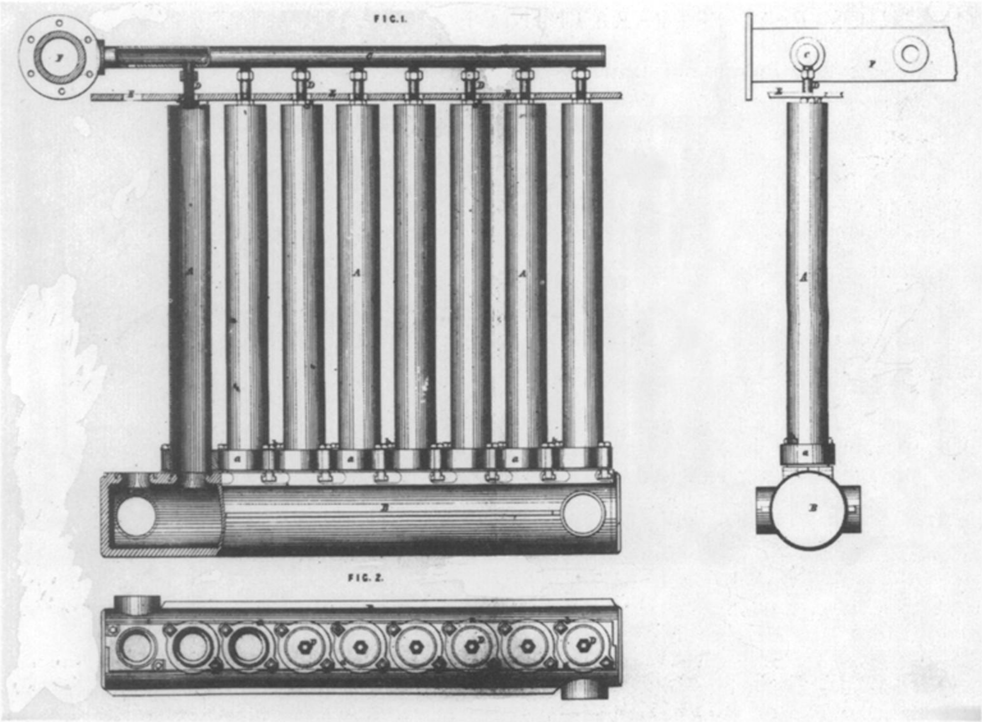

Figure 8.

impressive. The large capacity vacuum filtration appliances and 'pressure tubes' appear to be early inventions. Perkin describes his 'pressure tubes' also as 'Howard's patent safety boiler'. Perkin's figure of the alkaline melting and alizarin separation plant (not reproduced) is not clear with respect to this apparatus. However, the sketches of 1870, a more detailed drawing (Figure 7) and description from *Muspratt's Chemistry as applied to the Arts and Manufactures* (of about 1880) and the drawings of the relevant patents of Howard and Bousfield of 1866 (Figure 8) permit an understanding of Perkin's text, and clarify the origin.[45] The apparatus in use at Greenford Green was constructed of wrought-iron tubes and had a capacity of 150 gallons. It could withstand a pressure of 300 lb/sq. inch (about 50 atm.). It was easily emptied under pressure of steam and cleaned with water. Its function was that of a high-pressure digester of a much larger capacity than those already in use in the dyestuffs industry. The apparatus could well be considered as an adaptation of an important recent innovation in high-pressure steam generation to the needs of the alizarin industry.[46]

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[45] C. W. Vincent (ed.), *Chemistry, Theoretical, Practical and Analytical, Applied to the Arts and Manufactures* (no date, *c.* 1880), i, 518. This dictionary is generally called after its first editor, *Muspratt's Chemistry.*

The 'water-tube boilers' of J. Howard and E. T. Bousfield were protected by a long series of British and French patents. The most relevant are the first patents, British patent no. 226 and nos. 1811, 1866, and the equivalent French patent no. 72393.

[46] Perkin, op. cit. (42), 596.

THE INDUSTRIAL PREPARATION OF ALIZARIN IN 1874

Contemporary continental publications on alizarin chemistry and technology, in particular those written by Ott (1874), Wurtz (1875, 1876), Graebe and Liebermann (1876), and Auerbach (1873, 1877), permit the reconstruction of the industrial preparation of alizarin along the anthraquinone route as operated around 1874.[47]

Adolphe Wurtz's 1876 illustrated edition of his essay '*Progrès de l'industrie des matières colorantes artificielles*' is especially informative. His description is straightforward, and distinguishes three steps in the manufacturing process: (1) oxidation of anthracene, (2) sulphonation of anthraquinone resulting in anthraquinone disulphonic acid, followed by the preparation of the sodium salt, and (3) melting of this salt with caustic alkali, and the precipitation of alizarin.

From Ott (1874) and Graebe and Liebermann (1876) it is clear that, of the three alternative processes enumerated by Wurtz for *anthracene oxidation*, only the oxidation by potassium dichromate and dilute sulphuric acid was of practical importance. Ott described lead-lined tanks, the contents of which were heated by direct steam, not unlike Perkin's oldest appliances. Graebe and Liebermann mention an increase in yield by using finely divided anthracene or appropriate solutes (e.g. glacial acetic acid). The anthraquinone, prepared in this way, needed further purification. The best method was, according to Ott (1874) and Graebe and Liebermann (1876), treatment with three parts of concentrated sulphuric acid (66 °B) at 110 °C in vessels fitted with a steam jacket, followed by crystallization on trays, boiling with water, and filtration.

The *sulphonation process*, according to Wurtz, was carried out by heating anthraquinone and concentrated sulphuric acid at 260 °C in enamelled or lead-lined vessels equipped with a stirrer. These were mounted in a second vessel, serving as an oil bath, and built into a furnace under a hood (Figure 9).[48] However, Ott described sulphonation with Nordhausen sulphuric acid, which Graebe and Liebermann claimed was used exclusively in industry (40 per cent SO_3). Wurtz, therefore, was hardly up-to-date. The preparation of the sodium salt followed in the usual way, as in Perkin's early method. Ott adds that by fractional crystallization from the hot solution of the sodium salt at a density of 20 °B a salt separates, which by alkaline melting results in the blue shade ('*blaustich*') alizarin, and that from the salt separating after evaporation of the filtrate the red or yellow shade ('*gelbstich*') alizarin is obtained.

The *alkaline melting process* is illustrated by Wurtz (1876) with a drawing of a cast-iron melting apparatus very similar to his sulphonation reactor: the mixture of the sodium salt of anthraquinone-disulphonic acid and caustic soda was heated at 200–280 °C (Ott 170–220 °C) until a blue violet colour was reached. The melt was cooled, dissolved in water and the alizarin precipitated with mineral acid, filtered and washed. Some manufacturers, according to a footnote in Wurtz (1876), add 5–10 per cent potassium chlorate to the melt resulting in a more violet product. He explains, in error, that this occurs by the oxidative formation of purpurin from alizarin. Auerbach (1877) mentions the dividing of the alkaline melting process in two operations: when the melt had reached the proper consistency in the original reactor it was spread in thin layers on trays and heated in a kind of baking oven that permitted good contact of the product with air: this to prevent reduction of the alizarin

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[47] A concise but informative description of industrial alizarin preparation via anthraquinone is given by A. Ott, *Deutsche Industriezeitung* (1874), 425; A. Wurtz, *Progrès de l'industrie des matières colorantes artificielles*, Paris, 1876, is an illustrated separate edition of his contribution, under the same title, to the official French report on the 1873 International Exhibition in Vienna, published 1875; C. Graebe and C. Liebermann, *Das künstliche Alizarin*, Braunschweig, 1876, intended for the German report on the same exhibition, was only published separately; interesting technical information and its contemporary theoretical interpretation can also be found in G. Auerbach, *Das Anthracen und seine Verbindungen*, Berlin, 1873, and in the English edition: G. Auerbach, *Anthracen, etc.*, translated from a revised manuscript by W. Crookes, London, 1877.

[48] Wurtz, op. cit. (47), plate IV, fig. 12 (legends p. 192), descriptions, pp. 173–4.

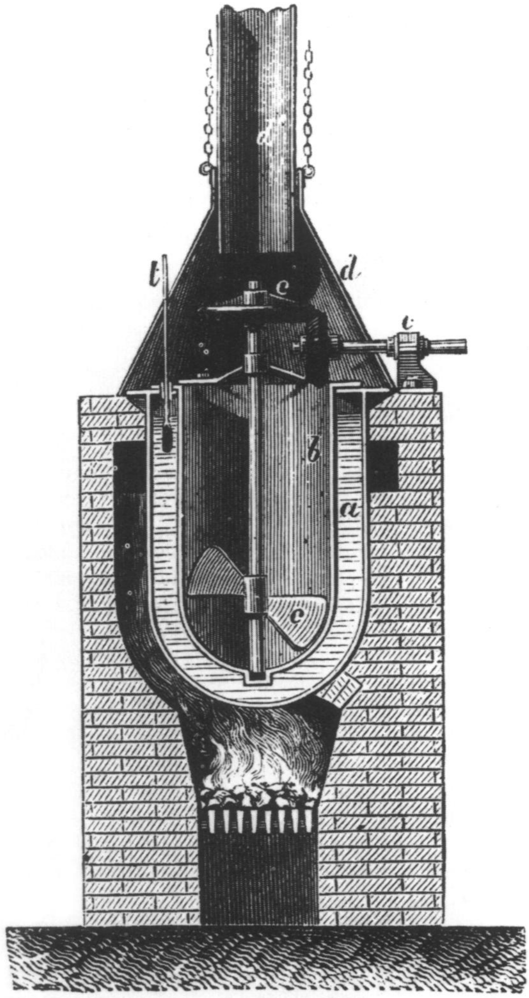

Figure 9.

already formed. To prevent losses, Auerbach advises that the melting should be completed in one apparatus: a strong iron boiler which can be closed and is capable of withstanding high pressure. 'As on melting under pressure a considerable amount of hydrogen is evolved, which reduces the sulpho-anthraquinonic acid to anthraquinon ... some manufacturers add chlorate of potash to the melt, which gives off oxygen at elevated temperatures and thus renders the hydrogen harmless.'[49] Graebe and Liebermann (1876) do not mention the addition of potassium chlorate nor the sodium salts separation method, which are both important innovations. Consequently, their essay was behind the times. Presumably this was because they were bound through their contractual obligations to BASF to keep this information secret.[50]

[49] Auerbach (1877), op. cit. (47), 152.

[50] Two letters from Graebe to Caro, dated 2 May and 8 June 1874 (SSDM 1987, 1988) and a letter from Liebermann to Caro of 12 July 1874 (SSDM 2094) clarify Caro's influence on the contents of Graebe and Liebermann (1876).

The variations and changes in production methods are associated with uncertainties and disputes with respect to the chemistry of the processes involved. The nature of the products of anthraquinone sulphonation and of the alkaline melting process was a source of considerable confusion. Graebe and Liebermann had concluded in 1871 that the sulphonation process resulted in anthraquinone mono- and disulphonic acid, and that the sodium salts are both transformed into alizarin by the alkaline melting process. This was also Auerbach's position in 1873. Ott reported in 1874 that, according to the manufacturers, the monosulphonic salt leads to yellow shade alizarin, and the disulphonic salt to blue shade alizarin. He himself presumes, however, the presence of an unknown yellow dye in '*gelbstich*' alizarin. Graebe and Liebermann concluded in 1876 from new researches that, depending on the proportions, anthraquinone-monosulphonic acid $C_{14}H_7O_2SO_3H$ and -disulphonic acid $C_{14}H_6O_2(SO_3H)_2$ are produced, the first leading to alizarin (violet shade), the second, mainly, if not completely, to isopurpurin (alizarin red shade). The alkaline melting process implies the substitution of one sulphonic acid group (HSO_3) by a hydroxy group (OH) and of one hydrogen atom (H) by a hydroxy group (OH), i.e. oxidation. Auerbach accepted this position in the reviewed edition (1877) of his survey of anthracene chemistry. We have already seen that the role of potassium chlorate in the alkaline melting process was also explained in different ways.

Clearly, halfway through the 1870s alizarin chemistry was not yet fully understood and alizarin technology along the anthraquinone route was not yet completely established: innovations which, in retrospect, appear to be very important were not sufficiently communicated or articulated. These innovations and their incorporation into alizarin technology only became common knowledge during the 1878 International Exhibition in Paris.

With respect to alizarin production along the dichloro-anthracene route the situation in 1874 was different. We might presume that Perkin's 1879 paper in the *Journal of the Society of Arts*[51] described the plant at Greenford Green in 1874, at the time he sold the factory to Brooke, Simpson & Spiller.

Anthracene purification was operated along the 1870 design: extraction of impurities with petroleum spirit, followed by dry distillation of the residue mixed with caustic soda. The last process was only understood after Graebe published in 1880 the isolation of carbazol from the residue of the dry distillation.[52]

Anthracene chlorination, a well-known laboratory process, was scaled up by Perkin to an efficient and safe industrial process. The preparation of sulphoanthraquinone acids from dichloroanthracene and the transformation of the acids into sodium salts, resulted from methods similar to those starting from anthraquinone. The separation of the sodium salts in those of mono- and disulpho-anthraquinonic acids was certainly not practised at Greenford Green before 1876, if ever. Perkin also mentioned the addition of potassium chlorate to the alkaline melt in his pressure tubes. However, high-pressure tubes were necessary, as long as the alkaline melting process in closed vessels was connected with the production of hydrogen, which is repressed by the addition of potassium chlorate. Perkin's solution to the pressure problem consequently became obsolete. Again, it is doubtful whether potassium chlorate was ever added at Greenford Green. Perkin perhaps updated his paper in 1879 without actual knowledge of manufacturing practice.

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[51] Perkin, op. cit. (42).

[52] C. Graebe, *Annalen der Chemie* (1880), **202**, 19–31.

There is, however, no doubt that Perkin's alizarin plant at Greenford Green in 1873 was a sophisticated, well-organized combination of operations and appliances far removed from a scaled-up chemical laboratory. It was capable of producing over a twelve-month period a quantity of 435 tons of 10 per cent alizarin paste.

THE INDUSTRIAL PREPARATION OF ALIZARIN IN 1878

We might presume that the dichloroanthracene route developed by Perkin at Greenford Green was not followed elsewhere. The process was more effective for the red shades (isopurpurin) than for the violet shades (alizarin). The process via anthraquinone, however, could be directed at will, and the main difficulties along this route were solved successively. We are well informed about the details of the alizarin production process for the anthraquinone route around 1878 via contemporary articles of Adolphe Kopp (1878), Graebe and Liebermann (1879), and Adolphe Kopp and Charles Girard (1880).[53] They used new information mainly originating from private communications of Bindschedler, one of the partners of the firm Bindschedler & Busch in Basle, to Kopp and to Graebe and Liebermann. Graebe and Liebermann presented the information as nearly literal citations and Kopp's formulations are almost identical. In the first supplement of the *Dictionnaire de Chimie* two illustrations explicitly originate from Bindschedler & Busch.[54]

Anthracene purification at Bindschedler & Busch started from 50–60 per cent anthracene. It was heated in a flat plate-iron retort at up to 200 °C, and sublimated with the help of a stream of superheated steam, which transported the anthracene vapour to a chamber, where it was condensed by a fine shower of cold water. The resulting anthracene was 95 per cent pure. Anthraquinone was prepared, as usual, by oxidation of a 200 kg charge of anthracene with potassium dichromate and diluted sulphuric acid, in 600 l lead-lined vats agitated by stirrers and heated by a stream of superheated steam. Filtration, followed by washings and centrifugation resulted in a still very impure product. Purification by solution in concentrated sulphuric acid at 100 °C, followed by crystallization and precipitation in boiling water and filtration in a filter press resulted in 122 kg anthraquinone, 90 per cent pure. Subsequent sublimation, similar to that for anthracene purification gave a 98 per cent pure product.

The sulphonation was carried out with fuming sulphuric acid (45 per cent SO_3) in the proportions of 100 kg anthraquinone to 100 or 200 kg sulphuric acid for the preparation of nearly pure alizarin (no V, 'violet') or alizarin containing isopurpurin and flavopurpurin ('*nuance jaune*') respectively. The sulphonation apparatus shown in Wurtz (1880) is reproduced from Wurtz (1876). Neutralization of the sulphonated anthraquinone with caustic soda lye gave, after cooling, a precipitate of the sodium salt of anthraquinone monosulphonic acid, the starting material for alizarin 'violet'. Concentration of the filtrate to 30 °B resulted in precipitation of sodium sulphate. Filtration and evaporation until dry give the starting material for red shade alizarin ('*nuance jaune*').

The most interesting part of the Bindschedler & Busch alizarin plant is the alkaline melting apparatus. neither in Kopp (1878) nor in Graebe and Liebermann (1879) do we

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[53] The most informative source is A. Kopp, 'Anthracène et alizarine artificielle', *Moniteur Scientifique* (1878), **20**, 1147–68, which is a part of his report 'L'industrie chimique à l'Exposition universelle de 1878' in this periodical. C. Graebe and C. Liebermann, *Moniteur Scientifique* (1879), **21**, 394–428 is a translation into French of their essay *Das künstliche Alizarin* of 1876, supplemented with new information. The article 'Alizarine artificielle (Industrie)', of A. Kopp and C. Girard, in Wurtz (1880), op. cit. (35), i, pp. 93–101, leans heavily on Kopp's *Moniteur Scientifique* article and on Wurtz's (1876), op. cit. (47), essay.

[54] Wurtz (1880), op. cit. (35), i, fig. 4, 5, p. 95, and fig. 8, p. 100, fig. 8 is reproduced here as Figure 10.

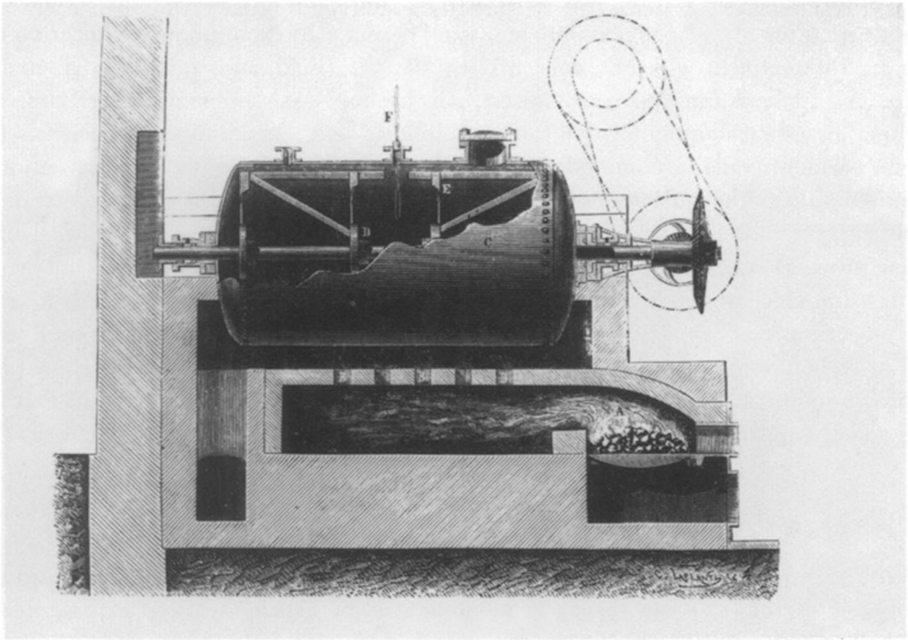

Figure 10.

find a description. However, Wurtz (1880) gives a detailed engraving, obtained from Bindschedler & Busch, which shows a horizontal cylindrical closed reactor, 'similar to a steam boiler', supplied with agitator and thermometer (Figure 10).

> The apparatus was charged with sodium salt, caustic soda solution and potassium chlorate, and heated to 165–170 °C. When the melt was ready (after two days) the reactor was emptied by the pressure of steam and the alizarin was precipitated with acid, and filtered and washed in a filter press.

From later publications we learn that the pressure reactor was in use over a long period.[55] It clearly belonged to the tradition starting from the ordinary steam boiler, adapted for chemical reactions and extraction: fat hydrolysis as in the apparatus of Delapchier (1854) and Droux (1876), and magenta extraction as in the apparatus shown by Girard and de Laire (1873). High-capacity steam boiler technology could be put to use for alizarin production when the production of hydrogen during the alkaline melting process, causing very high pressures, could be suppressed by addition of potassium chlorate. It is remarkable that, in his 1879 paper, Perkin did not mention this important innovation. His paper wrongly suggests that the 'pressure tubes' in use at Greenford were a common and stable feature of the two pathways.

Comparing the alizarin technology as presented by Adolphe Kopp, by Graebe and Liebermann, and by Kopp and Girard, with the later descriptions, it can be concluded that the main problems of alizarin production using the anthraquinone route were solved by

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[55] See I. Levinstein, *J. Soc. Chem. Industry* (1883), 213–27; M. l'Abbé Vassart, *Étude sur l'alizarine artificielle*, Paris, 1887, 70; P. Bolley, E. Kopp, R. Gnehm and R. Meyer, *Die Theerfarbstoffe*, Braunschweig, 1895–97, 1661–86.

1878. Anthracene purification was perfected by improved extraction and sublimation methods resulting in a 95 per cent pure industrial product. Anthraquinone purification was perfected by treatment with hot, concentrated sulphuric acid, an invention attributed by Graebe and Liebermann (1876) to Gessert, and by improved sublimation methods. The sulphonation of anthraquinone with fuming sulphuric acid was economical when this acid became a widely available commodity during the first half of the 1870s. The separation of the sodium salts of the anthraquinone sulphonic acids, described in 1874 by Ott, was of the greatest importance for the preparation of products of consistent quality. The alkaline melting process became very effective after the introduction of pressure boilers and the use of potassium chlorate, both credited to Koch, a chemist of Gessert in Elberfeld. Most of these inventions can be placed before 1874 but were presumably kept secret. It took seven years or so before the processes described in the original patents could be developed into full-grown industrial processes, partly because the basic technological inventions that had to be added required a few years for their transfer across the fences of the factories.[56]

PHTHALEINS, TRIPHENYLMETHANE AND AZO DYES

Next to the introduction of synthetic alizarin and the further extension of the substituted rosaniline dyes, the 1870s saw the introduction of three process innovations with significant industrial consequences.

The first was Adolf Baeyer's condensation of phthalic anhydride (an oxidation product of naphthalene) with phenols into the so-called 'phthaleins'. The most conspicuous phthalein compound was fluorescein, an extremely powerful coloured substance, prepared from phthalic anhydride and resorcinol.[57] However, it was not a dye. In close cooperation with Baeyer, Caro found in 1874 that the product of bromination of fluorescein was a remarkably good dye, and it was marketed in the same year as 'eosin'.

Soon other halogen-, nitro-, and alkyl- substitution products of fluorescein appeared to be brilliant dyes. It is striking that most of these discoveries were not covered by patents. Caro and Baeyer hoped, in vain, that the processes could be kept secret. Hofmann quickly

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[56] We have the opportunity to note a manufacturer's perspective of early alizarin technology in Carl Glaser, 'Erlebnisse und Erinnerungen nach meinem Eintritt in die BASF im Jahre 1869', typescript, Heidelberg, 1921, held at the archives of BASF, Ludwigshafen. During the 1870s Glaser was responsible for the development of the alizarin plant of the BASF.

The main obstruction preventing regular alizarin production at BASF was, according to Glaser, the preparation of the product through fusion of sodium sulphoanthraquinonate with caustic soda. The simple and effective laboratory process could not be scaled up. After almost two years of unsuccessful experimentation, Glaser was informed that Hoechst had obtained good results by using a kind of baking oven in which the molten mixture was heated on trays. Its introduction towards the end of 1871 removed the last hindrance to industrial production. It took another five years (until 1876) before the oxidation involved was uncovered, and the improvement brought about by adding oxidants to the mixture and melting in pressure boilers was introduced. Again the acquisition of 'classified' information was essential: a former employee of Gessert informed Glaser that the firm used horizontal high-pressure reactors with stirring appliances and added potassium chlorate.

A similar story can be reconstructed from Dr Rose, 'Alizarinrot oder Entwicklung der Alizarinfabrikation', in *Geschichte und Entwicklung der Farbenfabriken vorm. Friedr. Bayer & Co, Elberfeld, in den ersten 50 Jahren*, Munich, 1918, 291–6 (not published, held at the archives of Bayer AG, Leverkusen).

[57] A. Baeyer. *Berichte der Deutschen Chemischen Gesellschaft* (1871), **4**, 555–8, 658–65 (1875), **8**, 146–8.

recognized eosin as a derivative of the already well-known compound fluorescein and the publication of his results opened the field to many competitors.[58] At the 1878 International Exhibition thirteen phthalein dyes were shown under a variety of names, sold by several manufacturers.[59]

The second important discovery, also from Baeyer's laboratory, now in Munich, was the recognition of rosaniline, the base of magenta, as triamino-triphenylcarbinol $HO \cdot C(C_6H_4NH_2)_3$, and the proof of this structure by synthesis, as carried out by E. and O. Fischer. It was recognized that the rosaniline dyes and many phthaleins have close chemical relationships to a common 'mother substance': triphenylmethane $CH(C_6H_5)_3$. These theoretical results opened new synthetic pathways for triphenylmethane dyes. The first one prepared on the basis of the new insights was malachite green made by condensation of benzotrichloride and dimethylaniline, patented by Doebner on 26 February 1878, and by condensation of benzaldehyde and dimethylaniline, a process discovered by O. Fischer in 1877, and developed afterwards into the most economical method of preparation. Before 1888 some fifteen dyes prepared with the new condensation methods were marketed. Most of these dyes, or better the processes, were protected: fifty-two German patents on condensations leading to triphenylmethane dyes during the period 1877–87 (of 420 patents in class 22).[60]

The third and, in retrospect, most spectacular innovation of the 1870s was the discovery of the azo dyes, resulting from the 'coupling reaction' of diazo compounds (i.e. unstable compounds of aromatic amines and nitrous acid, already well known from the research of Peter Griess in the late 1850s and the 1860s) and aromatic amines or phenols. The self-professed discoverers of the azo dyes (Z. Roussin, H. Caro, O. Witt and P. Griess) all tried to keep the process secret. Again Hofmann appeared to be able to uncover the secret by analysing two of the first azo dyes shortly after they were marketed. Witt and Griess claimed 'scientific priority' by publishing part of their results.[61] Then a long series of patents on azo dyes, 130 German patents in the period 1877–87, and 105 marketed dyes reflected the intensive innovative activity in this field.[62]

The development of the new laboratory processes into industrial methods did not offer problems to the industry. The condensation reactions leading to triphenylmethane dyes could be realized with appliances already in use. The coupling reactions for azo dyes called for very simple reactors fitted with mechanical stirrers; adequate cooling could be achieved by addition of ice, then already an available commodity, to the reaction mixture. The isolation and purification of the dyes produced could be carried out with known methods

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[58] A. W. Hofmann, *Ber.* (1875), **8**, 62–6.

[59] C. Lauth, *Exposition Universelle Internationale de 1878 à Paris*. Rapport sur les produits chimiques et pharmaceutiques. Group V, Classe 47, Ch. 1: Matières premières de l'industrie des couleurs artificielles, Paris, 1881.

[60] This is based on information in E. Fischer and O. Fischer, *Ber.* (1878), **11**, 195–201, 612–13, 1079–82, 1598–9, 2095–9; (1879), **12**, 791–6, 796–803, 2344–53; *Ann.* (1878), **194**, 242–303; O. Doebner, German patent (DRP) no. 4322, 26 February 1878; O. Fischer, *Ber.* (1877), **10**, 1623–6; O. Doebner, *Ber.* (1878), **11**, 2274–7; and patent statistics derived from Friedländer (1888), op. cit. (2), and market information from Schultz and Julius, op. cit. (13).

[61] A. W. Hofmann, *Ber.* (1877), **10**, 213–18, 1378–81; O. Witt, *Ber.* (1877), **10**, 654–62; (1879) **12**, 259–62; P. Griess, *Ber.* (1877), **10**, 525–30; (1880), **12**, 483–9.

[62] Derived from Friedländer (1888), op. cit. (2), and Schultz and Julius, op. cit. (13).

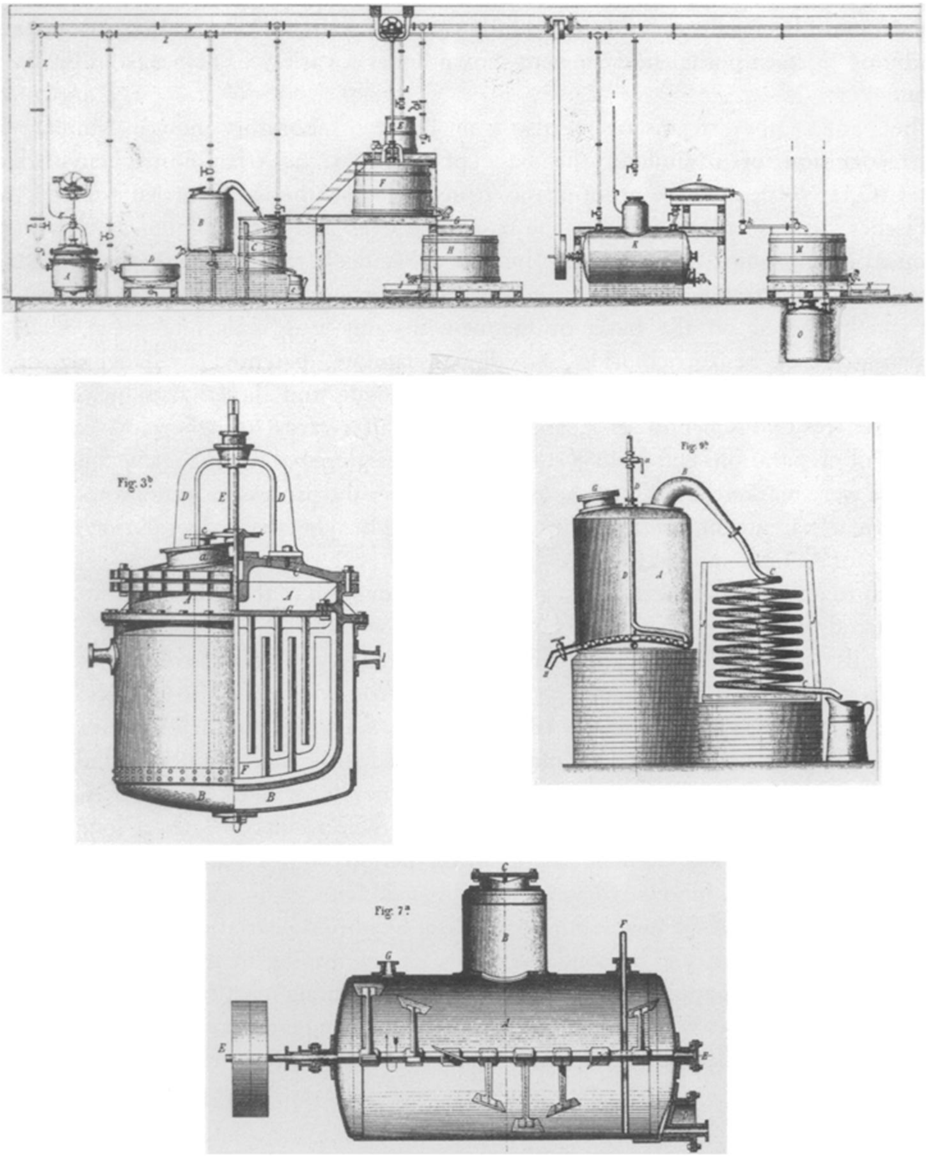

Figure 11.

and available appliances. Also the development of the laboratory preparations for intermediates into industrial processes profited from the experiences of the first twenty years of the synthetic dye industry.

A clear view on the state of the art during the second half of the 1880s can be obtained from a series of articles on dyestuffs manufacture in *Dinglers polytechnisches Journal* by Otto Mühlhäuser (from 1885 to 1887); from Karl Heumann's monograph *Die Anilinfarben* *und ihre Fabrikation* (1888), which leans heavily on these articles, and from Mühlhäuser's *Die Technik der Rosanilinfarbstoffe* (1889), which supplies detailed technical drawings of industrial appliances and complete plants. (The latter are missing in his articles in *Dinglers polytechnisches Journal* except for the plant for magenta production.) The drawings of the malachite green plant, and of a few of its details, are shown and explained as a demonstrative example.

Figure 11 shows the reactor *A* for the preparation of 'leucobase' of malachite green (i.e. the colourless reduced base of the dye) from benzaldehyde, dimethylaniline and chloride of zinc. The distillation apparatus *B*, *C* removed unused dimethylaniline by steam distillation, while the evaporator *D* separated the leucobase. The latter was transported to the reactor *F* for oxidation in an acid solution with lead peroxide, and for the subsequent precipitation of the lead as sulphate. The hot fluid passed through the filter box *G* to enter the vessel *H* where an insoluble malachite green–zinc chloride compound was precipitated by adding salt and zinc chloride, which compound was separated in the filter box *J*. In the extraction apparatus *K* the malachite green–zinc chloride compound was treated with hot water and, in molten form, filtered through the pressure filter *L* into *M*. Here ammonia was added which precipitated the base, separated by filtration through the filter box *N* and dried by centrifugation (not shown). The transformation into the oxalate and the crystallization is not shown here. Detailed drawings of *A*, *B*, *C*, and *K* are reproduced.

It is interesting to note that these appliances appear also as parts of other plants shown by Mühlhäuser (e.g. the magenta production plant). He lists, for every dye, the appliances needed for the industrial production just by giving names (e.g. extraction boilers, evaporation pans, steam distillators) and by specifying their capacities. The plants appear as organized combinations of standardized apparatus. A comparison of the apparatus and plants in Mühlhäuser's monograph with those of later publications justifies the conclusion that at the end of the 1880s dyestuffs technology can be considered a well-established practice, ready for the theoretical 'unit operations' approach of the twentieth century.[63]

CONCLUSIONS

The detailed descriptions and analyses in this paper allow some general conclusions:

1. Innovation in the synthetic dye industry before 1890 was, in the first place, process innovation. Few appliances were protected by patents of dyestuffs chemists or manufacturers. This is in sharp contrast with other branches of chemical manufacturing, the coal-tar distilleries included.
2. The appliances used in the synthetic dye industry developed towards more or less standardized formats for general use, although special problems called for special solutions.
3. It is not adequate to characterize the industrial appliances used in the synthetic dye industry as scaled-up laboratory apparatus: reactors with steam jackets, pressure filters, extraction boilers etc. do not originate from the bench.
4. Much apparatus was derived from other technologies such as steam technology, the hydrolysis of fats, the purification of fatty acids, and the extraction processes for natural dyes. William Perkin and others may have started from scratch but they were

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[63] Bolley, Kopp, Gnehm and Meyer (1896), op. cit. (55).

quick to borrow ideas and techniques from more developed engineering-based industries.

5 Communication of new knowledge about processes was extremely rapid via the patent system. Secrecy about chemical processes leading to marketed dyes was negligible after 1877. It was by then clear that secrecy about processes could only give a lead of a few months.

6 The description of new knowledge about chemical appliances was much slower. Because of lack of recognized innovative content it was not possible to take out patents. Retaining secrets about appliances longer than a few years was impossible, if not because of industrial espionage then because of the mobility of chemists and technicians.

7 The role of the International Exhibitions in the dissemination of dyestuffs technology was very important and suggests further research. We have no overview of the material distributed by chemical industries and no insight into the communication between the participants from industry and science. Poirrier and Bindschedler & Busch seem to have followed a much more communicative policy than other manufacturers.

8 The investigation of chemical technological illustration promises interesting contributions to the history of chemical technology. Illustrations are important for the characterization of innovations in apparatus. Sources are generally not mentioned. A genealogy of technical illustrations could be helpful for the construction of a chronology of technical innovations.