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978-1-316-60693-3 - The Chemistry of Dyestuffs: A Manual for Students of
Chemistry and Dyeing

M. Fort and L. L. Lloyd

Excerpt

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CHAPTER I

HISTORICAL INTRODUCTION TO THE CHEMISTRY OF THE DYESTUFFS

IN 1856 Perkin obtained a colouring matter from crude aniline by oxidation and put it on the market as "Mauve¹." Until that date the whole of the available colouring matters were of natural origin, chiefly vegetable, along with a few insect products like cochineal and lac dye, and a few mineral pigments, e.g., Prussian blue and chrome yellow. Since Perkin's discovery there has arisen a synthetic dyestuff industry developing with unequalled rapidity, until now the human taste for colour in all kinds of fabrics and tissues, in paints, varnishes, foodstuffs, etc., is almost entirely met by employment of synthetic products which did not previously exist in Nature, the materials and methods of scores of earlier generations being discarded wholesale, except in a few instances where natural dyestuffs are still able to compete with the synthetic products for special requirements. The old established natural dyestuffs have not been displaced without a struggle, and even

¹ This colouring matter was in use for postage stamps until the end of Queen Victoria's reign, long after it had been superseded for other purposes.

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now one finds remnants of a diminishing prejudice against "aniline dyes" in the popular mind, but scientifically regarded the distinction between natural and artificial dyestuffs is an arbitrary one, relating only to their origin. Thus we now have Alizarin, an artificial dyestuff, replacing Madder, not, however, by providing merely an imitation, for Alizarin is the actual colouring matter contained in Madder, only in a pure form produced synthetically.

The economic changes wrought by this revolution in the colouring industries have been far-reaching; large areas of land have had to be turned to fresh uses, and on the other hand a growing importance has become attached to certain materials previously regarded as waste products. Although the industry of dyestuff manufacture is relatively speaking quite young, economic changes of considerable import have occurred, and when war broke out Germany was the seat of the industry, while Switzerland held a distant second place as a producer of synthetic dyestuffs, Great Britain coming third. The reasons for this country's failure to retain the lead given to the home of a new industry are still the subject of occasional debate, but it may be stated that, although the accident of birth of "Mauve" was apparently greatly in Great Britain's favour, Germany was in every way more fitted to develop an industry which necessarily had to rest more and more on an absolutely scientific basis. As this gradually came about, the development naturally proceeded most rapidly in Germany, where the influence of Liebig and others had given a dignity and importance to chemical science such as it obtained in no other country. In consequence an army of workers in this branch of

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Excerpt

[More information](#)*Historical Introduction*

3

technical science was more readily mobilised, as was also capital for working industrial enterprises having a chemical basis. Other causes, such as the patent laws and the restrictive measures against the use of alcohol—an absolute necessity in the early days of the synthetic dyestuff industry—have also operated in Great Britain's disfavour.

Unfortunately it has been treated by certain German scientists and statesmen as a fair occasion for self-congratulation and a proof of superior national genius that this great industry should have found its chief seat in Germany. In the middle of last century British genius and capital were being applied to colonial expansion and the development of mechanical inventions which have since brought changes even more sweeping than have followed from the discovery of Mauve—and be it added, immensely more profitable to Great Britain than the coal tar dyestuff industry has yet been to Germany. The outbreak of war in 1914 however cut off the German supply and brought up the question as to whether the time had not come to encourage British enterprise in this industry. It is greatly to be hoped that the attempt will be successful, which it can, only by receiving scientific aid.

Of the comparatively few British chemists who have given serious attention to this branch of technical science, a relatively large number, comparing favourably with those of any other country, have achieved international fame, and as the British industry comes to demand more there need be no doubt of their being found.

Previous to the discovery of Mauve, picric acid and rosolic acid had been produced artificially without

1—2

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Excerpt

[More information](#)

4

Chemistry of Dyestuffs

finding commercial use as colouring matters, although since then both have been used as such. Perkin's discovery was made valuable by an almost contemporary event, i.e., Mansfield's success in separating benzene from coal tar, in which it had been discovered by Hofmann. The benzene was crude, and on nitration and reduction gave a crude aniline, which was the substance employed by Perkin.

Research at that time was at an empirical stage, and aniline was treated indiscriminately with all kinds of reagents. In 1859 Verguin obtained Magenta, Fuchsin or Rosaniline from crude aniline. Girard and de Laire in 1860 obtained a spirit-soluble blue by heating Magenta with aniline. In 1862 Nicholson sulphonated Aniline Blue and made it water-soluble, thus obtaining the first true acid dye, the Soluble Blues, which are still in extensive use, as is also Magenta. In 1863 came Hofmann Violets, soon to be superseded by the Methyl Violets. About this time the researches of Hofmann, Rosenstiehl, and E. and O. Fischer, went far towards explaining syntheses in the triphenyl-methane series, comprising Magenta and its derivatives. The period of activity in discovery of Rosaniline derivatives lasted until about 1877. Meanwhile colouring matters of other groups were being discovered: in 1862 Phosphine, the first yellow dye, by Nicholson; in 1863 Safranine, by Perkin; in 1864 Bismarck Brown, the first azo dye, and Martins Yellow, both by Martins and Caro.

The formulation of Kekulé's theory of the benzene ring in 1865 gave great impetus to synthesis in the field of dyestuffs. Empirical methods gave way before scientific methods of research, and the new era of

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Excerpt

[More information](#)*Historical Introduction*

5

scientific progress was strikingly inaugurated by the synthesis of Alizarin in 1869 by Graebe and Liebermann. The next ten years were very productive of new discoveries, especially in the class of azo dyes, now by far the most numerous class of dyestuffs in use. A corresponding falling-off in the discovery of Rosaniline derivatives was experienced, and since then activity in the production of new colouring matters of this class has subsided until now it is almost quiescent. On the contrary new azo dyes are constantly being brought out, and patent literature is still actively concerned with the registration of many valuable additions to the class.

In 1880 Adolf von Baeyer accomplished the first synthesis of indigo. Artificial indigo did not however become a commercial product for many years, and its present success is one of the most noteworthy achievements of chemical science backed by industrial enterprise.

The first direct cotton dye, Congo Red, was discovered in 1884 by Böttiger, and in 1887 the first cotton dye to be developed by diazotisation *in situ* on the fibre was discovered by Green, and appeared on the market as Primuline. Meanwhile the new class of insoluble azo dyes, produced on the fibre by successive treatments of cotton with the requisite components, was introduced in 1880 with Para-nitraniline Red (Para Red) by the firm of Holliday.

In 1893 Vidal patented the first important sulphide dye, Vidal Black, and a period of great activity in the discovery of new dyes of this class began, which has lasted up to the present but now shows distinct signs of falling off, at any rate until a more intimate knowledge of the structure of these compounds is rendered

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[More information](#)

available. The last stage of development is marked by the discovery of Indanthrene Blue by Bohn in 1901, which was the beginning of a new series of vat dyestuffs, since enriched by many syntheses of indigo derivatives. Synthetic indigo had meanwhile begun to seriously compete with the natural product, and from 1906 to 1914 the acreage under indigo cultivation in India fell from 420,000 to 150,000. The cutting off of German synthetic indigo by the European war again stimulated indigo planting, but there are no available data.

At present great activity prevails in the synthesis of vat dyestuffs, which possess a unique degree of fastness along with valuable tinctorial properties. The demand for greater fastness has been most successfully met, not only by the introduction of new vat dyestuffs, but by many and great improvements amongst the older classes of synthetic dyes, notably in mordant dyes admitting of improved methods of dyeing. The term "aniline dye" or "coal tar dye" now only conveys reproach where densest ignorance prevails, and as this is yet by no means uncommon, it is carefully ministered to in certain cases, as in the Oriental carpet trade, where the steady demand for native workmanship has not prevented, nor been at all impaired, by the unobtrusive replacement of vegetable dyes used since remote antiquity by the generally superior synthetic colouring-matters, products entirely of our own age.

In close conjunction with the progress of the synthetic dyestuff industry has been the development of other synthetic aromatic products derived from the raw materials found in coal tar. New drugs, artificial perfumes, explosives, disinfectants, and many important bodies which do not fall into any of these classes, as

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Excerpt

[More information](#)

Historical Introduction

7

for example saccharine, have been discovered and are manufactured by the colour firms as side-products of the great coal tar dyestuff industry.

Additional reference may be made to the trade journals from the outbreak of war in August 1914 to the establishment of the Government scheme in 1915. Also to the following papers:

“The Artificial Colour Industry,” F. M. Perkin, *Jour. Soc. Dyers*, p. 338, 1914.

“The Coal Tar Colour Industry of England,” I. Singer, *Jour. Soc. Dyers*, p. 124, 1910.

“Tinctorial Chemistry: Ancient and Modern,” R. Meldola, *Jour. Soc. Dyers*, p. 123, 1910.

“The Relative Progress of the Coal-Tar Industry in England and Germany,” A. G. Green, British Assoc. 1901, *Jour. Soc. Dyers*, p. 285, 1901.

CHAPTER II

TAR DISTILLATION

Production of Tar

I. THE most plentiful supply of tar is obtained during the decomposition of bituminous coals for the production of coal gas. The coal is heated in retorts at about 900° C. to 1000° C., at slightly reduced pressure, to remove the gas from the hot retorts as quickly as possible. The gas is cooled artificially in order to condense the substances of low boiling point. After cooling, it is necessary to remove tar that is suspended in a very finely divided condition in the gas. This is done by passing the gas under about 20 inches of water pressure through a “Tar Separator.” The whole of the

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[More information](#)

condensed portion is then allowed to mix. This separates into an aqueous upper layer and a lower layer of tar. The aqueous layer contains ammonia and small quantities of tarry substances in solution.

II. A large, increasing supply of tar is obtained from coke ovens. The coal is heated to a higher temperature than in the production of coal gas.

The tar is much thicker and contains a larger quantity of free carbon than coal gas tar.

III. A fairly large amount of tar is obtained by cooling the waste gases from blast furnaces, and this tar contains phenols of high molecular weight and of high germicidal value, with a large amount of free carbon.

IV. During the preparation of charcoal by the distillation of wood, there is obtained a distillate which separates into two layers; the upper aqueous layer is used for the manufacture of acetone, methyl alcohol, and acetic acid; the lower layer furnishes wood tar from which creosote (crude guaiacol) is obtained.

Different classes of tar are also obtained from the following processes: the distillation of bituminous shale; the manufacture of oil gas; the partial decomposition of oils by "cracking," the oils being delivered in thin streams into very hot retorts, the distillation of crude mineral oils, etc.

A different variety of coal tar is obtained by the distillation of coal at comparatively low temperature, viz., at about 400° C. to 450° C.

Composition of Tar.

The composition of tar varies with the source, and in the case of coal tar with the coal and temperature of distillation.

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M. Fort and L. L. Lloyd

Excerpt

[More information](#)*Tar Distillation*

9

Fatty and aromatic hydrocarbons have been extracted from coal by means of solvents, but the amounts of such substances are usually very small. Paraffin hydrocarbons and hexahydrofluorene have been obtained.

The yield, as well as the relative amounts of the constituents of the tar, varies with the class of coal. The brown or young coals (lignite) give more fatty compounds and also more tar than the short flaming or older coals. The older or the less bituminous the coals, the smaller will be the amount of low boiling point constituents in the tar, and the higher will be the amount of anthracene and like compounds.

By the distillation of coal, for the manufacture of patent fuel, at low temperature, viz. 400° C. to 450° C., there is obtained a tar, which is fairly rich in low boiling hydrocarbons, a large percentage consisting of paraffin hydrocarbons. The so-called benzol from this tar, on account of the presence of other than aromatic hydrocarbons, is of no use for the manufacture of nitrobenzene.

In the distillation of caking coals, for the manufacture of coal gas, it is general to calculate upon a yield of 10 gallons of tar per ton of coal. This figure is only a rough guide, the quantity varying very much with the kind of coal.

It has been shown recently by Pictet and others that coal from Montrambert yields a mixture of hydrocarbons by extraction with boiling benzol. Among others hexahydrofluorene has been separated. By the distillation of coal in vacuum a tar is obtained, free from phenolic substances, containing a large proportion of basic compounds, but practically free from the aromatic bodies naphthalene, anthracene. This vacuum tar is decomposed by ordinary distillation with production of benzol,

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naphthalene and anthracene. From this it appears that the aromatic compounds in tar are pyrogenetic decomposition products.

At about 900° C. to 1000° C. there is a maximum yield of benzene compounds with a good illuminating gas; higher temperatures give more gas, but of less illuminating power, and the tar is richer in the more complex aromatic compounds.

Coal tar is a black viscous liquid, Sp. Gr. 1·1 to 1·2, and contains many aromatic compounds, the chief of which are now given.

Hydrocarbons: benzene, toluene, xylenes and other homologues, naphthalene and its homologues, acenaphthene, fluorene, anthracene, phenanthrene, pyrene, chrysene, etc.

Neutral compounds: carbon disulphide, thiophene and its homologues, carbazol, etc.

Bases: pyridine and its homologues, quinoline, isoquinoline, aniline, acridine, etc.

Phenolic substances: carbolic acid, cresylic acids, naphthols, etc. .

Practically all of these compounds are employed in the colour industry, although many are not separated as such from tar, but may be made from a more easily obtainable constituent, e.g., aniline from benzene, naphthols from naphthalene.

Gas tar contains roughly about 2 per cent. benzol, 0·5 per cent. toluol, 0·6 per cent. phenol, 5 to 6 per cent. naphthalene and 0·6 per cent. anthracene.

On distillation the tar is divided, as described later, into four or five parts.

The **light oil** contains roughly 5 to 15 per cent. phenols, 1 to 3 per cent. basic substances, 0·1 per cent.