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Fibre-Reactive Dyes

W. F. BEECH



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Foreword

One cannot be certain whether dyeing or fermentation is the more ancient manifestation of man's interest in applied chemistry. Both derive from the desire to satisfy subjective rather than objective needs. Both played their part in the ancient mysteries. Oddly enough, this connection, remote in time, was remade in the more recent period since it was while employed by a brewery that Peter Griess discovered in 1862 the diazo reaction, which provides the basis for the azo chromogenic system. This is unknown in nature and provides the most important single chromogen in the whole gamut of synthetic dyes. However, in modern times every man feels qualified to pronounce on the quality of his ale while dyeing and colour in general are still viewed as a mystery exciting appreciative wonderment. The maintenance of this differentiation is interesting because the manufacture of synthetic dyes is over a hundred years old, has provided the origins of the organic chemical industry; and supports at the present time a very large research and technical effort on an international scale.

Although Perkins' discovery of Mauveine in 1856 was initiated by chance, it was not long before chemists were able to decide the general kind of chemical structures required for particular end uses. Some thirty years after Perkins' discovery, Böttiger produced the theories and results that have provided the basis ever since for the synthesis of dyes with good affinity for cellulose. Colour chemistry became, from that point, more than just a hopeful search among coloured organic chemicals for useful dyes. It began to develop its own ideas and systems and established itself in that period as an academic discipline at Leeds. The essence of Böttiger's conclusions was that good economy in use and good fastness to washing could be conferred on a dye structure by introducing particular molecular configurations.

This is not the only way of achieving these objectives, however, and much of the driving force leading to progress and variety in dyestuffs research has been the desire to achieve high fastness to wet treatments by any means possible. Among the many ingenious solutions to this problem which have been examined and found to be of value, one of the earliest to be considered was the binding of dye molecules to substrates by the formation of a covalent link. The idea was shown to be feasible by Cross and Bevan as early as 1895 but the practical difficulties remained insurmountable until 1956, when fibre-reactive dyes appeared for the coloration of cellulose fibres.

It is the work of the past seventy or so years, and in particular the last fifteen, which provides the material for Dr. Beech's book. He has seen the developments take place at close hand and has taken the necessary step of drawing together the current knowledge before it becomes too diffuse for ready examination. Few dyestuff classes have expanded more rapidly in number and variety than has that of the fibre-reactive dyes. From three dyes available in 1956 and a few relevant patent specifications the number of fibre-reactive dyes has leapt into the hundreds, exceeded in rate growth only by the weight of patent specifications. A guide book has clearly become necessary, particularly for those not closely involved in the developments from the beginning and it is this which Dr. Beech has been able to provide.

Leeds,
November, 1969

I. D. RATTEE

Preface

Although nearly 15 years have passed since Rattee and Stephen succeeded in solving a major problem, which had engaged the attention of many able dyestuffs chemists during the previous 60 years, no textbook has yet appeared either in English or in German describing the vast new technology created by their fundamental discovery. Admittedly, several excellent reviews on fibre-reactive dyes and related topics have been published from time to time, but a definite need now appears to exist for something much more comprehensive, such as would collate the vast and rather scattered literature and prove useful not only in providing the research worker with a coherent record of what has already been achieved and of the relevant literature but also in helping the student of colour chemistry to master the essentials of one of the most important branches of his subject. Additionally, there would appear to be a need to provide for the more general type of reader who wishes to keep up to date in recent technological developments, and for those engaged in the more practical aspects of the textile dyeing and printing industries who wish to learn more about the scientific background of the processes they operate.

In the present work, therefore, an attempt has been made to cater for all of these interests, despite the obvious difficulties of so doing. To a large extent, these difficulties stem from the very diversity which the subject has now assumed. Although the theoretician, for example, might well regard the study of fibre-reactive dyes to be of interest mainly from the point of view of reaction mechanisms and kinetics, those involved in the large-scale commercial dyeing and printing of textiles will naturally be mainly concerned with the more practical aspects of the subject. In trying to steer a middle course the author has taken the view that although the treatment of a technological subject should rest on an essentially practical basis, underlying theories should

be stated in sufficient detail to enable the various aspects of the subject to be related, as far as possible, to a common background rather than left as an incoherent collection of empirical facts. Although it is obviously impossible in a general work to enter into detailed discussion of the finer points of the more abstruse theories, on the one hand, or of the highly practical processes of manufacture and application, on the other, ample references have been included to indicate where such detail might be found if required.

Although the author was not himself involved in research on fibre-reactive dyes until considerably later, he was nevertheless a departmental colleague of one of the inventors throughout the critical period of discovery and early development, and was thus in a very favourable position to fully appreciate the magnitude of the contribution made by Dr. W. E. Stephen towards almost every aspect of the transformation of the reactive dyeing of cellulose, from a laboratory curiosity of no commercial application to a technique of such predominant technological and economic significance as to rank among the major advances of dyestuffs chemistry. This preface would therefore seem to be a suitable place for the author to pay personal tribute to the excellence and breadth of Dr. Stephen's work, which, together with the very important contribution made by Mr. (now Professor) I. D. Rattee, was very appropriately recognised by the subsequent joint award of a Gold Medal by the Society of Dyers and Colourists.

Although every care has been taken to check statements with the original literature sources wherever possible and to obtain advice from specialists whenever doubt has arisen, it is probably too much to hope that a work of the present scope will be entirely free from mistakes. The author will therefore be grateful to be informed of any errors which might have escaped his notice.

The author is greatly indebted to all those who have assisted him in various ways, and would like to thank Professor I. D. Rattee, of the Department of Colour Chemistry of the University of Leeds, for his interest and helpful advice; Dr. R. R. Davies, of Research Department, ICI Dyestuffs Division, for providing facilities and for critically reading the whole of the manuscript and suggesting various improvements; and those of his colleagues of ICI Dyestuffs Division who have critically read and

offered helpful suggestions in connection with the various parts of the subject in which they themselves are specialists. In the latter connection, he would especially thank Drs. N. S. Corby, D. W. Ramsay and C. V. Stead, and Messrs. A. C. Farthing and C. Morris, of Research Department; and Messrs. F. R. Alsberg, M. R. Fox, J. F. Lewis, W. J. Marshall, J. Shore and H. H. Sumner, of Application Research and Technical Service Department. His thanks are also due to Mr. B. Lamble, of Research Department, for help in the correction of proofs. Finally, the author would like to express his gratitude to the publishers for their courtesy and consideration, which have gone far towards helping to make his task pleasant.

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Acknowledgements

I wish to express my gratitude to the many authors of papers and articles, whose names are referred to in the text in connection with specific items, for their kindness in permitting me to reproduce certain tables, figures and other matter from their publications. My grateful thanks are also due to the publishers of the journals in which these papers and articles first appeared, for allowing me use of their copyright for the present purpose. I am thus indebted to the Society of Dyers and Colourists (Bradford) for general permission to reproduce material from their *Journal*; and to the publishers of the *American Dyestuff Reporter* (New York), *Angewandte Chemie* and the *International Edition* thereof (Weinheim), *Chimia* (Zürich), *Helvetica Chimica Acta* (Basle), the *International Dyer and Textile Printer* (London), the *Journal of the Chemical Society* (London) and *Melliand Textilberichte* (Heidelberg) for permission to reproduce the specific items associated with the names of these journals in the text. I also wish to thank the Textile Technical Federation of Canada for permission to reproduce several items from the paper by Mr. H. H. Sumner and Dr. T. Vickerstaff in the 7th Seminar Book of Papers of the Canadian Textile Society (Kingston, Ontario); the American Cyanamid Company for permission to quote solubilities given on page 84 from their brochure *Aero Cyanuric Chloride*; and Academic Press (London) Limited and Dr. T. E. Peacock for permission to reproduce the figure on page 89 showing the charge density distribution for nitrogen heterocycles, from the latter's book, *Electronic Properties of Aromatic and Heterocyclic Molecules*.

W. F. B.

References and Symbols

With few exceptions, abbreviations of the names of journals and other periodicals are those recommended in the *World List of Scientific Periodicals*. For patent specifications the following are used:

Austrian P.	Austrian Patent Specification
Belg.P.	Belgian Patent Specification
B.P.	British Patent Specification
Fr.P.	French Patent Specification
Ger.P.	German Patent Specification
Jap.P.	Japanese Patent Specification
Sw.P.	Swiss Patent Specification
U.S.P.	United States Patent Specification

All temperatures are stated in degrees Celsius.

The symbol \longrightarrow , when used between the name of a diazotisable amine and the name of a compound capable of undergoing azo coupling, means "diazotised and coupled with"; e.g. aniline \longrightarrow β -naphthol refers to the azo compound obtained by diazotising aniline and coupling the diazonium salt with β -naphthol, i.e. 1-phenylazo-2-naphthol.

The symbol $-\text{O} \cdot \text{Cell.}$ refers to a cellulose molecule minus one hydrogen atom; e.g. $\text{Me} \cdot \text{O} \cdot \text{Cell.}$ would indicate a monomethyl ether of cellulose.

Abbreviations of Names of Dyestuffs Manufacturers

<i>Abbreviation</i>	<i>Name of firm and place of headquarters</i>
ACNA	Aziende Colori Nazionali Affini ACNA, Milan
Amer. Aniline	American Aniline Products Inc., New York
Amer. Cyanamid	American Cyanamid Company, Dyestuffs Department, Bound Brook, N.J.
BASF	Badische Anilin- und Soda-Fabrik A.-G., Ludwigshafen/Rhein
Bayer	Farbenfabriken Bayer A.-G., Leverkusen
Cassella	Cassella Farbwerk Mainkur A.-G., Frankfurt/Main
CFMC	Compagnie Française des Matières Colorantes, Paris
CIBA	Gesellschaft für Chemische Industrie in Basle (Society of Chemical Industry, Basle)
Du Pont	E. I. du Pont de Nemours & Co. Inc., Wilmington, Delaware
Durand & Huguenin	Durand and Huguenin S.A., Basle
Francolor	see CFMC
Geigy	J. R. Geigy A.-G., Basle
Gen. Aniline	General Aniline & Film Corporation, New York
Hoechst	Farbwerke Hoechst A.-G., Frankfurt/Main
ICI	Imperial Chemical Industries Limited, Dyestuffs Division, Manchester

IG	Interessen Gemeinschaft für Farben- industrie A.-G., Frankfurt/Main (dissolved in 1945)
Interchemical Corp.	Interchemical Corporation, Hawthorne, N.J.
Kodak	Eastman Kodak Company, Rochester, New York
Kuhlmann	Établissements Kuhlmann (Ugine Kuhlmann), Paris
Sandoz	Sandoz Limited, Basle
Southern Dyestuffs	Southern Dyestuffs Corporation, Charlotte, N.C.

Manufacturers' Trade Marks

The following are trade marks belonging to the companies indicated in the table below :

Basazol (BASF)	Inthion (Hoechst)
Calcobond	Lanasol (CIBA)
(Amer. Cyanamid)	Levafix (Bayer)
Carbolan (ICI)	Permafix (Bayer)
Cavalite (Du Pont)	Primazin (BASF)
Chlorantine (CIBA)	Procilan (ICI)
Cibacrolan (CIBA)	Procinyl (ICI)
Cibacron (CIBA)	Procion (ICI)
Cibalan (CIBA)	Reacna (ACNA)
Coranil (Hoechst)	Reactone (Geigy)
Drimalan (Sandoz)	Reatex (CFMC)
Drimarene (Sandoz)	Remalan (Hoechst)
Dykolite	Remazol (Hoechst)
(Southern Dyestuffs)	Remazolan (Hoechst)
Elisiane (CFMC)	Solidazol (Cassella)
Hydrosol (Cassella)	Supramine (IG)

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I

Introduction

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1. Deficiencies of Non-reactive Dyes

Throughout the long history of the tinctorial arts, the dyer of textiles has been confronted with the problem of trying to match the permanence of his colorations as closely as possible with the useful life of the fabric. Until little more than a century ago, his choice of colorants was limited to natural dyes, although the range of fast shades which could be produced was greatly extended by the use of a variety of mordants. Indigo, Tyrian Purple and mordanted Madder were outstanding among natural dyes in giving dyeings of fastness unsurpassed by other colorants.

Perkin's discovery of Mauveine (1856) did not of itself represent any evolution in dyeing methods.¹ Although of unusual brightness and fastness to light by the standards of its time, it merely fitted into the usual pattern by having high affinity for silk and low affinity for cotton. To dye cotton with Mauveine, it was still necessary to use a mordant, e.g. tannic acid and a metallic oxide.

Dyeing of cotton without the use of a mordant became possible with Böttiger's discovery of Congo Red in 1884, but this and most other similar direct cotton dyes afforded dyeings of comparatively poor fastness to wet treatments and to light. Development subsequently of vat and azoic dyes enabled very fast dyeings to be produced, but both of these classes are more expensive and less easily applied than direct dyes.

Dyeing of cotton with direct and with vat or azoic dyes typifies two of the three possible ways² of attaching dyes to

textile fibres, viz (1) by physical adsorption, (2) by mechanical retention and (3) by chemical reaction.

Dyeing with direct dyes depends upon the affinity of the dye for the substrate, which, in the case of cotton, arises from comparatively weak forces of van der Waals type possibly reinforced to some degree by hydrogen bonding.³ With fibres such as wool the presence of ionogenic groups does not of itself cause any marked increase of fastness; the presence of opposite charges on dye and fibre does, however, mean that there is no electro-potential effect restraining the approach of dye molecules to the surface and allowing other short-range bonding forces to develop, as is the case with cellulosic substrates and acid dyes. With either wool or cotton, therefore, such a system exhibits reversible distribution of dye between substrate and aqueous phase, so that even in theory it is impossible to obtain the highest fastness to wet treatments. All reversibly bound dyes depend upon physical adsorption, and the equilibrium situation is modified by electrical potential effects without being determined by them. When a sulphonated dye molecule penetrates cellulose, it introduces a negative charge, repelling further molecules. Fastness is limited by rapid diffusion unless large molecules are used, and high exhaustion occurs only when the surface potential field effect is limited by using high electrolyte concentrations, as is common in dyeing cotton with direct dyes.

A much higher standard of fastness results when insoluble colours are formed within the interstices of cotton fibre with azoic dyes, but the highest fastness of which any particular azoic combination is capable is obtained only when the dyeing is subjected to an aftertreatment, e.g. with boiling soap solution, to secure aggregation of the pigment so that it becomes completely trapped within the fibre. Such aftertreatment is an essential part of the azoic dyeing process, which exemplifies attachment of dye to fibre by mechanical retention.

The causes of poor or indifferent fastness of dyeings may lie in instability of the dye molecule itself, in weakness of its attachment to the fibre or in both. Dye molecules vary very greatly among themselves (according to chemical constitution) in stability towards the agencies to which dyed fabrics are exposed during normal wear and usage, i.e. light, water, cleansing agents and air; in industrial areas the latter may be highly polluted not

only with carbonaceous matter but also with oxides of sulphur and nitrogen. The search for faster dyes must therefore always include not only a search for more stable coloured molecules but also a search for ways of attaching them more firmly to fibres.

Great progress was made during the first half of the present century in discovering or inventing dye structures characterised by great inherent stability, typical examples being Indanthrone, Thioindigo, Caledon Jade Green, Hydron Blue, the Neolan dyes and Monastral Fast Blue. In view of the early use of mordants, it is not surprising that metallisation began to play an increasingly important part in the development of fast dyes, especially after the structures of metallic complexes of azo dyes had been established with reasonable certainty by the work of Pfeiffer, Morgan, Drew and their co-workers.⁴ Nevertheless, until the 1950s all commercial dyes still depended fundamentally upon either physical adsorption or mechanical retention for their attachment to fibres, even though much effort was devoted to devising structures and application procedures in which these processes were deployed to maximum advantage. In the latter connection, there may be mentioned, for example, the various aftertreatments used for securing improved fastness with direct dyes, such as diazotisation and coupling on the fibre, and treatment with formaldehyde or copper salts; with at least some of these improved wet fastness probably results from a lowering of water solubility and consequent decrease in the rate at which the dye is desorbed from the fibre by water.⁵ Attempts were also made to "animalise" cellulosic fibres by treatment with reactive compounds such as ethylene imine, so producing modified fibres containing basic centres capable of forming salt links with dyes of the acid wool type.⁶

The possibility of attaching dyes to fibres by chemical reaction has for long been attractive to dyestuffs chemists because attachment by physical adsorption and by mechanical retention both possess serious disadvantages. It must be pointed out that in this context "chemical reaction" implies the formation of a covalent bond between the dye and the fibre, and does not include the formation of salt links such as are formed between acid dyes and wool. As already mentioned, physical adsorption involves a reversible equilibrium, so that it is theoretically impossible to obtain the highest degree of wet fastness. Although the wet

fastness may be improved by altering the shape of the dye molecule so as to increase the forces of adsorption, such modifications of structure usually reduce water solubility and increase the tendency of the dye to aggregate, and these properties combined with higher affinity for the fibre make the production of level dyeings more difficult.²

Mechanical retention forms the basis of dyeing with vat, sulphur and azoic dyes, and of the mass coloration of man-made fibres. High wet fastness is achieved through the virtual insolubility of the pigment in water or soap solution, together with mechanical retention of pigment particles by the fibre substance in which they are embedded. The process of introducing the insoluble pigment into the fibre is, however, comparatively complicated and troublesome, and occasionally difficulty may arise from growth of pigment particles or deposits of loose dye particles on the surface of the fibres.² Vat dyes tend to be expensive and rather restricted in range of shade, and mixtures of azoics are sometimes not easy to process and do not always give the expected results.⁷ Although cost of dyeing is not an overwhelming disadvantage in the production of high-quality goods, there is obvious scope for a type of dye capable of giving fast bright shades on cotton without the use of specialised dyeing equipment.

Interest in the possibility of attaching dyes to fibres by chemical reactions giving rise to covalent linkages between dye and fibre arose from the supposition that high wet fastness would result from uniting the dye and the fibre to form a single molecule. The stability of such a molecule must, of course, depend upon the resistance of the covalent linkage to reagents, and this will vary with the nature of the link itself. An ester link, for example, might hydrolyse fairly rapidly under conditions of alkaline soap boiling. Rubbing fastness with chemically linked dyes should present no problem, because the dye could be rubbed away only by removal of the fibre substance itself.

Another factor contributing towards the urge to investigate and develop reactive dyes was the increasing interest that became evident in the 1930s in continuous dyeing methods. Rattee⁸ has pointed out that Böttiger's Congo Red and the ranges of direct cotton dyes which were developed subsequently were devised to suit the methods employed in the dyeing trade at the time, which