

Table of Contents

1 The Development of Dyes	1
1.1 Introduction	1
1.2 Pre-Perkin Era — The Natural Dyes	1
1.2.1 Introduction	1
1.2.2 Yellow Dyes	2
1.2.3 Red Dyes	4
1.2.4 Purple Dyes	4
1.2.5 Blue Dyes	5
1.2.6 Black Dyes	5
1.3 Perkin and Beyond — The Synthetic Dyes	5
1.3.1 Introduction	5
1.3.2 Perkin's Discovery of Mauveine	6
1.3.3 The Post-Mauveine Era	8
1.3.4 Kekulé's Contribution	10
1.3.5 Alizarin	11
1.3.6 Indigo	13
1.3.7 The Introduction of Novel Chromogens	15
1.4 Future Trends	19
1.5 Summary	21
1.6 Bibliography	21
2 Classification and Synthesis of Dyes	23
2.1 Introduction	23
2.2 Classification of Dyes	23
2.2.1 Azo Dyes	23
2.2.2 Anthraquinone Dyes	24
2.2.3 Vat Dyes	24
2.2.4 Indigoid Dyes	24
2.2.5 Polymethine Dyes	25
2.2.6 Aryl-Carbonium Dyes	26
2.2.7 Phthalocyanine Dyes	27
2.2.8 Nitro Dyes	27
2.2.9 Miscellaneous Dyes	27

2.3	Synthesis of Dye Intermediates	28
2.3.1	Synthesis of Aromatic Carbocycles	28
2.3.2	Synthesis of Aromatic Heterocycles	47
2.4	Synthesis of Dyes	57
2.4.1	Azo Dyes	57
2.4.2	Anthraquinone Dyes	66
2.4.3	Vat Dyes	77
2.4.4	Phthalocyanine Dyes	80
2.4.5	Indigoid Dyes	82
2.4.6	Polymethine Dyes	85
2.4.7	Di- and Tri-Arylcarbonium Dyes	89
2.5	Summary	93
2.6	Bibliography	94
3	Azo Dyes	95
3.1	Introduction	95
3.2	Basic Structure of Azo Dyes	95
3.3	Tautomerism	96
3.3.1	Tautomerism of Hydroxyazo Dyes — Azo-Hydrazone Tautomerism	96
3.3.2	Hydroxyazo Dyes of the Naphthalene Series	99
3.3.3	Hydroxyazo Dyes of the Benzene Series	104
3.3.4	Tautomerism of Aminoazo Dyes — Amino-imino Tautomerism	108
3.3.5	Protonated Azo Dyes — Azonium-Ammonium Tautomerism	112
3.4	Metal Complex Azo Dyes	116
3.4.1	Introduction	116
3.4.2	Medially Metallised Azo Dyes — Nature of the Bonding by the Azo Group	116
3.4.3	Types of Dyes and their Stability	117
3.4.4	Structure and Stereochemistry	118
3.4.5	Commercial Uses of Metal Complex Azo Dyes	119
3.4.6	Properties of the Metallised Dyes	120
3.4.7	Terminally Metallised Dyes	121
3.5	Colour and Constitution	121
3.5.1	Introduction	121
3.5.2	Early Theories	121
3.5.3	Modern Theories	124
3.5.4	Experimental Observations. Monoazo Dyes — Derivatives of 4-Aminoazobenzene	126
3.5.5	Application of VB and MO Theories	131
3.5.6	Protonated Azo Dyes	142
3.5.7	Azo-Hydrazone Tautomers	146
3.5.8	Polyazo Dyes	148
3.5.9	Steric Effects	152
3.6	Summary	158
3.7	Bibliography	159

4 Anthraquinone Dyes	163
4.1 Introduction	163
4.2 Structure of Anthraquinone Dyes	163
4.3 Tautomerism	164
4.3.1 Tautomerism of Hydroxyanthraquinone Dyes	164
4.3.2 Reduced Hydroxyanthraquinone Dyes — <i>Leuco-Quinizarin</i>	166
4.3.3 Aminoanthraquinone Dyes	168
4.3.4 Reduced Aminoanthraquinone Dyes	168
4.4 Protonated and Ionised Anthraquinone Dyes	169
4.4.1 Introduction	169
4.4.2 Anthraquinone	169
4.4.3 Aminoanthraquinone Dyes	169
4.4.4 Hydroxyanthraquinone Dyes	171
4.4.5 Aminohydroxyanthraquinone Dyes	173
4.5 Metal Complexed Anthraquinone Dyes	173
4.5.1 Introduction	173
4.5.2 Commercial Dyes	173
4.5.3 Structure and Properties	174
4.6 Colour and Constitution	174
4.6.1 Introduction	174
4.6.2 Experimental Results	175
4.6.3 VB/MO Explanation of Colour and Constitution	186
4.6.4 Steric Effects	195
4.7 Summary	197
4.8 Bibliography	198
5 Miscellaneous Dyes	200
5.1 Introduction	200
5.2 Vat Dyes	200
5.2.1 Introduction	200
5.2.2 The Anthraquinonoid Vat Dyes	201
5.2.3 Sulphur-containing Vat Dyes	205
5.2.4 Colour and Constitution of Anthraquinonoid Vat Dyes	206
5.3 Indigoid Dyes	208
5.3.1 Introduction	208
5.3.2 Structure and Unusual Features of Indigo	208
5.3.3 Colour and Constitution of Indigoid Dyes	211
5.3.4 Other Indigoid Dyes	215
5.3.5 Protonation and Ionisation	217
5.3.6 Commercial Indigoid Dyes	218
5.4 The Phthalocyanines	219
5.4.1 Introduction	219
5.4.2 The Discovery of the Phthalocyanines	219
5.4.3 Elucidation of the Structure of Phthalocyanine	220
5.4.4 Colour and Constitution of Porphyrins and Phthalocyanines	221
5.4.5 Copper Phthalocyanine Dyes	226

5.5	Polymethine Dyes	226
5.5.1	Introduction	226
5.5.2	Oxonols and Merocyanines	227
5.5.3	Cyanine Dyes and their Derivatives	227
5.5.4	Colour and Constitution	231
5.6	Di- and Tri-aryl Carbonium Dyes and their Derivatives	242
5.6.1	Introduction	242
5.6.2	Structural Interrelationships	243
5.6.3	General Colour-Structure Properties	244
5.6.4	Steric Effects	247
5.6.5	Phenolphthalein	249
5.6.6	Heterocyclic Derivatives of Di- and Tri-phenylmethanes	249
5.7	Nitro (and Nitroso) Dyes	253
5.7.1	Introduction	253
5.7.2	Nitrodiphenylamine Dyes	253
5.7.3	Nitroso Dyes	257
5.8	Summary	257
5.9	Bibliography	259
6	Application and Fastness Properties of Dyes	262
6.1	Introduction	262
6.2	Textile Fibres — Types and Structures	262
6.2.1	Introduction	262
6.2.2	Natural Fibres	263
6.2.3	Semi-Synthetic Fibres	265
6.2.4	Synthetic Fibres	267
6.3	Application and Wet Fastness of Dyes	271
6.3.1	Introduction	271
6.3.2	Physical Adsorption	271
6.3.3	Solid Solutions	273
6.3.4	Insoluble Aggregates within the Fibre	275
6.3.5	Ionic Bonds	277
6.3.6	Covalent Bonds	278
6.4	Light Fastness of Dyes	281
6.4.1	Introduction	281
6.4.2	Test Methods	282
6.4.3	Basic Photochemical Principles	284
6.4.4	Mechanism of Fading	285
6.4.5	Effect of Aggregation on Light Fastness	294
6.4.6	Catalytic Fading	294
6.4.7	Phototendering of Dyed Fibre	297
6.5	Photochromism	298
6.6	Heat Fastness of Dyes	299
6.7	Bleach Fastness of Dyes	301
6.8	Metamerism	302
6.9	Solvatochromism	303

6.10 Summary 303

6.11 Bibliography 304

Appendix I 305

Appendix II 306

Author Index 307

Subject Index 310