

Contents

Preface XIX

List of Contributors XXI

Part I

1 Introduction to Inorganic High Performance Pigments 3

Gunter Buxbaum

- 1.1 Introduction 3
- 1.2 Survey of Inorganic Pigments 4
- 1.3 New Candidates on the Catwalk of Color 5
- 1.4 Challenges for the Future 6

2 Bismuth Vanadates 7

Hartmut Endriss

- 2.1 Introduction 7
- 2.2 Historical Background 7
- 2.3 Manufacture 8
- 2.4 Properties and Applications 8
 - 2.4.1 Chemical Properties 8
 - 2.4.2 Physical Properties 9
 - 2.4.3 Coloristic Properties 9
 - 2.4.4 Dispersibility 10
 - 2.4.5 Light Fastness and Weather Resistance 10
 - 2.4.6 Chemical and Solvent Resistance 10
- 2.5 Applications 10
 - 2.5.1 Coatings 10
 - 2.5.2 Plastics 11
 - 2.5.2.1 Properties 11
 - 2.5.2.2 Applications 11

2.5.2.3	Conformity of Pigments for Plastics Coloration to Food and Drug Regulations	11
---------	---	----

2.6	Toxicology	12
-----	------------	----

2.6.1	Acute Toxicity	12
-------	----------------	----

2.6.2	Chronic Toxicity	12
-------	------------------	----

2.7	Ecology	12
-----	---------	----

3 Cadmium Pigments 13

Paul Dunning

3.1	Introduction	13
-----	--------------	----

3.2	Pigment History	13
-----	-----------------	----

3.2	Raw Materials	15
-----	---------------	----

3.2.1	Cadmium	15
-------	---------	----

3.2.2	Selenium	15
-------	----------	----

3.3	Chemistry of Cadmium, Selenium and Cadmium Sulfide	16
-----	--	----

3.3.1	Cadmium	16
-------	---------	----

3.3.2	Selenium	16
-------	----------	----

3.3.3	Substitution in the CdS Lattice	17
-------	---------------------------------	----

3.4	Method of Pigment Manufacture	17
-----	-------------------------------	----

3.4.1	General Points	17
-------	----------------	----

3.4.2	Cadmium Oxide Formation	19
-------	-------------------------	----

3.4.3	Cadmium Metal Dissolution	19
-------	---------------------------	----

3.4.4	Other Solution Making	20
-------	-----------------------	----

3.4.5	Precipitation	20
-------	---------------	----

3.4.6	Filtration and Washing	21
-------	------------------------	----

3.4.7	Drying	21
-------	--------	----

3.4.8	Calcination	21
-------	-------------	----

3.4.9	Wet Milling	22
-------	-------------	----

3.4.10	Removal of Soluble Cadmium	22
--------	----------------------------	----

3.4.11	Final Drying and Milling	22
--------	--------------------------	----

3.5	Physical Properties	22
-----	---------------------	----

3.6	Regulatory Issues	24
-----	-------------------	----

3.7	Uses	25
-----	------	----

4 Cerium Pigments 27

Jean-Noel Berte

4.1	Introduction	27
-----	--------------	----

4.2	Rare Earth Sulfides and the Origins of their Color.	28
-----	---	----

4.3	Cerium Sulfide Pigment: Manufacture	31
-----	-------------------------------------	----

4.4	Properties and Applications	34
-----	-----------------------------	----

4.4.1	Coloration of Plastics	34
-------	------------------------	----

4.4.2	Paint and Coatings Application	38
-------	--------------------------------	----

4.4.3	Miscellaneous Applications	39
-------	----------------------------	----

4.5	Toxicology and Environmental Aspects	39
-----	--------------------------------------	----

4.6	Toxicological and Environmental Concerns during the Manufacturing Process	40
-----	---	----

5 Complex Inorganic Color Pigments: An Overview. 41

James White

5.1	Introduction	41
5.2	Structures of CICPs	42
5.3	Production of CICPs	44
5.4	Titanate Pigments	44
5.4.1	Rutile Titanates	45
5.4.2	Spinel Titanates	46
5.4.3	Other Titanates	47
5.5	Aluminate Pigments	47
5.6	Cobalt Aluminates	47
5.7	Cobalt Chromium Aluminates	48
5.8	Chromites and Ferrites	49
5.9	Black CICPs	49
5.10	Brown Pigments	50
5.11	Green Chromites	51

6 Titanate Pigments: Colored Rutile, Priderite, and Pseudobrookite Structured Pigments 53

John Maloney

6.1	Introduction	53
6.2	History	55
6.2.1	Doped-Rutile (DR) Pigments	57
6.2.2	Priderite Pigments	58
6.2.3	Pseudobrookite Pigments	58
6.3	Synthesis	58
6.3.1	DR Pigments	59
6.3.2	Priderite Pigments	61
6.3.3	Pseudobrookite Pigments	62
6.4	Applications	62
6.5	Properties	63
6.5.1	Spectral Properties	63
6.5.1.1	Visible Spectral Characterization	63
6.5.1.2	UV and NIR Spectral Characterization	66
6.5.2	Physical Properties	66
6.5.2.1	Particle Size Distribution	66
6.5.2.2	X-ray Diffraction Characterization	67
6.5.2.3	Specific Gravity	68
6.5.2.4	Oil Absorption and Specific Surface Area	69
6.5.2.5	Powder Flow and Dusting	70
6.5.3	Chemical Properties	70

- 6.5.3.1 pH Measurement 70
- 6.5.3.2 Weathering 71
- 6.5.3.3 Particle Chemistry 72

Part II

7 Special Effect Pigments 77

Gerhard Pfaff

- 7.1 Introduction 77
- 7.2 Pearlescent and Interference Pigments 78
 - 7.2.1 Optical Principles of Pearlescent and Interference Pigments 79
 - 7.2.2 Substrate-Free Pearlescent Pigments 82
 - 7.2.2.1 Natural Pearl Essence 82
 - 7.2.2.2 Basic Lead Carbonate 82
 - 7.2.2.3 Bismuth Oxychloride 82
 - 7.2.2.4 Micaceous Iron Oxide 83
 - 7.2.2.5 Titanium Dioxide Flakes 83
 - 7.2.3 Pigments Formed by Coating of Substrates 84
 - 7.2.3.1 Metal Oxide-Mica Pigments 84
 - 7.2.3.2 Silica Flake Pigments 90
 - 7.2.3.3 Alumina Flake Pigments 94
 - 7.2.3.4 Borosilicate-based Pigments 96
 - 7.3 Effect Pigments Formed by Coating of Metal Flakes 96
 - 7.4 Pigments Formed by Grinding a Film 97
 - 7.5 Pigments Based on Liquid Crystal Polymers 98
 - 7.6.1 Diffractive Pigments 101
 - 7.6.2 Pigments Based on Holography and Gratings 102
- Acknowledgments 103

8 Crystal Design of High Performance Pigments 105

Martin Schmidt

- 8.1 Introduction 105
- 8.2 Crystal Engineering of Organic Pigments 106
 - 8.2.1 Close Packing 106
 - 8.2.2 Crystal Energy 108
 - 8.2.3 Specific Interactions 109
- 8.3 Crystal Structure Determination 113
- 8.4 Crystal Structure Calculation 115
 - 8.4.1 General Methods 115
 - 8.4.2 Crystal Structure Calculations of Pigments 116
 - 8.4.3 Crystallochromy 118
 - 8.4.4 Morphology Calculation 119

- 8.4.5 Pigment Morphologies 121
- 8.5 Control of Interfacial Properties Through Tailor-Made Additives 122

Part III 129

9 The Global Market for Organic High Performance Pigments 131

Fritz Brenzikofer

- 9.1 Introduction 131
- 9.2 The 1999 Market for Organic High Performance Pigments 132
- 9.3 The Producers of High Performance Pigments 133
- 9.4 The Demand for HPP by Consumer Market Segments 133
 - 9.4.1 The Demand by Regions 134
 - 9.4.2 The Trade Balance of HPP among these Regions 134
- 9.5 Demand Factors for HPPs 137
 - 9.5.1 Market Requirements and Trends 138
 - 9.5.1.1 Industrial/Decorative Paints 138
 - 9.5.1.2 Plastics 138
 - 9.5.1.3 New Markets 138
 - 9.5.2 Marketing Strategies of Main HPP Producers 138
 - 9.5.3 Globalization Prozess 138
- 9.6 Conclusions/Outlook 138

10 Benzimidazolone Pigments and Related Structures 139

Hans-Joachim Metz and Frank Morgenroth

- 10.1 Introduction 139
- 10.2 Historical Background 143
- 10.3 Method of Manufacture 145
- 10.4 Typical Properties and Major Reasons for Use 146
- 10.5 Pigment Grades, Discussion of Individual Pigments 154
- 10.6 Pigment Manufacturers, Economics 158
- 10.7 Safety, Health and Environmental Aspects 164

11 Diketopyrrolopyrrole (DPP) Pigments 165

Olof Wallquist and Roman Lenz

- 11.1 Introduction 165
 - History 165
- 11.2 Syntheses 166
 - 11.2.1 Reformatsky Route 166
 - 11.2.2 Succinic Ester Route 168
 - 11.2.3 Succinic Amide Route 169
 - 11.2.4 Miscellaneous Routes 169
- 11.3 Molecular Structure and Properties 170
 - 11.3.1 Spectral Properties 170

11.3.2	Spectral Properties – Fluorescence	172
11.3.3	Single X-ray Structure Analysis	174
11.4	Chemical Properties	176
11.4.1	Electrophilic Aromatic Substitution	177
11.4.2	Nucleophilic Aromatic Substitution	177
11.4.3	N-Alkylation	178
11.4.4	Transformations on the Carbonyl Group	179
11.5	Solid-State Properties	180
11.5.1	General Properties	180
11.5.2	Particle Size Control	180
11.5.3	Polymorphism	181
11.5.4	Solid Solutions	182
11.5.5	Surface Modifications	184
11.6	Conventional Applications	185
11.7	Nonconventional Applications	190
12	Dioxazine Violet Pigments	195
	<i>Terence Chamberlain</i>	
12.1	Introduction	195
12.1.1	The Chemistry of Dioxazine Pigments	195
12.2	Synthesis	196
12.2.1	Dianil Formation	197
12.2.2	Cyclization of the Dianil	197
12.3	Pigmentation and Properties	202
12.3.1	Pigment Violet 23	202
12.3.2	Pigment Violet 37	203
12.4	Recent Developments	203
12.4.1	Preparation/Production Methods	203
12.4.2	New Products	204
13	Disazocondensation Pigments	205
	<i>Fritz Herren</i>	
13.1	Introduction	205
13.2	Historical Background	205
13.3	Chemistry	206
13.3.1	Commercialized Pigments (Past and Present [4])	207
13.3.2	Recent Developments	212
13.4	Synthesis and Manufacture	214
13.5	Characterization, Properties, Application	216
13.5.1	Physical Characterization	216
13.5.2	Available Grades	216
13.5.3	Properties and Applications	217

14 Isoindoline Pigments 221*Volker Radtke, Peter Erk, and Benno Sens*

- 14.1 Introduction 221
- 14.2 Historical Background 224
- 14.3 Methods of Manufacture 226
- 14.4 Typical Properties and Major Reasons for Use 229
- 14.5 Crystal Structures of Isoindoline Pigments 229
 - 14.5.1 Structure Determination 229
 - 14.5.2 Discussion 232
 - 14.5.3 ESA Data 233
- 14.5 Pigment Grades; Discussion of Individual Pigments 236
- 14.6 Pigment Manufacturers; Economics 239
- 14.7 Toxicology and Ecology 240

15 Isoindolinone Pigments 243*Abul Iqbal, Fritz Herren, and Olof Wallquist*

- 15.1 Introduction 243
- 15.2 Chemistry 244
 - 15.2.1 Azomethine-Type Isoindolinones 244
 - 15.2.2 Methine-Type Isoindolinones 252
 - 15.2.3 Metal Complexes Based on Isoindolinones 253
- 15.3 Physicochemical Properties 254
- 15.4 Commercial Products and Applications 257

16 Perylene Pigments 261*Brian Thompson*

- 16.1 Definition of Perylene Pigments 261
 - 16.1.1 History 261
 - 16.1.2 Color Index and Identity 261
- 16.2 Synthesis of Perylenes 263
 - 16.2.1 Conversion of Perylenes: Acenaphthene to Perylene Tetracarboxylic Acid Diimide (PTCI, Pigment Violet 29) 263
 - 16.2.2 Synthesis of Perylene Tetracarboxylic Acid Dianhydride (PTCA) by Hydrolysis of PTCI to PTCA, and PTCA as a Pigment (Pigment Red 224) 265
 - 16.2.3 Alkylation of PTCI to Pigment Red 179 and other Perylene Pigments 265
 - 16.2.4 Synthesis of Perylene Pigments and Mixed Crystals by Condensation of PTCA with Amines 266
 - 16.2.5 Half Imide, Half Anhydrides of PTCA (10) 266
 - 16.2.6 Derivatives of Perylene as Performance Enhancers 267
- 16.3 The Conditioning of Perylene Diimide Pigments 267
- 16.4 Mixed Crystals and Solid Solutions of Perylene Diimide Pigments 268

16.5	Drying of Perylene Pigments	268
16.6	Physical Chemistry and Color Physics of Perylene Pigments	269
16.7	Perylene Pigments and their Applications	270
16.8	Perylenes as Functional Colorants	271
16.9	Current Producers	271
16.10	Pricing Trends and Economics of Use	272
16.11	Health, Safety, and Environmental Considerations	272

17 Phthalocyanines – High Performance Pigments and Their Applications 275

Masao Tanaka

17.1	Introduction	275
17.2	Application of Optical Properties	276
17.2.1	Color Filters for Liquid Crystal Display Devices	276
17.2.2	Ink Jet Inks	277
17.2.3	Infrared Ray Absorbents	279
17.2.4	CD-R	281
17.3	Application of Optoelectronic Properties	282
17.3.1	Electrophotographic Photoreceptor	282
17.3.2	Nonlinear Optical Devices	286
17.4	Application of Catalysis	287
17.4.1	Deodorizers	287
17.4.2	Photodynamic Therapy	288
17.5	Conclusion	289

18 Quinacridone Pigments 293

Terence R. Chamberlain (modification of original chapter by Edward E. Jaffe)

18.1	Introduction	293
18.2	Historical Background	293
18.3	Quinacridone Syntheses	295
18.3.1	The Synthesis of DMSS from Dimethyl Succinate	295
18.3.1.1	By-Products Produced During the Synthesis and Isolation of DMSS	295
18.3.2	Synthesis of DMSS from Diketene (Methyl 4-Chloroacetoacetate)	297
18.3.3	Synthesis of Quinacridones by the Thermal Process	298
18.3.4	Synthesis of Quinacridones by the PPA Process	300
18.3.5	Synthesis of Quinacridones by Application of the Ullmann Reaction	303
18.4	Recently Introduced Quinacridone Products	304
18.5	Structural Data and Spectra	305
18.6	Polymorphism	308
18.7	Substituted Quinacridones	311
18.8	Photostability and a Suggested Mechanism	313
18.9	Quinacridonequinone	315
18.10	Other 6,13-Disubstituted Quinacridones	317

18.11	Solid Solutions	318
18.12	Conditioning and Surface Treatment of Quinacridones	323
18.13	Applications	325
18.14	Health and Safety Factors	326
18.15	Business Aspects	326
19	Quinophthalone Pigments	331
	<i>Volker Radtke</i>	
19.1	Introduction	331
19.2	Historical Background	333
19.3	Methods of Manufacture	334
19.4	Typical Properties and Major Reasons for Use	335
19.5	Pigment Grades and Discussion of Individual Pigments	336
19.5.1	Discussion of Individual Pigments	338
19.6	Pigment Manufacturers: Economics	339
19.7	Toxicology and Ecology	340
20	Imidazolone-Annellated Triphenedioxazine Pigments	341
	<i>Martin U. Schmidt</i>	
20.1	Introduction	341
20.2	On the Structure of Pigment Violet 23	342
20.3	Imidazolone-Annellated Triphenedioxazine Pigments	344
20.3.1	Syntheses	345
20.3.2	Properties	346
20.3.2.1	Pigment Blue 80	346
20.3.2.2	Other Imidazolone-Annellated Triphenedioxazine Pigments	347
20.3.3	Crystal Engineering on Imidazolone-Annellated Triphenedioxazine Pigments	347
20.3.3.1	Structure Determination from X-Ray Powder Data	348
20.3.3.2	Crystal Structures of Pigment Blue 80 and the Dimethyl Derivative (4b)	349
20.3.3.3	Crystal Engineering: Pigment Violet 57	351
	Part IV	355
21	Chemical and Physical Characterization of High Performance Organic Pigments	357
	<i>Constantinos Nicolaou</i>	
21.1	Introduction	357
21.2	Visible Spectrophotometry	359
21.2.1	Introduction	359
21.2.2	Applications of Visible Spectroscopy	362
21.2.2.1	Copper Phthalocyanines	362

21.2.2.2	Visible Spectra of Quinacridone Pigments	364
21.2.2.3	Visible Spectra of Other Pigments	366
21.3	Applications of FT-IR Spectroscopy	368
21.3.1	Introduction	368
21.3.2	Applications of Infrared Spectroscopy	370
21.4	Mass Spectrometry Techniques	373
21.4.1	Introduction	373
21.5	High-Performance Liquid Chromatography	378
21.5.1	Introduction	378
21.5.2	HPLC Applications	378
21.6	Powder X-ray Diffraction	380
21.6.1	Introduction	380
21.6.2	XRD Sample Preparation	382
21.6.3	Applications of XRD	382
21.7	Particle Sizing Techniques	390
21.7.1	Introduction	390
21.7.2	Transmission Electron Microscopy	393
21.7.2.2	Sample Preparation for TEM Analysis	393
21.7.2.3	Applications of TEM	394
21.7.3	Optical Microscopy	396
21.7.3.1	Introduction	396
21.7.3.2	Applications of Optical Microscopy	397
21.7.4	Particle Size by Ultracentrifugal Sedimentation and Comparison to TEM	398
21.7.4.1	Introduction	398
21.7.4.2	Applications of Particle Sizing by Ultracentrifugation	399
21.8	Thermal Analysis and Decomposition Temperatures of HPOPs	404
21.9	Product Safety and Environmental Testing of HPOPs	407
22	Regulatory Affairs for High Performance Pigments: North America	409
	<i>Harold F. Fitzpatrick, Esq. and Glenn C. Merritt, Esq.</i>	
22.1	Introduction	409
22.2	Toxic Substances Control Act	409
22.3	Canada	411
22.3.1	Assessment of the Canadian DSL	412
22.4	Mexico	413
22.5	Toxic Release Inventory Reporting	414
22.6	Regulation of <i>de minimis</i> Levels	414
22.7	Food and Drug Administration	415
22.8	Color Pigments in General	415
22.9	PBT-TRI Rules	418
22.10	Nanotechnology and Regulation	420
22.11	High Production Volume (HPV) Substances	423
22.12	Phthalocyanine Pigments	424

- 22.13 Quinacridone Pigments 424
- 22.14 Carbazole Violet Pigments 425
- 22.15 Perylene Pigments 426
- 22.16 Inorganic Pigments 426
- 22.16.1 Complex Inorganic Color Pigments 426
- 22.16.2 Cadmium Pigments 427
- 22.17 Conclusion 428

23 Regulatory and Legislative Aspects of Relevance to High Performance Pigments: Europe 431

Eric Clarke and Herbert Motschi

- 23.1 Introduction 431
- 23.2 The European Union and its Institutions 431
- 23.2.1 European Commission 432
- 23.2.2 European Parliament (E.P.) 433
- 23.2.3 The Council of the European Union and other Institutions 434
- 23.2.4 Legal Instruments 434
- 23.3 The Major EU Directives Governing Chemical Control 435
- 23.3.1 Dangerous Substances (Commission Directive 67/548/EEC) 436
- 23.3.1.1 Some Differences between EU and US Requirements 437
- 23.3.1.2 Notification 438
- 23.3.1.3 Classification and Labeling 440
- 23.3.2 Dangerous Preparations (E.P. and Council Directive 1999/45/EEC) 444
- 23.3.3 Safety Data Sheets (Commission Directive 2001/58/EC) 444
- 23.3.4 Existing Substances, Priority Lists, Risk Assessment (Council Regulation EEC 793/93) 444
- 23.3.5 Restrictions of Marketing and Use 445
- 23.3.6 REACH 447
- 23.3.7 Pollution Control 448
- 23.3.8 Packaging and Packaging Waste (E.P. and Council Directive 94/62/EC) 448
- 23.3.9 Eco-Labels 448
- 23.3.10 Food Packaging Legislation 449
- 23.3.11 Technical Barriers to Trade 452
- 23.4 National Regulations 452
- 23.4.1 Germany 453
- 23.4.1.2 Wassergefährdungsklassen (Water-Hazard Classes) 453
- 23.4.1.3 Dioxin Limits 454
- 23.4.2 France 455
- 23.4.3 Switzerland 457
- 23.5 Future Enlargement of the EU (PHARE and similar programs) 458
- 23.6 Nonregulatory Initiatives 460
- 23.6.1 High Production Volume (HPV) Chemicals Testing Initiative 460
- 23.6.2 Precautionary Principle 460

- 23.6.3 Black-listing 461
- 23.7 Confidentiality 462
- 23.8 Availability of Information on Current Regulations 462
- 23.9 Future Outlook 463

24 Infrared Reflecting Complex Inorganic Colored Pigments 467

Terry Detrie and Dan Swiler

- 24.1 Introduction 467
- 24.2 Background/Physics 468
 - 24.2.1 Source of Infrared Light 468
 - 24.2.2 Heating Mechanisms 469
 - 24.2.3 Cooling Mechanisms 470
- 24.3 Measurement 471
 - 24.3.1 ASTM E903: Integrating Sphere Spectrophotometer [3] 471
 - 24.3.2 ASTM C1549: Portable Solar Reflectometer [4] 471
 - 24.3.3 ASTM E1918: Pyranometer [5] 472
 - 24.3.4 ASTM D4803: Heat Buildup [6] 472
- 24.4 Pigments 473
 - 24.4.1 Introduction 473
 - 24.4.2 Doped Rutile Titanate Yellows and Tans 473
 - 24.4.3 CICP Tans and Browns 475
 - 24.4.4 CrFe and Other CICP IR Blacks 476
 - 24.4.5 New Inorganic IR Black Pigments 479
 - 24.4.6 Blue Pigments 480
 - 24.4.7 Green CICP Pigments 481
- 24.5 Formulation with IR Pigments 482
 - 24.5.1 Opacity 483
 - 24.5.2 Absorptions 484
- 24.6 Market Driving Forces 485
 - 24.6.1 Studies 485
 - 24.6.2 Specifications on "Cool Roof" 486
 - 24.6.3 Rebate Programs 486
- 24.7 Conclusions 487

25 Toxicology and Ecotoxicology Issues with High Performance Pigments 489

Robert Mott (revision of original chapter by Hugh M. Smith)

- 25.1 Introduction 489
- 25.2 Recent Toxicological Testing of High Performance Pigments 489
- 25.3 Past Confusion in Assessment of HPPs 490
 - 25.3.1 Confusion between Water Soluble Salts of Inorganic Metals and Related but Insoluble Pigments 490
 - 25.3.2 Confusion bBetween Pigments and their Associated Impurities 491
 - 25.3.3 False Positives in Genotoxicity Testing of Organic HPPs 491

25.3.3	Over-Reliance on Structure Activity Relationship (SAR) Assessment of HPPs	491
25.3.4	Confusion over Inaccurate “PBT” Classifications of HPPs	492
25.3.4	Inadequacy of Recent Computer-Driven Models for Substance Profiling	492
25.3.5	Inadequacy of Partition Coefficient Calculations in Evaluating Bioaccumulation	492
25.3.6	Continued Polarization Between Environmental NGOs and Industry Groups	493
25.4	Current Programs for Toxicological and Ecotoxicological Assessment of HPPs	493
25.5	The Way Ahead	494
25.5.1	Future Protocols for HPPs	494
25.5.2	Implementation of the Prior Informed Consent (PIC) Treaty	494

Appendix	497
-----------------	-----

Index	503
--------------	-----

