

High Performance Pigments

Second, Completely Revised and Extended Edition

Edited by

Edwin B. Faulkner and Russell J. Schwartz



WILEY-
VCH

WILEY-VCH Verlag GmbH & Co. KGaA

High Performance Pigments

Edited by

Edwin B. Faulkner and

Russell J. Schwartz

Related Titles

Freitag, W. (ed.)

Paints, Coatings and Solvents 3rd Edition

2009

ISBN: 978-3-527-31690-8

Ghosh, S. K. (ed.)

Functional Coatings by Polymer Microencapsulation

2006

ISBN: 978-3-527-31296-2

Hunger, K. (ed.)

Industrial Dyes Chemistry, Properties, Applications

2009

ISBN: 978-3-527-31401-0

Buxbaum, G., Pfaff, G. (eds.)

Industrial Inorganic Pigments

2005

ISBN: 978-3-527-30363-2

Pfaff, G. (ed.)

Encyclopedia of Applied Color

2008

ISBN: 978-3-527-31551-2

Herbst, W., Hunger, K.

Industrial Organic Pigments Production, Properties, Applications

2004

ISBN: 978-3-527-30576-6

Streitberger, H.-J., D-ssel, K.-F. (eds.)

Automotive Paints a nd Coatings

2008

ISBN: 978-3-527-30971-9

High Performance Pigments

Second, Completely Revised and Extended Edition

Edited by

Edwin B. Faulkner and Russell J. Schwartz



WILEY-
VCH

WILEY-VCH Verlag GmbH & Co. KGaA

The Editors

Edwin B. Faulkner

Sun Chemical Corporation
Performance Pigments
5020 Spring Grove Avenue
Cincinnati, OH 45232
USA

Russell J. Schwartz

Sun Chemical Corporation
Colors Technology
5020 Spring Grove Avenue
Cincinnati, OH 45232
USA

Cover Illustration:

Original artwork by Maria da Rocha, formerly manager of Analytical Services with the Colors Group on Sun Chemical, and chair person of CPMA's Analytical Committee. The work represents the expansive palette of colors now possible with today's organic and inorganic high performance pigments.

■ All books published by Wiley-VCH are carefully produced. Nevertheless, authors, editors, and publisher do not warrant the information contained in these books, including this book, to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

Library of Congress Card No.: applied for
British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library.

Bibliographic information published by
the Deutsche Nationalbibliothek The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available in the Internet at <http://dnb.d-nb.de>.

© 2009 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

All rights reserved (including those of translation into other languages). No part of this book may be reproduced in any form – by photostripping, microfilm, or any other means – nor transmitted or translated into machine language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

Printed in the Federal Republic of Germany.
Printed on acid-free paper.

Typesetting Kühn & Weyh, Satz und Medien,
Freiburg
Printing
Bookbinding

ISBN: 978-3-527-31405-8

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	<i>N</i> -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*Terence Chamberlain*

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*Fritz Herren*

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

Volker Radtke

- 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

Martin U. Schmidt

- 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

Constantinos Nicolaou

- 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/EC) 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
<i>Terry Detrie and Dan Swiler</i>		
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
<i>Robert Mott (revision of original chapter by Hugh M. Smith)</i>		
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 between 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

Preface

High performance pigments are an important segment of the diverse and rich field of color and visual effect technology. The sub-category of pigments referred to as “high performance” generally denotes members of the larger body of pigments, both organic and inorganic, that exhibit enhanced durability. The most salient durability feature is generally regarded as resistance to visible and ultraviolet radiation (lightfastness), but heat stability and chemical resistance are also critical attributes.

The distinctions within the various pigment sub-classes are not always consistent with this definition and can cause some confusion to new participants in the field. For example, copper phthalocyanine pigments typically exhibit the excellent fastness characteristics associated with high performance pigments but are often relegated to the category of classical or commodity pigments due to their prolific use in lower cost applications (e. g. publication printing inks) where durability is of minimal consequence or value. The characterization of pigments as high performance or classical types by cost is unreliable and ill advised.

The situation is further complicated by the relatively broad range of durability within the high performance pigment class. Though many organic high performance pigments exhibit sufficient stability for long-term outdoor applications, they are still not as lightfast or heat stable as the most durable inorganic members of the field. Yet another complicating factor is that application systems can significantly influence the performance. For example, copper phthalocyanine pigment may exhibit extremely poor resistance to sodium hypochlorite in one paint system and excellent resistance in another, while a mixed metal oxide performs equally well in both. Pigment surface treatments can also confound the classification situation. Lead chromate and aluminum pigments can be rendered more stable by encapsulating them with a dense amorphous layer of silica. Without this surface treatment these pigments could hardly be considered high performance in many applications.

Though it is challenging to summarize trends in such a technically diverse industry there are a few worth mentioning because they may provide some relevance and context with regard to the ongoing technical evolution. The first is that as product stewardship has gained a more prominent role in the chemical industry it has influenced the technical efforts of companies and universities engaged

in high performance pigment research and development. The Dyes & Pigments journal reported that over 60% of the research papers it receives pertain to environmental and product stewardship issues such as effluent treatment and toxicology. Most high performance pigments fall into the category of nano-particles which recently have been defined by the United States Environmental Protection Agency as particles having at least one dimension less than 100 nm. Nano-particle technology is receiving intensive scrutiny due to concerns over possible toxicological effects. The second trend is an increase in research directed toward elaborating high performance pigments for enhanced performance in emerging technologies such as digital printing, electronic displays, and solar cells, to name a few.

The chapters to follow are authored by some of the most knowledgeable innovators and practitioners in the field. Collectively, they have hundreds of patents and many have lectured throughout the world in their respective areas of expertise. Of equal importance to their technical depth is their knowledge of the commercial aspects which will influence the future of the technology and the industry. Their insights will hopefully prove to be valuable to the reader and their contributions to this collection are greatly appreciated.

Finally, thank you to Sun Chemical Corporation for its commitment and support of the project.

November 2008

Ed Faulkner
Russell Schwartz

List of Contributors

Jean-Noel Berte

Rhodia
Electronics & Catalysis
Pigments, Ceramics and Additives
21-26 rue Chef de Baie
La Rochelle, Cedex 1
France

Fritz Brenzikofer

Pigments and Additives Division
Clariant International Ltd.
65926 Frankfurt/Main
Germany

Gunter Buxbaum

Consultant
Holzapfelweg 2
47802 Krefeld
Germany

Terence Chamberlain

Sun Chemical Corporation
Colors Group
5020 Spring Grove Avenue
Cincinnati, Ohio 45232
USA

Eric Clarke

ETAD
4005, Basel 5
Switzerland

Terry Detrie

Ferro Corporation
251 W. Wylie Avenue
PO Box 519
Washington, PA 15301
USA

Paul Dunning

Johnson Matthey
Pigments and Dispersions
Liverpool Road East
Kidsgrove, Stoke-on-Trent
ST73AA
UK

Hartmut Endriss

BASF AG
67056 Ludwigshafen
Germany

Harold F. Fitzpatrick Esq.

Fitzpatrick & Waterman
333 Meadowlands Parkway, 4th Floor
P.O. Box 3159
Secaucus, New Jersey 07096
USA

Michael Greene

Bayer Corporation
Coating & Colorants Division
P.O. Box 118088
Charleston, South Carolina 29423
USA

Fritz Herren

Ciba Inc.
4002 Basel
Switzerland

Abul Iqbal

IQChem, Inc.
Post Office Box 212
4005 Basel
Switzerland

Roman Lenz

Ciba Inc.
4002 Basel
Switzerland

John Maloney

Ferro Corporation
P.O. Box 6550
Cleveland, Ohio 44101
USA

Glenn C. Merritt Esq.

Fitzpatrick & Waterman
333 Meadowlands Parkway, 4th Floor
P.O. Box 3159
Secaucus, New Jersey 07096
USA

Hans-Joachim Metz

Clariant GmbH
Pigments and Additives Division
PTRF 6G384
65926 Frankfurt/Main
Germany

Frank Morgenroth

Clariant GmbH
Pigments and Additives Division
PTRF 6G384
65926 Frankfurt/Main
Germany

Herbert Motschi

ETAD
4005, Basel 5
Switzerland

Robert Mott

Sun Chemical Corporation
5020 Spring Grove Avenue
Cincinnati, OH 45232
USA

Constantinos Nicolaou

Sun Chemical Corporation
Colors Group
5020 Spring Grove Avenue
Cincinnati, Ohio 45232
USA

Gerhard Pfaff

Merck KGaA
Pigments Division
Postfach
64271 Darmstadt
Germany

Volker Radtke

BASF AG
EFO/MP-J550
67056 Ludwigshafen
Germany

Benno Sens

BASF AG
ZDP/P-J550
67056 Ludwigshafen
Germany

Martin U. Schmidt

Goethe University
Institute of Inorganic and Analytical Chemistry
Max-von-Laue-Straße 7
60438 Frankfurt am Main
Germany

Dan Swiler

Ferro Corporation
251 West Wylie Avenue
PO Box 519
Washington, PA 15301
USA

Masao Tanaka

Dainippon Ink & Chemicals
18 Higashifukashiba Kamisu-Machi
Kashima-Gun, Ibaraki-Ken 314-02
Japan

Brian Thompson

Sun Chemical Corporation
5020 Spring Grove Avenue
Cincinnati, OH 45232
USA

Olof Wallquist

Ciba Inc.
4002 Basel
Switzerland

James White

The Shepherd Color Co.
4539 Dues Drive
Cincinnati, Ohio 45246
USA

Part I

1

Introduction to Inorganic High Performance Pigments

Gunter Buxbaum

1.1

Introduction

In 2005 the world production of inorganic pigments was approximately 6 million tonnes, representing a value of about \$14 billions. For high performance pigment applications the market in paints and coatings is of special interest and was estimated at 2.4 million tonnes representing a value of about \$5.6 billions. Some years ago the British Color Makers Association estimated the economic value of downstreamed colored industrial products using inorganic pigments at about the 80-fold of the pigment value.

In writing an introductory chapter to colored Inorganic High Performance Pigments, one is faced with a definitional dilemma, as the term “high performance pigment” is more usually met with in organic rather than inorganic literature. Cost alone is not the determining factor, otherwise the natural semiprecious stone lapis lazuli would have to be included, with its deep blue characteristics. One of the problems with high performance inorganic pigments is the limitation in available chemistry, so that very few really new compounds have been developed in recent decades.

Most inorganic pigment applications have thus been achieved by the well-known “workhorses” of conventional pigments, but the economic pressures of the last decade have dictated two main directions for product development: on the one hand an economization of existing pigment manufacture, in line with world price competition, and on the other hand, discovery and development of “new” and “improved” inorganic pigments with higher performing characteristics. Even in the more “commodity” or conventional inorganics such as chrome yellow, titanium dioxide, iron oxide, and carbon black, incrementally improved performance is required, e.g., in dust free preparations for the construction industry.

A third development started earlier. Driven by national laws and regulations in the ecological and toxicological area, “sustainable development” and substitution pressures have resulted in the replacement of formerly well known, and highly recommended inorganic pigments, such as red lead, lead molybdate, and chrome orange, by more “environmentally friendly” or less toxic substances, which can surely be considered as “high performance” pigments.

Finally, in the field of “functional pigments” such as corrosion inhibiting or optically variable types, the development of “high performance” types has been necessary.

1.2

Survey of Inorganic Pigments

When we consider a short survey of today’s major inorganic pigments, we are faced with the realization that the three major pigment families: titanium dioxide, carbon black, and iron oxides, accounting for more than 90% of the worldwide tonnage, as shown in Table 1.1, are all outside of our subject matter. They are well known to everyone, and have already been discussed in depth in recent handbooks [1, 2].

Further inspection of Table 1.1, however, reveals a selection of “high performance” pigments classified according to their chemical composition. In particular, the families of complex (or mixed) metal oxides, and functional pigments show a wide variety in their chemical composition.

Table 1.1 Inorganic pigments, classified by composition.

Class	Pigment	High performance
Elements		
	Carbon black	+
	Al-flakes	+
	Oxide coated Al, Zn/Cu flakes	+
	Zn-dust	
	Nanoscale silicon	#
Oxides/hydroxides		
	Metal-oxide flakes	+
	TiO_2	
	Fe_2O_3	
	FeOOH	
	Fe_3O_4	
	Cr_3O_3	
	Pb_3O_4	
Mixed metal oxides		
	ZnFe_2O_4	+
	CoAl_2O_4	
	$(\text{Co}, \text{Ni}, \text{Zn})_2\text{TiO}_4$	+
	$\text{Ti}(\text{Ni}, \text{Nb})\text{O}_2$	+
	$\text{Ti}(\text{Cr}, \text{Nb})\text{O}_2$	+

Table 1.1 Continued

Class	Pigment	High performance
Sulfides		
	ZnS	
	ZnS/BaSO ₄ (lithopone)	
	CdS	+
	Ce ₂ S ₃	+
Oxide/nitride		
	(Ca,La)Ta(O,N) ₃	#
Chromates		
	Pb(Cr,S)O ₄	
	Pb(Cr,Mo,S)O ₄	
Vanadates		
	BiVO ₃	+
Silicates		
	Na ₃ Al ₆ Si ₆ O ₂₄ S ₃ (ultramarine)	
	Mica, SiO ₂ and glass-based effect pigments	+
Cyanides		
	KFe[Fe(CN) ₆]	

Note: # not yet in industrial scale

In every pigment class illustrated, one will find at least one grade with a high performance characteristic, which may be the determining factor, or driver, for the end user to purchase this pigment in their application. It is self-evident, therefore, that degree of performance for a pigment depends on the demands imposed upon it for its intended application.

1.3

New Candidates on the Catwalk of Color

Bearing in mind the limitation in the color of inorganic pigments, one has to be surprised at the numbers of new compounds introduced with good pigment performance. More and more, specialized physical effects appear to dominate over variation in chemical composition. In Table 1.1, for example, we must point out that mica-based effect pigments, being still a “young” pigment class, have already become well established since their “breakthrough” introduction. Again, while bismuth vanadate yellow is in the early stages of its growth potential, cerium sulfides

are in their industrial infancy, and are attempting to carve out a niche for themselves in applications where the well-established cadmium sulfide family is no longer the pigment of choice. On the more experimental side, “nanoscale silicon,” with particle size below 5 nm, is now available as a laboratory curiosity in microgram quantities as the first in the series of “quantum effect pigments” predicted by theoretical physicists [3]. Nearer to introduction is another new family, the calcium, lanthanum, tantalum oxide-nitrides [4]. Reproducibility, however, must be proven first. Their published properties, *viz.*, brilliance of color coupled with non-toxicity, appear ideal for inclusion in the high-performance category.

A study of the “old fashioned” and almost forgotten workhorse pigment ultramarine blue could also be significant in the light of its revival through recently introduced new manufacturing technology. And so it is possible that, in the future, development of new manufacturing processes for “old” pigments and enhancement of their properties might well revitalize these products to the point where they could also join the ranks of truly high performance pigments.

1.4

Challenges for the Future

This leads us to consider challenges for new high performance pigments, which can be designated as *Three Essential Es*:

<i>Effectiveness</i>	=	Technical performance
<i>Economy</i>	=	Benefits for the customer
<i>Ecology</i>	=	Environmental and toxicological safety

Better effectiveness could include higher tinting strength, greater ease of dispersion, better fineness of grind, higher saturation, and so on.

Better economy could include widening the fields of application for known high performance pigments by giving the customer enhanced value-in-use. And better ecology is today’s task for industry as a whole, and is self-evident.

All three “E” will be optimized further on. New inventions will be made, hand-in-hand with steady process and product development. And as we can learn from a study of today’s lowercost pigments, such as lead chromate, where the encapsulated specialties of yesteryear are now the norm for coatings application, the high performance pigments of today will become the conventional standards of tomorrow, with those of tomorrow having to be invented now. And so the development of high performance inorganic pigments is, in reality, a never-ending story.

References

- 1 P.A. Lewis, ed., *The Pigment Handbook*, 2nd edn., Wiley, New York, 1988.
- 2 G. Buxbaum and G. Pfaff, eds., *Industrial Inorganic Pigments*, 3rd edn., Wiley-VCH, Weinheim, 2005.
- 3 A.G. Cullis and L.T. Canham, *Nature* 353 (1991) 335.
- 4 M. Jansen and H.P. Letschert, *Nature* 404 (2000) 980–982.