

High Performance Pigments

Second, Completely Revised and Extended Edition

Edited by

Edwin B. Faulkner and Russell J. Schwartz



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., Dessel, K.-F. (eds.)

Automotive Paints and 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 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 photoprinting, 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	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

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 ultra-violet 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 two 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 Higashifukushiba 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 ₂ O ₃	
	FeOOH	
	Fe ₃ O ₄	
	Cr ₃ O ₃	
	Pb ₃ O ₄	
Mixed metal oxides		+
	ZnFe ₂ O ₄	+
	CoAl ₂ O ₄	
	(Co,Ni,Zn) ₂ TiO ₄	+
	Ti(Ni,Nb)O ₂	+
	Ti(Cr,Nb)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.