

Willy Herbst, Klaus Hunger

# **Industrial Organic Pigments**

Production, Properties, Applications

Third, Completely Revised Edition

With Contributions by  
Gerhard Wilker, Heinfred Ohleier,  
and Rainer Winter



WILEY-VCH Verlag GmbH & Co. KGaA



W. Herbst, K. Hunger

**Industrial  
Organic Pigments**

## Further Titles of Interest:

K. Hunger (Ed.)

**Industrial Dyes**

2002

ISBN 3-527-30426-6

G. Buxbaum (Ed.)

**Industrial Inorganic Pigments**

Second, Completely Revised Edition

1998

ISBN 3-527-28878-3

H. M. Smith (Ed.)

**High Performance Pigments**

2002

ISBN 3-527-30204-2

H. G. Völz

**Industrial Color Testing**

**Fundamentals and Techniques**

Second, Completely Revised Edition

2001

ISBN 3-527-30436-3

W. Freitag, D. Stoye (Eds.)

**Paints, Coatings and Solvents**

Second, Completely Revised Edition

1998

ISBN 3-527-28863-5

J. Bieleman (Ed.)

**Additives for Coatings**

2000

ISBN 3-527-29785-5

Willy Herbst, Klaus Hunger

# **Industrial Organic Pigments**

Production, Properties, Applications

Third, Completely Revised Edition

With Contributions by  
Gerhard Wilker, Heinfred Ohleier,  
and Rainer Winter



WILEY-VCH Verlag GmbH & Co. KGaA

Dr. Willy Herbst  
Frankfurter Straße 10  
D-65719 Hofheim  
Germany

Dr. Klaus Hunger  
Johann-Strauß-Straße 35  
D-65779 Kelkheim  
Germany

Gerhard Wilker  
Clariant GmbH  
Div. PA/BU Pigmente  
BG Lack  
Industriepark Höchst, C 653  
D-65926 Frankfurt am Main  
Germany

Heinfred Ohleier  
Clariant GmbH  
Div. PA/BU Pigmente  
BG Kunststoff  
Industriepark Höchst, C 653  
D-65926 Frankfurt am Main  
Germany

Rainer Winter  
Clariant GmbH  
Div. PA/BU Druckpigmente-AT, LTG  
Industriepark Höchst, C 653  
D-65926 Frankfurt am Main  
Germany

This book was carefully produced. Nevertheless, authors and publisher do not warrant the information contained therein 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  
A catalogue record for this book is available from the British Library

Bibliographic information published by  
Die Deutsche Bibliothek  
Die Deutsche Bibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data is available in the Internet at <<http://dnb.ddb.de>>

First Edition 1993  
Second Edition 1997  
Third Edition 2004

© 2004 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 a 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 acid-free and low chlorine paper  
Printed in the Federal Republic of Germany

Composition: Detzner Fotosatz, Speyer  
Printing: Druckhaus Darmstadt GmbH,  
Darmstadt  
Bookbinding: Litges & Dopf Buchbinderei  
GmbH, Heppenheim

ISBN 3-527-30576-9

# Preface to the Third Edition

The second edition of our book has again found a favourable reception worldwide, triggering even a reprint of that edition some time ago. We are therefore pleased to present the third edition, again as a comprehensively reviewed and updated version. Due to the friendly acceptance of the former editions, principle and basic concepts of the book have not been changed.

Although Willy Herbst has resigned from work on this new edition, we were able to win three experts on the applications of organic pigments as new coauthors to help continue maintaining the expected standard of *Industrial Organic Pigments*.

Together with Heinfred Ohleier, Gerhard Wilker and Rainer Winter of Clariant Deutschland GmbH, we thoroughly reviewed and updated all parts of the book and included many pigments newly launched into the market since the second edition, with all properties and applications which were available to us.

Again, we are grateful for comments, advice and additions from colleagues from chemical companies, especially from Clariant, Ciba Specialty Chemicals and Engelhard USA. Furthermore, we express our gratitude to the publishing team of Wiley-VCH, in particular to Karin Sora, who, as always, accompanied our work with great devotion.

Kelkheim and Frankfurt  
January 2004

K. Hunger, H. Ohleier, G. Wilker, R. Winter





# Preface to the Second Edition

The current trend in the manufacture and use of organic pigments is a steady increase, the present worldwide consumption being estimated as 160 000 tons, with an equivalent value of about 3 billion dollars.

As a result of the favorable reception of the first edition of this book, we decided to maintain its structure and conception to the greatest possible extent in this new edition. Thus, we have tried to include comprehensively all organic pigments available on the market. The book has been thoroughly reviewed and carefully updated with regard to production, properties, test methods, application, chemical formulas, and the list of commercially available organic pigments. We have considered all the information accessible to us about pigments newly launched on the market as well as additional information about pigments described in the previous edition. The list of commercially available pigments was further supplemented by more C.I. Formula numbers and CAS numbers. Section 1.6.1 (Coloristic Properties) has been kindly revised by Dr. Glaser, DPP pigments (3.5) and quinophthalone pigments (3.9) are now included in Chapter 3. The index was completely revised and considerably extended by a great many additional terms.

For several reasons, ranges of pigments have been rationalized in recent years, causing a withdrawal of a considerable number of pigments from the market. The rationale behind the removal of these pigments, when known to us, is given. Since these brands will still be used for some years, for example in automotive repair finishes, we have continued to describe their properties in the new edition.

The introduction of newly developed, especially high-performance pigments, may take a considerable period of time. Owing to the outdoors weathering tests required, the extensive and comprehensive testing procedures of very lightfast and weatherfast pigments for automotive finishes or certain plastics applications may last two years or even longer. Because of the dependence of lightfastness and weatherfastness on the entire application media, correspondingly comprehensive testing procedures have to be performed by the pigment manufacturer, i.e., the paint company or plastics processor. For this reason, high-performance pigments may often take several years to reach the market.

We thank the management and several colleagues of the Division Specialty Chemicals of Hoechst AG for supporting us again by providing relevant information and scientific sources. Furthermore, we express our gratitude to colleagues at Ciba-Geigy AG in Basel for assistance, which greatly helped to improve our knowledge of DPP pigments. We are grateful to several colleagues from other companies for their advice and suggestions.

VIII *Preface to the Second Edition*

The cooperation with our publisher, WILEY-VCH, was again a pleasure for us, and we thank Ms. K. Sora and Ms. C. Grossl in particular for their devotion to making this book a successful one.

Hofheim and Kelkheim  
April 1997

W. Herbst, K. Hunger

# Preface to the First Edition

Organic pigments - the increasingly most important group of organic colorants worldwide - have never yet been treated comprehensively with respect to their industrial significance and their application properties. In this book we have tried to give an account of the chemistry, the properties, and applications of all commercially produced organic pigments.

This book is intended for all those who are interested in organic pigments, especially chemists, engineers, application technicians, colorists, and laboratory assistants throughout the pigments industry and in universities and technical colleges. We have specifically avoided an in-depth discussion of the underlying scientific and theoretical framework, but there are references to the pertinent literature.

The initial part is devoted to chemical and physical characterization of pigments and discusses important terminology connected with pigment application. This is followed by three chapters describing the chemistry and synthesis, the properties and application of individual pigments. In these chapters pigments are classified according to their chemical structure and listed by their Colour Index Name instead of their trade name. The Colour Index, published by the Society of Dyers and Colourists, lists all those pigments and dyes which have been registered by the pigment and dye manufacturers. The products are listed by their Colour Index (C.I.) Generic Name, followed by a Constitution Number, provided the chemical structure has been published. An example is C.I. Pigment Yellow 1, 11680. The last chapter discusses questions of ecology and toxicology. The literature references listed at the end of each dual-numbered subchapter have been limited to a selection covering the most important topics. The appendix shows general structural equations for the syntheses of individual groups of pigments and lists all pigments mentioned in this book, including the respective CAS (Chemical Abstracts Service) registry numbers.

The technical and fastness properties of different pigments have been assessed by unified, usually standardized test methods. Lightfastness measurements, however, had to be carried out by comparison to the Blue Scale - despite serious objections which are explained in the text. This was the only technique which made it possible to list comparative values for all pigments described in this book.

After careful deliberation we have reluctantly refrained from listing data on pigment economics. Reliable data on organic pigments have only been published in a few countries. Moreover, many of the other data turned out to be either contradictory or so incomplete that it was impossible to elicit reliable information from them.

We are pleased to present here the English version of our book, which is an update of the German edition of 1987, supplemented by all appropriate and newly published data. Also included are those commercial organic pigments which have recently been introduced to the market.

We would like to thank Mrs. Barbara Hoeksema for her work in translating this book.

We would like to express our gratitude to the management of the Fine Chemicals and Colors Division of Hoechst AG for their support and for making the scientific and technical resources available to us. We would also like to thank the numerous colleagues, both at other companies - especially at BASF AG and at Ciba/Geigy AG - and in-house colleagues, who through their stimulation, critique, and suggestions supported us considerably. We would like to express our particular gratitude to Dr. F. Glaser, who wrote Chapter 1.6.1.

Our appreciation is also extended to our families and friends, without whose consideration and patience it would not have been possible to write this book.

It is a pleasure to express our gratitude to the VCH publishing company who helped us greatly through their stimulation and their compliance with many of our wishes.

Frankfurt-Höchst  
December 1992

W. Herbst, K. Hunger

# Contents

<b>1</b>	<b>General</b>	
1.1	Definition: Pigments–Dyes . . . . .	1
1.1.1	Organic-Inorganic Pigments. . . . .	2
1.2	Historical . . . . .	3
1.3	Classification of Organic Pigments . . . . .	4
1.3.1	Azo Pigments . . . . .	5
1.3.1.1	Monoazo Yellow and Orange Pigments . . . . .	5
1.3.1.2	Disazo Pigments . . . . .	5
1.3.1.3	$\beta$ -Naphthol Pigments . . . . .	6
1.3.1.4	Naphthol AS Pigments (Naphthol Reds) . . . . .	6
1.3.1.5	Azo Pigment Lakes (Salt Type Pigments) . . . . .	6
1.3.1.6	Benzimidazolone Pigments . . . . .	7
1.3.1.7	Disazo Condensation Pigments . . . . .	7
1.3.1.8	Metal Complex Pigments . . . . .	7
1.3.1.9	Isoindolinone and Isoindoline Pigments . . . . .	7
1.3.2	Polycyclic Pigments . . . . .	8
1.3.2.1	Phthalocyanine Pigments . . . . .	8
1.3.2.2	Quinacridone Pigments . . . . .	8
1.3.2.3	Perylene and Perinone Pigments . . . . .	9
1.3.2.4	Diketopyrrolo–Pyrrole (DPP) Pigments . . . . .	9
1.3.2.5	Thioindigo Pigments . . . . .	9
1.3.3	Anthraquinone Pigments . . . . .	9
1.3.3.1	Anthrapyrimidine Pigments . . . . .	10
1.3.3.2	Flavanthrone Pigments . . . . .	10
1.3.3.3	Pyranthrone Pigments . . . . .	10
1.3.3.4	Anthanthrone Pigments . . . . .	10
1.3.4	Dioxazine Pigments . . . . .	10
1.3.5	Triarylcarbonium Pigments . . . . .	11
1.3.6	Quinophthalone Pigments . . . . .	11
1.4	Chemical Characterization of Pigments . . . . .	11
1.4.1	Hue . . . . .	12
1.4.1.1	Crystal Modification and Crystal Structure . . . . .	16

## XII Contents

1.4.2	Tinctorial Strength . . . . .	17
1.4.3	Lightfastness and Weatherfastness . . . . .	20
1.4.4	Solvent and Migration Fastness . . . . .	21
1.5	Physical Characterization of Pigments . . . . .	24
1.5.1	Specific Surface Area . . . . .	26
1.5.2	Particle Size Distribution . . . . .	31
1.5.2.1	Determination of Particle Size by Ultrasedimentation . . . . .	31
1.5.2.2	Determination by Electron Microscopy . . . . .	33
1.5.2.3	Data Representation . . . . .	37
1.5.3	Polymorphism . . . . .	41
1.5.4	Crystallinity . . . . .	44
1.6	Important Application Properties and Concepts . . . . .	47
1.6.1	Coloristic Properties (by F. Gläser) . . . . .	47
1.6.1.1	Color . . . . .	47
1.6.1.2	Color Depth . . . . .	50
1.6.1.3	Color Differences . . . . .	51
1.6.1.4	Optical Behaviour of Pigmented Coatings . . . . .	51
1.6.1.5	Tinctorial Strength . . . . .	53
1.6.1.6	Hiding Power . . . . .	55
1.6.1.7	Transparency . . . . .	55
1.6.2	Fastness to Solvents and Special Application Fastness . . . . .	56
1.6.2.1	Organic Solvents . . . . .	56
1.6.2.2	Water, Soap, Alkali, and Acids . . . . .	57
1.6.2.3	Pigment Performance in Special Applications . . . . .	59
1.6.2.4	Textile Fastness Properties . . . . .	61
1.6.3	Migration . . . . .	62
1.6.3.1	Blooming . . . . .	63
1.6.3.2	Bleeding/Overspraying Fastness . . . . .	65
1.6.4	Disturbances During the Processing of Pigmented Systems . . . . .	69
1.6.4.1	Plate-Out . . . . .	70
1.6.4.2	Overpigmentation/Chalking . . . . .	70
1.6.4.3	Distortion/Nucleation in Polymers . . . . .	71
1.6.5	Dispersion . . . . .	72
1.6.5.1	General Considerations . . . . .	72
1.6.5.2	Desagglomeration of Pigment Particles . . . . .	74
1.6.5.3	Wetting of Pigment Particle Surfaces . . . . .	74
1.6.5.4	Distribution of the Dispersed Pigment in its Medium . . . . .	78
1.6.5.5	Stabilization . . . . .	79
1.6.5.6	Dispersion and the Critical Pigment Volume Concentration . . . . .	80
1.6.5.7	Test Methods . . . . .	81
1.6.5.8	Flush Pastes . . . . .	86
1.6.5.9	Pigment Preparations . . . . .	87
1.6.6	Lightfastness and Weatherfastness . . . . .	87
1.6.6.1	Definition and General Information . . . . .	87
1.6.6.2	Evaluation Techniques and Equipment . . . . .	88

1.6.6.3	Factors Determining the Lightfastness . . . . .	91
1.6.7	Thermal Stability . . . . .	98
1.6.8	Flow Properties of Pigmented Systems . . . . .	104
1.6.8.1	Rheological Properties . . . . .	104
1.6.8.2	Viscoelastic Properties . . . . .	107
1.6.8.3	Influence on the Flow Properties . . . . .	108
1.6.8.4	Correlation between Flow Behavior and Rheological Parameters . . . . .	108
1.6.8.5	Rheological Measurements . . . . .	110
1.7	Particle Size Distribution and Application Properties of Pigmented Media . . . . .	118
1.7.1	Tinctorial Strength . . . . .	118
1.7.2	Hue . . . . .	120
1.7.3	Hiding Power, Transparency . . . . .	125
1.7.4	Lightfastness and Weatherfastness . . . . .	130
1.7.5	Dispersibility . . . . .	133
1.7.6	Gloss . . . . .	134
1.7.7	Solvent and Migration Fastness . . . . .	136
1.7.8	Flow . . . . .	140
1.8	Areas of Application for Organic Pigments . . . . .	142
1.8.1	Printing Inks . . . . .	143
1.8.1.1	Offset/Letterpress Printing . . . . .	144
1.8.1.2	Gravure Printing . . . . .	148
1.8.1.3	Flexo and Screen Printing and Other Printing Processes . . . . .	152
1.8.1.4	Security Printing . . . . .	152
1.8.2	Coatings . . . . .	153
1.8.2.1	Oxidatively Drying Paints . . . . .	153
1.8.2.2	Oven Drying Systems . . . . .	154
1.8.2.3	Emulsion Paints . . . . .	159
1.8.3	Plastics . . . . .	160
1.8.3.1	Polyolefins . . . . .	164
1.8.3.2	Polyvinyl Chloride (PVC) . . . . .	167
1.8.3.3	Polyurethane . . . . .	171
1.8.3.4	Polyamide, Polycarbonate, Polyester, Polyoxymethylene . . . . .	172
1.8.3.5	Polystyrene, Styrene-Copolymers, Poly(Methyl Methacrylate) . . . . .	173
1.8.3.6	Elastomers . . . . .	174
1.8.3.7	Thermosets (Thermosetting Plastics) . . . . .	175
1.8.3.8	Spin Dyeing . . . . .	176
1.8.4	Other Areas of Application . . . . .	179

**2 Azo Pigments**

2.1	Starting Materials, Synthesis . . . . .	184
2.1.1	Diazo Components . . . . .	185
2.1.2	Coupling Compounds . . . . .	188

XIV Contents

2.1.3	Important Intermediates . . . . .	192
2.2	Synthesis of Azo Pigments . . . . .	193
2.2.1	Diazotization . . . . .	194
2.2.1.1	Diazotization Mechanism . . . . .	195
2.2.1.2	Methods of Diazotization . . . . .	196
2.2.2	Coupling . . . . .	197
2.2.2.1	Coupling Techniques . . . . .	199
2.2.3	Finishing . . . . .	201
2.2.4	Filtration, Drying, Milling . . . . .	203
2.2.5	Azo Pigment Synthesis by Continuous Operation . . . . .	204
2.2.6	Production Units for Azo Pigment Manufacture by Batch Operation . . . . .	207
2.3	Monoazo Yellow and Orange Pigments . . . . .	210
2.3.1	Chemistry, Manufacture . . . . .	211
2.3.1.1	Non-laked Monoazo Yellow and Orange Pigments . . . . .	211
2.3.1.2	Monoazo Yellow Pigment Lakes . . . . .	214
2.3.2	Properties . . . . .	215
2.3.2.1	Non-laked Monoazo Yellow and Orange Pigments . . . . .	215
2.3.2.2	Monoazo Yellow Pigment Lakes . . . . .	216
2.3.3	Application . . . . .	216
2.3.4	Commercially Available Monoazo Yellow and Orange Pigments . . . . .	217
2.4	Disazo Pigments . . . . .	236
2.4.1	Diarylide Yellow Pigments . . . . .	237
2.4.1.1	Chemistry, Manufacture . . . . .	237
2.4.1.2	Properties . . . . .	239
2.4.1.3	Application . . . . .	241
2.4.1.4	Commercially Available Diarylide Yellow and Orange Pigments . . . . .	243
2.4.2	Bisacetoacetarylide Pigments . . . . .	260
2.4.2.1	Commercially Available Bisacetoacetarylide Pigments and Their Properties . . . . .	261
2.4.3	Disazopyrazolone Pigments . . . . .	264
2.4.3.1	Chemistry, Manufacture . . . . .	264
2.4.3.2	Properties . . . . .	265
2.4.3.3	Application . . . . .	265
2.4.3.4	Commercially Available Pigments . . . . .	265
2.5	$\beta$ -Naphthol Pigments . . . . .	270
2.5.1	Chemistry, Manufacture . . . . .	271
2.5.2	Properties . . . . .	273
2.5.3	Application . . . . .	274
2.5.4	Commercially Available $\beta$ -Naphthol Pigments . . . . .	275
2.6	Naphthol AS Pigments . . . . .	280
2.6.1	Chemistry, Manufacture . . . . .	282
2.6.2	Properties . . . . .	283
2.6.3	Application . . . . .	284



2.6.4	Commercially Available Naphthol AS Pigments . . . . .	286
2.7	Red Azo Pigment Lakes . . . . .	313
2.7.1	$\beta$ -Naphthol Pigment Lakes . . . . .	314
2.7.1.1	Chemistry, Manufacture . . . . .	314
2.7.1.2	Properties . . . . .	315
2.7.1.3	Application . . . . .	316
2.7.1.4	Commercially Available Pigments . . . . .	316
2.7.2	BONA Pigment Lakes . . . . .	323
2.7.2.1	Chemistry, Manufacture . . . . .	324
2.7.2.2	Properties . . . . .	324
2.7.2.3	Application . . . . .	325
2.7.2.4	Commercially Available BONA Pigment Lakes . . . . .	325
2.7.3	Naphthol AS Pigment Lakes . . . . .	336
2.7.3.1	Chemistry, Manufacture, and Properties . . . . .	336
2.7.3.2	Commercially Available Naphthol AS Pigment Lakes . . . . .	336
2.7.4	Naphthalene Sulfonic Acid Pigment Lakes . . . . .	340
2.7.4.1	Chemistry, Manufacture, and Properties . . . . .	340
2.7.4.2	Commercially Available Pigments . . . . .	340
2.8	Benzimidazolone Pigments . . . . .	343
2.8.1	Chemistry, Manufacture . . . . .	345
2.8.1.1	Yellow and Orange Benzimidazolone Pigments – Coupling Component . . . . .	345
2.8.1.2	Red Benzimidazolone Pigments – Coupling Component . . . . .	346
2.8.1.3	Pigment Synthesis and Aftertreatment . . . . .	346
2.8.1.4	Results of Crystal Structure Analyses . . . . .	347
2.8.2	Properties . . . . .	348
2.8.3	Application . . . . .	349
2.8.4	Commercially Available Benzimidazolone Pigments . . . . .	351
2.9	Disazo Condensation Pigments . . . . .	369
2.9.1	Chemistry, Manufacture . . . . .	369
2.9.2	Properties . . . . .	372
2.9.3	Application . . . . .	373
2.9.4	Commercially Available Pigments . . . . .	374
2.10	Metal Complex Pigments . . . . .	388
2.10.1	Chemistry, Synthesis . . . . .	389
2.10.1.1	Azo Metal Complexes . . . . .	390
2.10.1.2	Azomethine Metal Complexes . . . . .	391
2.10.2	Properties . . . . .	392
2.10.3	Application . . . . .	393
2.10.4	Commercially Available Pigments . . . . .	393
2.11	Isoindolinone and Isoindoline Pigments . . . . .	401
2.11.1	Chemistry, Synthesis, Starting Materials . . . . .	403
2.11.1.1	Azomethine Type: Tetrachloroisoindolinone Pigments . . . . .	403
2.11.1.2	Methine Type: Isoindoline Pigments . . . . .	407

2.11.2	Properties . . . . .	409
2.11.3	Application . . . . .	410
2.11.4	Commercially Available Isoindolinone and Isoindoline Pigments . . . . .	410

### **3 Polycyclic Pigments**

3.1	Phthalocyanine Pigments . . . . .	422
3.1.1	Starting Materials . . . . .	423
3.1.2	Manufacture . . . . .	424
3.1.2.1	Phthalonitrile Process . . . . .	425
3.1.2.2	Phthalic Anhydride/Urea Process . . . . .	428
3.1.2.3	Manufacturing the Different Crystal Modifications . . . . .	432
3.1.2.4	Phase- and Flocculation-Stabilized Copper Phthalocyanine Blue Pigments . . . . .	434
3.1.2.5	Manufacture of Green Types . . . . .	435
3.1.2.6	Metal-free Phthalocyanine Blue . . . . .	436
3.1.3	Properties . . . . .	437
3.1.4	Application . . . . .	439
3.1.5	Commercially Available Pigments . . . . .	440
3.2	Quinacridone Pigments . . . . .	452
3.2.1	Manufacture, Starting Materials . . . . .	453
3.2.1.1	Thermal Ring Closure . . . . .	454
3.2.1.2	Acidic Ring Closure . . . . .	455
3.2.1.3	Dihalo Terephthalic Acid Process . . . . .	456
3.2.1.4	Hydroquinone Process . . . . .	457
3.2.1.5	Substituted Quinacridones . . . . .	457
3.2.1.6	Quinacridone Quinone . . . . .	458
3.2.1.7	Polymorphism . . . . .	459
3.2.2	Properties . . . . .	461
3.2.3	Application . . . . .	462
3.2.4	Commercially Available Quinacridone Pigments . . . . .	462
3.3	Vat Dyes Prepared as Pigments . . . . .	472
3.4	Perylene and Perinone Pigments . . . . .	473
3.4.1	Perylene Pigments . . . . .	474
3.4.1.1	Preparation of the Starting Materials . . . . .	474
3.4.1.2	Chemistry, Manufacture . . . . .	475
3.4.1.3	Properties . . . . .	476
3.4.1.4	Application . . . . .	476
3.4.1.5	Commercially Available Perylene Pigments . . . . .	477
3.4.1.6	Various Other Perylene Tetracarboxylic Acid Pigments . . . . .	482
3.4.2	Perinone Pigments . . . . .	483
3.4.2.1	Preparation of the Starting Materials . . . . .	483
3.4.2.2	Chemistry, Manufacture . . . . .	484

3.4.2.3	Properties . . . . .	484
3.4.2.4	Commercially Available Perinone Pigments and Their Application . . . . .	484
3.5	Diketopyrrolo-Pyrrole (DPP) Pigments . . . . .	487
3.5.1	Chemistry, Manufacture . . . . .	487
3.5.2	Properties and Application . . . . .	489
3.5.3	Commercially Available DPP Pigments . . . . .	490
3.6	Thioindigo Pigments . . . . .	495
3.6.1	Chemistry, Manufacture . . . . .	495
3.6.2	Properties . . . . .	497
3.6.3	Commercially Available Types and Their Application . . . . .	498
3.7	Various Polycyclic Pigments . . . . .	501
3.7.1	Aminoanthraquinone Pigments . . . . .	501
3.7.1.1	Anthraquinone-Azo Pigments . . . . .	502
3.7.1.2	Other Aminoanthraquinone Pigments . . . . .	504
3.7.1.3	Properties and Application . . . . .	507
3.7.2	Hydroxyanthraquinone Pigments . . . . .	509
3.7.2.1	Properties and Application . . . . .	511
3.7.3	Heterocyclic Anthraquinone Pigments . . . . .	511
3.7.3.1	Anthrapyrimidine Pigments . . . . .	511
3.7.3.2	Indanthrone and Flavanthrone Pigments . . . . .	513
3.7.4	Polycarbocyclic Anthraquinone Pigments . . . . .	520
3.7.4.1	Pyranthrone Pigments . . . . .	520
3.7.4.2	Anthanthrone Pigments . . . . .	524
3.7.4.3	Isoviolanthrone Pigments . . . . .	527
3.8	Dioxazine Pigments . . . . .	530
3.8.1	Preparation of the Starting Materials . . . . .	530
3.8.2	Chemistry, Manufacture . . . . .	531
3.8.3	Properties . . . . .	532
3.8.4	Commercially Available Dioxazine Pigments and Their Application . . . . .	533
3.9	Quinophthalone Pigments . . . . .	537
3.9.1	Chemistry, Manufacture . . . . .	537
3.9.2	Properties and Application . . . . .	539
3.10	Triarylcarbonium Pigments . . . . .	540
3.10.1	Inner Salts of Sulfonic Acids (Alkali Blue Types) . . . . .	541
3.10.1.1	Chemistry, Manufacture . . . . .	542
3.10.1.2	Properties . . . . .	546
3.10.1.3	Commercially Available Types and Their Application . . . . .	546
3.10.2	Dye Salts with Complex Anions . . . . .	549
3.10.2.1	Chemistry, Manufacture . . . . .	550
3.10.2.2	Properties . . . . .	557
3.10.2.3	Application . . . . .	557
3.10.2.4	Important Representatives . . . . .	557

XVIII *Contents*

**4        Miscellaneous Pigments**

4.1	Aluminum Pigment Lakes . . . . .	567
4.2	Pigments with Known Chemical Structure Which Cannot be Assigned to Other Chapters . . . . .	570
4.3	Pigments with Hitherto Unknown Chemical Structure . . . . .	578

**5        Legislation, Ecology, Toxicology**

5.1	Introduction . . . . .	585
5.2	Legislation . . . . .	586
5.2.1	General . . . . .	586
5.2.2	Legislation Concerning Organic Pigments . . . . .	586
5.2.2.1	Food Packaging . . . . .	589
5.2.2.2	Toys . . . . .	591
5.2.2.3	Consumer Goods . . . . .	592
5.3	Ecology . . . . .	593
5.4	Toxicology . . . . .	594
5.4.1	Acute Toxicity . . . . .	594
5.4.2	Irritation of Skin and Mucous Membrane . . . . .	595
5.4.3	Toxicity After Repeated Application . . . . .	595
5.4.4	Mutagenicity . . . . .	596
5.4.5	Chronic Toxicity – Carcinogenicity . . . . .	596

<b>Review of Chemical Structures and Chemical Reactions . . . . .</b>	<b>601</b>
---	------------

<b>List of Commercially Available Pigments . . . . .</b>	<b>637</b>
--	------------

<b>Subject Index . . . . .</b>	<b>647</b>
--------------------------------	------------

# 1 General

## 1.1 Definition: Pigments–Dyes

Colorants are classified as either pigments or dyes. Pigments are inorganic or organic, colored, white or black materials which are practically insoluble in the medium in which they are incorporated. Dyes, unlike pigments, do dissolve during their application and in the process lose their crystal or particulate structure. It is thus by physical characteristics rather than by chemical composition that pigments are differentiated from dyes [1]. In fact, both are frequently similar as far as the basic chemical composition goes, and one structural skeleton may function either as a dye or as a pigment.

In many cases the general chemical structure of dyes and pigments is the same. The necessary insolubility for pigments can be achieved by avoiding solubilizing groups in the molecule or by forming insoluble organic structures. Carboxylic and especially sulfonic acid functional groups lend themselves to the formation of insoluble metal salts (lakes); formation of metal complex compounds without solubilizing groups and finally suitable substitution may decrease the solubility of the parent structure (e.g., carbonamide groups).

Pigments of many classes may be practically insoluble in one particular medium, yet dissolve to some extent in another. Partial solubility of the pigment is a function of application medium and processing conditions, especially of the processing temperature. Important application properties of pigments and/or pigmented systems, such as tinctorial strength, migration, recrystallization, heat stability, lightfastness and weatherability, are often determined by the portion of pigment that dissolves to a minor degree in the vehicle in which it is applied.

Monoazo yellow pigments of the Hansa Yellow type (e.g., P.Y.1, P.Y.3; Sec. 2.3.4) may serve as an example. Their solubility in air-dried alkyd resin systems is so negligible that they are considered insoluble; which explains their frequent use in such media. Since their solubility increases with increasing temperature, they migrate considerably in vehicles such as various oven-dried varnish systems or in plastics. This results in bleeding or blooming (Sec. 1.6.3). Strong migratory tendencies preclude their use in such high temperature applications. Even slight temperature changes in the course of pigment incorporation into its application medium may often determine the commercial fate of a pigment. Moreover, the inherent tinctorial properties of a product in a particular vehicle system are sometimes compro-

mised by difficulties such as recrystallization, which arises through a certain solubility of the pigment in its medium.

Under certain circumstances, it may even be advantageous to have a pigment dissolved to some degree in its binder system in order to improve certain application properties such as tinctorial strength and rheological behavior. Such conditions arise when special amine-treated diarylide yellow pigments are incorporated in toluene-based publication gravure inks (Sec. 1.8.1.2). In toluene, up to 5% of the amine-treated pigment may be either dissolved or dispersed to a nearly molecular level. This improves the tinctorial strength and decreases the viscosity, which in turn enhances the rheology of the pigmented ink. The performance of a colorant in its role as a commercial pigment is therefore defined by its interaction with the application medium under the conditions that govern its application.

### 1.1.1 Organic–Inorganic Pigments

In some application areas, inorganic pigments are also used to an appreciable extent, frequently in combination with organic pigments. A comparison of the respective application properties of inorganic versus organic pigments shows some fundamentally important differences between the two families.

Most inorganic pigments are extremely weatherfast (Sec. 1.6.6) and many exhibit excellent hiding power (Sec. 1.6.1.3). Their rheology is usually an advantage (Sec. 1.6.8), being superior to that of most organic pigments under comparable conditions. In white reductions, however, many inorganic pigments have much less strength than organic pigments. With the exception of Molybdate Red, Chrome Yellow, and cadmium-based pigments, inorganic pigments provide dull shades. Since there are only relatively few inorganic types, the spectral range that is accessible by inorganic pigments alone is very limited. Many hues cannot be produced in this manner.

Inorganic pigments not only exhibit coloristic limitations but also frequently present application problems. Ultramarine Blue, for instance, is not fast to acid; while Prussian Blue must not be exposed to alkalis. Such limitations preclude the application of especially Prussian Blue in paints that are to be applied to a basic substrate (e.g., exterior house paints). In the red range of the spectrum, iron oxide red pigments produce weak hues of comparatively little brilliance. Molybdate Reds and Chrome Yellows lend themselves to a host of applications but are nevertheless sensitive to acids and light. There are stabilized versions of such pigments which claim improved lightfastness and acid resistance. These products also claim to be chemically fast to hydrogen sulfide, which affects the brightness of a coating through sulfide formation. However, if the particle surfaces of such types are damaged in the course of the dispersion process, the above-mentioned deficiencies are apparent at the damaged site.

Poor tinctorial strength and lack of brilliance restricts the use of inorganic pigments in printing inks. There are areas of application, however, where it is hardly,

if at all, possible to replace the inorganic species by an organic pigment. The ceramics industry, for example, requires extreme heat stability, which precludes the use of organic compounds. Thus, the organic and inorganic classes of pigments are generally considered complementary rather than competitive.

## Reference for Section 1.1

- [1] DIN 55 943: Farbmittel, Begriffe. ISO 4618-1-1984 (TC 35): Paints and varnishes–Vocabulary, Part 1: General terms.

## 1.2 Historical

The history of pigment application dates back to prehistoric cave paintings, which give evidence of the use of ocher, hematite, brown iron ore, and other mineral-based pigments more than 30,000 years ago. Cinnabar, azurite, malachite, and lapis lazuli have been traced back to the third millennium BC in China and Egypt. With Prussian Blue in 1704 the first inorganic pigment was synthesized. It was not until a century later that Thenard produced his Cobalt Blue. Ever increasing expertise and technology led to the production of Chrome Yellow, Cadmium Yellow, several synthetic iron oxides covering parts of the ranges of yellow, red, and black hues; Chrome Oxide Green, and Ultramarine.

Important twentieth-century developments include the addition of Molybdate Red to the series of inorganic synthetic coloring matters in 1936; Titan Yellow followed in 1960.

Currently newly developed inorganic pigments were introduced to the market:

- bismuth-molybdenum-vanadium oxide pigments for lead-free formulation
- cerium sulphide pigments which can be used as a replacement for cadmium sulphide pigments

The beginning of organic pigment application dates to antiquity. It is certain that the art of using plant and animal “pigments” to extend the spectral range of available inorganic colorants by a selection of more brilliant shades had been practised thousands of years ago. However, for solubility reasons, most of these organic colors would now be classified as dyes rather than pigments. Even in antiquity, they were used not only for dyeing textiles but also, due to their ability to adsorb on mineral based substrate such as chalk and china clay, were used for solvent resistant coatings for decorative purposes. These materials later came to be known as lakes or toners. For thousands of years, derivatives of the flavone and anthraquinone series have been the major source of natural colors for such applications.

The beginning of the era of scientific chemistry was marked by the synthesis of large numbers of dyes for textile related purposes. Some of these were also applied to inorganic substrates by adsorption, for use as pigment toners. The commercially available soluble sodium salts of acid dyes were rendered insoluble, an essential property of pigments, by reacting them with the water soluble salts of calcium, barium or lead to form lakes. Basic dyes (commercially available as chlorides or as other water-soluble salts), on the other hand, were treated with tannin or antimony potassium tartrate to yield insoluble colorants, that is, pigments. Some of the early commercially important lakes, such as Lake Red C (Pigment Red 53:1) and Lithol Rubine (Pigment Red 57:1), released on to the market in 1902 and 1903, respectively, are still commercially important products (Sec. 2.7).

Entering the market in the late nineteenth century, the first water insoluble pigments that did not contain acidic or basic groups were the red  $\beta$ -naphthol pigments (Para Red P.R.1, 1885). Falling into the same chemical class are Toluidine Red (P.R.3, 1905) and Dinitroaniline Orange (P.O.5, 1907), two members of this class of pigments which still enjoy commercial importance today. In 1909, Hansa Yellow (P.Y.1) was introduced to the market as the first monoazo yellow pigment. The first red Naphthol AS pigments followed in 1912, and the first commercial pioneers of the diarylide yellow pigment range, some of which had been patented as early as 1911, appeared in 1935. Phthalocyanine blue pigments also appeared in 1935, followed by phthalocyanine green pigments a couple of years later [1]. The rapid advances in pigment chemistry led to such important classes of pigments as disazo condensation pigments in 1954, quinacridones in 1955, azo pigments of the benzimidazolone series in 1960, the isoindolinone pigments in 1964 [2], and the diketopyrrolo pyrrole pigments in 1986.

## References for Section 1.2

- [1] G. Geissler, DEFAZET Dtsch. Farben Z. 31 (1977) 152–156.
- [2] H. MacDonald Smith, Am. Ink Maker 55 (1977) 6.

## 1.3 Classification of Organic Pigments

Publications have over the course of the years proposed several classification systems for organic pigments. Basically, it seems appropriate to adopt a classification system by grouping pigments either by chemical constitution or by coloristic properties. Strict separation of the two classification systems is not very practical, because the categories tend to overlap; however, for the purposes of this book it is useful to list pigments according to chemical constitution.



A rough distinction can be made between azo and nonazo pigments; the latter are also known as polycyclic pigments. The commercially important group of azo pigments can be further classified according to structural characteristics, such as by the number of azo groups or by the type of diazo or coupling component. Polycyclic pigments, on the other hand, may be identified by the number and the type of rings that constitute the aromatic structure.

## 1.3.1 Azo Pigments

Azo pigments, subdivided into the monoazo and disazo pigments, have the azo group ( $-\text{N}=\text{N}-$ ) in common. The synthesis of azo pigments is economically attractive, because the standard sequence of diazonium salt formation and subsequent reaction with a wide choice of coupling components allows access to a wide range of products.

### 1.3.1.1 Monoazo Yellow and Orange Pigments

Monoazo yellow pigments that are obtained by coupling a diazonium salt with acetoacetic arylides as coupling components cover the spectral range between greenish and medium yellow; while coupling with 1-arylpyrazolones-5 affords reddish yellow to orange shades.

All members of this pigment family share good lightfastness, combined with poor solvent and migration resistance. These properties define and limit their application. Monoazo yellow pigments are used extensively in air-dried alkyd resin and in emulsion paints, and certain inks used in flexo and screen printing. Other applications are in letterpress and offset inks, as well as in office articles.

### 1.3.1.2 Disazo Pigments

There is a dual classification system based on differences in the starting materials. The first and most important group includes compounds whose synthesis involves the coupling of di- and tetra-substituted diaminodiphenyls as diazonium salts with acetoacetic arylides (diarylide yellows) or pyrazolones (disazo pyrazolones) as coupling components. The second group, bisacetoacetic arylide pigments, are obtained by diazotization of aromatic amines, followed by coupling onto bisacetoacetic arylides.

The color potential of disazo pigments covers the color range from very greenish yellow to reddish yellow and orange and red. Most show poorer lightfastness and weatherfastness; but better solvent and migration fastness than monoazo yellow and orange pigments. Their main applications are in printing inks and plastics, and to a lesser extent in coatings.

### 1.3.1.3 $\beta$ -Naphthol Pigments

$\beta$ -Naphthol pigments provide colors in the range from orange to medium red. The typical coupling reaction with  $\beta$ -naphthol as a coupling component yields such well-known pigments as Toluidine Red and Dinitroaniline Orange. Their commercial application in paints requires good lightfastness. Solvent resistance, migration fastness and lightfastness are comparable to the monoazo yellow pigments.

### 1.3.1.4 Naphthol AS Pigments (Naphthol Reds)

These pigments are obtained by coupling substituted aryl diazonium salts with arylides of 2-hydroxy-3-naphthoic acid (2-hydroxy-3-naphthoic acid anilide = Naphthol AS). They provide a broad range of colors from yellowish and medium red to bordeaux, carmine, brown, and violet; their solvent fastness and migration resistance are only marginal. Naphthol AS pigments are used mainly in printing inks and paints.

### 1.3.1.5 Azo Pigment Lakes (Salt Type Pigments)

In Europe pigments of this type are known as “toners”, but since this term is differently used elsewhere we refer to them as “lakes” throughout this book, although a chemically correct description would be “salt type pigments”.

Historically, “lakes” referred to the first type of synthetic organic pigments made from water soluble dyes by precipitation onto alumina hydrate (aluminium hydroxide).

These pigments are formed by precipitating a monazo compound which contains sulfo and/or carboxy groups. The coupling component in the reaction may vary:  $\beta$ -naphthol lakes are derived from 2-naphthol, BONA pigment lakes use 2-hydroxy-3-naphthoic acid (**B**eta-**O**xy-**N**aphthoic **A**cid); and Naphthol AS pigment lakes contain anilides of 2-hydroxy-3-naphthoic acid as a coupling component. Lakes may also be prepared from naphthalenesulfonic acids. Lake Red C is one of the commercially significant  $\beta$ -naphthol lakes. Limited lightfastness, which ranks far behind the non-laked  $\beta$ -naphthol counterparts, along with a tendency to migrate largely restricts their use mainly to the printing inks field.

Most BONA lake pigments provide an extra site for salt formation. Apart from the usual substituents, the diazo components of almost all BONA lake pigments contain a sulfonic acid function. Two acid substituents are thus available to form insoluble salts, which is the form in which these pigments are commercially available. Metal cations such as calcium, strontium, barium, magnesium, or manganese combine with the organic anion to produce shades between medium red and bluish red. Their use in printing inks exceeds their increasing use in plastics and paints.

The organic acid group of Naphthol AS pigment lakes is part of the diazo component; a second site for salt formation can be provided by the coupling component. The plastics industry is the main user of such lakes.

Naphthalenesulfonic acid lake pigments are based on naphthalenesulfonic acid as a coupling component; introduction of an additional  $\text{SO}_3\text{H}$  function as part of the diazo component is possible.

### 1.3.1.6 Benzimidazolone Pigments

Benzimidazolone pigments feature the benzimidazolone structure, introduced as part of the coupling component. The pigments that are obtained by coupling onto 5-acetoacetylaminobenzimidazolone cover the spectrum from greenish yellow to orange; while 5-(2'-hydroxy-3'-naphthoylamino)-benzimidazolone as a coupling component affords products that range from medium red to carmine, maroon, bordeaux, and brown shades. Pigment performance, including lightfastness and weatherability, is generally excellent. Pigments that satisfy the specifications of the automobile industry are used to an appreciable extent in automotive finishes. Benzimidazolone pigments are also used extensively to color plastics and high grade printing inks.

### 1.3.1.7 Disazo Condensation Pigments

These pigments can formally be viewed as resulting from the condensation of two carboxylic monoazo components with one aromatic diamine. The resulting high molecular weight pigments show good solvent and migration resistance and generally provide good heat stability and lightfastness. Their main markets are in the plastics field and in spin dyeing. The spectral range of disazo condensation pigments extends from greenish yellow to orange and bluish red or brown.

### 1.3.1.8 Metal Complex Pigments

Only a few azo metal complexes are available as pigments. Most of these are very lightfast and weatherfast. The chelating metal is usually nickel, and less commonly, cobalt or iron(II).

The azo group ( $-\text{N}=\text{N}-$ ) may be replaced by the analogous ( $-\text{CH}=\text{N}-$ ) moiety to form an azomethine complex pigment, usually with copper as a chelating metal. The number of commercially available products in this group is also restricted. They typically afford yellow shades. Those species that provide the required lightfastness and weather resistance are used in automotive finishes and other industrial coatings.

### 1.3.1.9 Isoindolinone and Isoindoline Pigments

Although of comparatively good light- and weatherfastness, solvent and migration resistance, only a few members of the isoindolinone and isoindoline families are commercially available as pigments. Chemically classified as heterocyclic azome-

thines, these pigments produce greenish to reddish yellow hues. Isoindolinone pigments are preferably supplied for the pigmentation of plastics and high grade coatings.

### 1.3.2 Polycyclic Pigments

Pigments with condensed aromatic or heterocyclic ring systems are known as polycyclic pigments. The several pigment classes that fall into this category do not reflect their actual commercial importance; only few are produced in large volume. Their chief characteristics are good light- and weatherfastness and good solvent and migration resistance; but, apart from the phthalocyanine pigments, they are also more costly than azo pigments.

#### 1.3.2.1 Phthalocyanine Pigments

Phthalocyanine pigments are derived from the phthalocyanine structure, a tetraaza tetrabenzoporphine. Although this basic molecule can chelate with a large variety of metals under various coordination conditions, today only the copper(II) complexes are of practical importance as pigments. Excellent general chemical and physical properties, combined with good economy, make them the largest fraction of organic pigments in the market today. Copper phthalocyanine blue exists in several crystalline modifications. Commercial varieties include the reddish blue alpha form, as stabilized and nonstabilized pigments; the greenish blue beta modification; and, as yet less important, the intense reddish blue epsilon modification. Bluish to yellowish shades of green pigments may be produced by introduction of chlorine or bromine atoms into the phthalocyanine molecule.

#### 1.3.2.2 Quinacridone Pigments

The quinacridone structure is a linear system of five anellated rings. These pigments perform largely like phthalocyanine pigments. Outstanding light- and weatherfastness, resistance to solvents and migration resistance justify the somewhat higher market price in applications for high grade industrial coatings, such as automotive finishes, for plastics, and special printing inks. Unsubstituted transquinacridone pigments are commercially available in a reddish violet beta and a red gamma crystal modification. One of the more important substituted pigments is the 2,9-dimethyl derivative, which affords a clean bluish red shade in combination with excellent fastness properties. Solid solutions of unsubstituted and differently substituted quinacridones and blends with quinacridone quinone resulting in reddish to yellowish orange pigments are commercially available; while 3,10-dichloroquinacridone as yet enjoys only limited success as a pigment.

### 1.3.2.3 Perylene and Perinone Pigments

Perylene pigments include the dianhydride and diimide of perylene tetracarboxylic acid along with derivatives of the diimide; while perinone pigments are derived from naphthalene tetracarboxylic acid.

Commercially available types provide good to excellent lightfastness and weatherability; some of them, however, darken upon weathering. A number of them have excellent heat stability, which renders them suitable for spin dyeing. They are also used to color polyolefins which are processed at high temperatures. The list of applications includes high grade industrial coatings, such as automotive finishes; and, to a lesser degree, special printing inks for purposes such as metal decoration and poster printing.

### 1.3.2.4 Diketopyrrolo-Pyrrole (DPP) Pigments

The basic skeleton of this newly developed group of pigments consists of two anelated five-membered rings each of which contains a carbonamide moiety in the ring.

This class of pigments has as yet some commercially used representatives, one of them with great importance in the market. In full shades and white reductions, the pigments afford shades in the color range from orange to medium and bluish reds. The pigments are used primarily in high grade industrial coatings, including automotive finishes and in plastics because of their excellent lightfastness and weatherfastness as well as their good heat stability.

### 1.3.2.5 Thioindigo Pigments

4,4',7,7'-Tetrachlorothioindigo with a reddish violet shade reigns supreme as a pigment among the derivatives of this indigo. It can be used for bordeaux shades in automotive refinishes. Thioindigo pigments are generally used in industrial coatings and plastics for their good lightfastness and weatherfastness in deeper shades.

## 1.3.3 Anthraquinone Pigments

Apart from some nonclassified pigments such as Indanthrone Blue (P.131.60), the anthraquinone pigments, which are structurally or synthetically derived from the anthraquinone molecule, can be divided into the following four groups of polycyclic pigments.

### 1.3.3.1 Anthrapyrimidine Pigments

The commercially leading member of this class, Anthrapyrimidine Yellow in very light white reductions affords a greenish to medium yellow with excellent weatherfastness. It lends itself primarily to application in industrial coatings such as automotive metallic finishes or to modify the shades of automotive finishes.

### 1.3.3.2 Flavanthrone Pigments

Flavanthrone Yellow, the only commercially used flavanthrone, is a moderately brilliant reddish yellow. Excellent lightfastness and weatherfastness, combined with good solvent and migration resistance, make this pigment an attractive supplement to Anthrapyrimidine Yellow, mainly in the automotive finish industry.

### 1.3.3.3 Pyranthrone Pigments

Commercial attention focuses on the derivatives of the pyranthrone molecule at a varying level of halogenation. Most are orange; but others exhibit a dull medium to bluish red shade. Due to their good weatherfastness pyranthrone pigments are used for high grade industrial finishes.

### 1.3.3.4 Anthanthrone Pigments

Dibromoanthanthrone is the only commercial pigment within this group. Qualities such as outstanding light- and weatherfastness justify the relatively high cost for application in high grade industrial coatings such as automotive finishes. The transparent pigment provides shades of scarlet for metallic finishes.

## 1.3.4 Dioxazine Pigments

The dioxazine molecule is derived from triphenodioxazine, a linear system of five anellated rings. Apart from Pigment Violet 37, the commercially most representative one is Pigment Violet 23, an extremely lightfast and weatherfast compound with good to excellent solvent and migration resistance. Applications include the pigmentation of coatings, plastics, printing inks, and for spin dyeing. Apart from producing violet shades, the pigment also lends itself to the shading of phthalocyanine blue pigments in colorations, particularly in coatings. It is also used to tone the light yellowish shade of titanium dioxide in whites and in shading carbon blacks that have a brownish cast.