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Klaus Hunger and Martin U. Schmidt

Industrial Organic Pigments

Production, Crystal Structures, Properties, Applications

Fourth, Completely Revised Edition

Klaus Hunger
Martin U. Schmidt

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With Contributions by
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WILEY-VCH
Verlag GmbH & Co. KGaA

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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 on the Internet at <http://dnb.d-nb.de>.

Print ISBN: 978-3-527-32608-2
ePDF ISBN: 978-3-527-64835-1
ePub ISBN: 978-3-527-64834-4
oBook ISBN: 978-3-527-64832-0

Cover Design Grafik-Design Schulz
Typesetting Thomson Digital, Noida, India
Printing and Binding

The printed edition of this book is printed with P.Y.12, P.R.57:1, P.B.15:3 and P.Bl.7

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Preface to the Fourth Edition

All chapters in the fourth edition have been thoroughly reviewed, revised, and updated. More than 130 formulae were added or revised. About 170 figures were added. The chapter on legislation, ecology, toxicology was completely rewritten and now represents the latest developments.

Actually "Azo pigments" do not exist. All single-crystal structure analyses as well as spectroscopic investigations reveal that no commercial "Azo pigment" contains an azo group, but they exhibit the hydrazone-tautomeric form instead[1)]. Consequently all commercial "azo pigments" should be called "hydrazone pigments". This nomenclature has been employed throughout this book. We hope, that the correct denomination "hydrazone pigment" finds its way to all publications on organic pigments as well as to the labelling of products etc.

The properties of organic pigments depend on their crystal structures. Correspondingly all available information on the crystal structures of all industrial organic pigments has now been included and almost every crystal structure is depicted by a figure. The effect of the crystal structure and the polymorphism of a pigment on its colouristic and physical properties is described in detail. The new co-author of this book, Prof. Dr. Martin U. Schmidt, has been researching organic pigments since 1995, with a focus on their polymorphism and their crystal structures.

Several sections have been moved to other chapters in the 4th edition. Most triarylcarbonium pigments and most metal complex pigments are neither hydrazone nor polycyclic pigments, hence their description now appears in chapter 4 (Miscellaneous Pigments). The section on isoindoline and isoindolinone pigments has been moved to chapter 3 (Polycyclic Pigments).

We pay tribute to our deceased colleagues Dr. Willy Herbst, who was the former coauthor of the book, and Prof. Dr. Erich F. Paulus (Goethe University, Frankfurt, formerly at Hoechst AG), who worked on polymorphism and single-crystal structure analyses of organic pigments for 43 years.

1) The only "real" azo pigments are the naphthalene sulfonic acid pigment lakes P.R.66 and P.R.67, which are unable to form tautomeric hydrazone species because they do not contain a hydroxy group in the ortho-position to the azo group.

The layout process for the fourth edition required considerable effort, both by the authors and the publisher, resulting in more than 10 consecutive proofs within a period of 5 years.

The authors thank Dipl.-Ing. Thomas Heber, Dr. Friedrich Reisinger, and Stefan Wannemacher (all from Clariant) for the review and revision of the sections 1.6 to 1.8 and updates in several other sections. We express our gratitude to numerous present and former colleagues at Clariant for many years of kind and intense cooperation, in particular Dr. Dieter Schnaitmann and Dr. Wolfgang Schwab for information on quinacridones and other polycyclic pigments, Dr. Hans Joachim Metz for information on hydrazone pigments, especially quinazolinediones, and Dr. Hans-Tobias Macholdt for information on non-impact printing. Dipl. Chem. Tanja Trepte (formerly at Goethe University) is kindly acknowledged for drawing the new formulae, and Dr. Stephanie Cronje (Goethe University) for improving the English.

Kelkheim and Frankfurt am Main, 2018 K. Hunger, M.U. Schmidt

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

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.

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

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

List of Abbreviations

ABS	acrylonitrile-butadiene-styrene
BET	Brunauer, Emmett and Teller
BONA	ß-oxy-naphthoic acid
BP	British patent
CF	copper ferrocyanide
C.I.	Colour Index
CIE	Commission internationale de l'éclairage (International Commission on Illumination)
CIELAB	L*a*b* system of the Commission internationale de l'éclairage
CH	Swiss patent or patent application
(C)PVC	(critical) pigment volume concentration
CuPc	copper phthalocyanine
DE-AS	Deutsche Anmeldungsschrift (German patent application)
DE-OS	Deutsche Offenlegungsschrift (German patent application)
DE-PS	Deutsche Patentschrift (German patent)
DIN	Deutsches Institut für Normung (German Institute of Standardization)
DPP	diketopyrrolopyrrole
DRP	Deutsches Reichs-Patent (German Patent before 1945)
EP	European patent
FATIPEC	Federation of Associations of Technicians for Industry of Paints in European Countries
HALS	Hindered Amine Light Stabilizers
HDPE	high density polyethylene
HOMO	highest occupied molecular orbital
JP	Japanese patent
LDPE	low density polyethylene
LUMO	lowest unoccupied molecular orbital
NAD	nonaqueous dispersion
NC	nitrocellulose
NMP	N-methyl -2-pyrrolidone
O.E.M	original equipment manufacture
PA	polyamide

PBT	persistant, bioaccumulating, toxic
P.B.	Pigment Blue
P.Bl.	Pigment Black
P.Br.	Pigment Brown
P.Gr.	Pigment Green
P.O.	Pigment Orange
P.R.	Pigment Red
P.V.	Pigment Violet
P.Y.	Pigment Yellow
PC	polycarbonate
PCB	polychlorobiphenyl
PCDD	polychlorinated dibenzodioxin
PCDF	polychlorinated dibenzofuran
PDF	pair-distribution function
PE	polyethylene
PET	polyethylene terephthalate
PM	phosphomolybdic acid
PMA	polymethyl acrylate
PMMA	polymethyl methacrylate
PVC	polyvinylchoride
POM	polyoxymethylene
POP	persistent organic pollutant
PP	polypropylene
PS	polystyrene
PT	phosphotungstic acid
PTM	phosphotungstomolybdic acid
PUR	polyurethane
PVC	polyvinyl chloride
QQ	quinolonoquinolone
SAN	styrene-acrylonitrile
SD	Standard Depth of shade
SM	silicomolybdic acid
TEM	transmission electron microscopy
THI	thiazine indigo
US	(In the reference section) US Patent
WO	International patent application