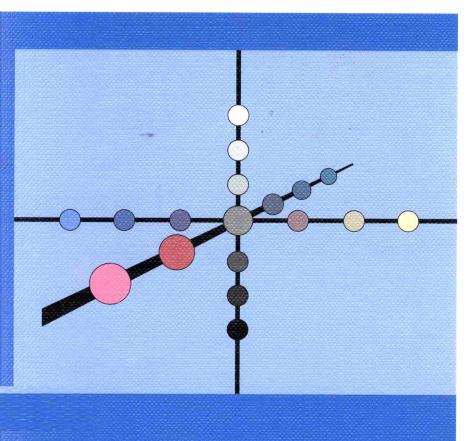
# Industrial Color Testing

Fundamentals and Techniques



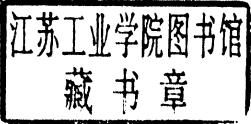


Hans G. Völz

# **Industrial Color Testing**

Fundamentals and Techniques

Translated by Ben Teague





Dr. Hans G. Völz Deswatines-Straße 78 (formerly: Bayer AG, Krefeld-Uerdingen) D-47800 Krefeld

This book was carefully produced. Nevertheless, author, translator 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.

Editorial Directors: Karin Sora, Dr. Ulrike Wünsch

Production Manager: Peter J. Biel

Library of Congress Card No. applied for.

A catalogue record for this book is available from the British Library.

Die Deutsche Bibliothek - CIP-Einheitsaufnahme Völz, Hans G.:

Industrial color testing: fundamentals and techniques / Hans G. Völz. - Weinheim; New York; Basel;

Cambridge; Tokyo: VCH, 1995

Dt. Ausg. u.d.T.: Völz, Hans G.: Industrielle Farbprüfung ISBN 3-527-28643-8

© VCH Verlagsgesellschaft mbH, D-69451 Weinheim (Federal Republic of Germany), 1995

Printed on acid-free and chlorine-free paper.

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. Composition: Hagedornsatz GmbH, D-68519 Viernheim. Printing: Druckhaus Diesbach, D-69469 Weinheim. Bookbinding: Industrie- und Verlagsbuchbinderei Heppenheim GmbH, D-64630 Heppenheim Printed in the Federal Republic of Germany

## **Preface to the English Edition**

The English version of my book is appearing just four years after the successful German edition entitled *Industrielle Farbprüfung*. It is closely based on the German text. Revisions have been necessary in only a few passages to correct errors and update (and sometimes expand) the literature citations. Furthermore, equations that are essential for theoretical understanding and practical application have been enclosed in boxes for emphasis.

New material in the colorimetric part includes the CIELAB 92 color-difference system (Section 2.3.3) and the RAL Design color-order system (Section 2.3.4). A greatly simplified and clearer description has been given for the proposition (important in the determination of tinting strength) that equality of the CIE tristimulus values Y in lightness matching implies equality of the Kubelka-Munk functions, that is, that  $\Delta Y = \Delta F_Y = 0$  (Sections 4.6.4 and 4.7.1). In connection with tests of significance, it is shown how the error of preparation can be separated into specific error components (Section 6.3.3). To aid the understanding of confidence levels in relation to acceptability, an explanatory paragraph has been inserted in Section 6.5.3, and the same chapter has been expanded by the new Section 6.5.4, "Acceptability and Test Errors."

The index of standards (Appendix 1) is completely new. Organized through keywords, it lists standards of the International Organization for Standardization (ISO), the European Committee for Standardization (CEN), and several national standards bodies: the American Society for Testing and Materials (ASTM), the British Standards Institution (BSI), the Association Française de Normalisation (AFNOR), the Japanese Industrial Standards (JIS), and the Deutsches Institut für Normung (DIN). An important role in the preparation of this table was again performed by Mr. E. Fritzsche of DIN, Berlin, to whom I would like to express my gratitude.

I am also grateful to my colleague and successor, Dr. H. Heine, Krefeld, for his generous assistance, to Mr. Ben Teague for a sympathetic translation, and to Mrs. Karin Sora of VCH Publishers for her helpful collaboration.

July 1994 Hans G. Völz

#### **Preface**

This book is directed chiefly to all technical personnel who are involved with pigments and dyes, whether as manufacturers, converters, or consumers. It is often not enough to be familiar with the procedure used in a test; more must be known about the quantity being measured and the way in which it varies as a function of other parameters – in brief, about its physicochemical habit, which is embedded in the well-known fields of chemistry and physics. This is especially important when test methods are to be rationalized; rationalization requires computers, and all computer use is based on applied mathematics. Effective rationalization is possible only when the mathematical and physical background of the quantities being measured is kept fully in view. The lack of suitable worked-out examples to illustrate test methods often creates difficulties in practice as well. This book should help close the gap by providing at least one practical example for each of the test methods described.

The book should, however, also offer some utility to the scientist engaged in research and development work on pigments and dyes. Discussion of principles makes up a substantial part of the text, and many suggestions and hints are included to further the scientist's work. On the other hand, anyone working in research or development but lacking a knowledge of both the principles and the state of the art will scarcely be in a position to advance the colorimetric properties of these substances.

A third audience – so the author hopes – will find the book beneficial: university lecturers and students in the natural sciences. The study of colorimetry in the testing of coloring material is a perfect example of the interdisciplinary effect of chemistry, physical chemistry, physics, theoretical physics, mathematics, and cybernetics (informatics). It goes without saying that one must understand the principles of each discipline before one can understand their interaction. There is, however, another point: The integrative components of the knowledge assembled in this book are hardly taught (if at all) in our universities and colleges of technology – colorimetry and Kubelka-Munk theory being just two examples. Even beyond the field of coloring materials, both these bodies of knowledge have significant roles to play in many other technical areas, and it is hard to comprehend that people with university-level diplomas even today are entering the colorant manufacturing and converting industries without ever having come in contact with either topic.

In choosing the contents of this book from the disciplines named, the author has adopted a standard that he considers trustworthy, one that has continually

aided him in distinguishing key topics from less important ones: He wanted to write the book he wishes had been available when he entered the field of pigment testing. Naturally, such a wish is a bit of a fantasy, for it is only now that this book could be written in its present form. Some three-quarters of the test methods described here did not even exist then. The same holds, in modified form, for the principles; while certain branches of knowledge had already been developed 30 years ago, they were not yet relevant for our field – the statistical analysis of color coordinates is one of many topics that might be mentioned. Finally, the introduction of the computer in colorimetric testing has led to major changes in recent years.

To avert misunderstandings, some special points relating to text selection should be stated in advance. The title of the book should be read as referring to the colorimetric examination of pigments and dyes in media; thus, all tests not carried out in mixtures with a lacquer, paint, plastic, or other coating are excluded (e.g., on textile fibers or in printing inks). The chapter on "Colorimetry" has been kept short even though it threatened to grow into another whole volume. In other words, this book does not wish to be mistaken for a textbook on colorimetry. The only aspects of that field that are covered are topics essential for the context of the book. Similarly, one will search in vain for instructions on color formulation and correction calculations. These operations do not come under the heading of pigment and dye testing, even if they must be preceded by testing. Similarly, the application of Mie theory in the determination of particle-size distributions is not covered, for it is based not on colorimetric methods but on general spectroscopic methods.

In Chapter 2, on the other hand, a comparatively large proportion has been devoted to the statistical analysis of color coordinates. The reasons for this are that these applications are relatively novel in practice and that key topics such as acceptability (tolerances) are related to them. New in Chapter 3 are the four-flux equations for specular substrates, which may prove to be of interest in the future. Chapter 4 offers – for the first time, as far as the author is aware – a theoretical mathematical justification for the universal practice of treating wideband measurements (e.g., reflectometer values) or color coordinates (e.g., CIE tristimulus values) as spectral values in Kubelka-Munk analysis and of matching not the tristimulus values but their Kubelka-Munk functions. In Chapter 5, instructions are given for extending Mie calculations to the particle-size distribution of anisometric (i.e., bladed or rod-shaped) pigments.

While the text was in preparation, a number of colleagues expressed willingness to read it and offer vital suggestions and corrections. The entire text was read by Dr. H. Heine (Krefeld-Uerdingen), Dr. S. Keifer (Krefeld-Uerdingen), and A. van Leendert (Krefeld). The following experts made themselves available to read portions of the text: Dr. L. Gall (Ludwigshafen), Dr. W. Herbst (Frankfurt-Höchst), Prof. G. Kämpf (Leverkusen), Prof. J. Krochmann (Berlin), Dr. H. Pauli (Basel), Dr. K. Sommer (Krefeld-Uerdingen), Dr. J. Spille (Leverkusen), Dr. J. Thiemann (Leverkusen), Dr. J. Wiese (Krefeld-Uerdingen), and Dr. K. Witt (Berlin). Mrs. E. Lechner and Mr. E. Fritzsche of DIN, Berlin, have prepared the exemplary listing of the standards cited. The author would

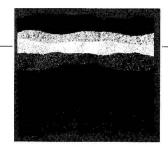
#### VIII Preface

like to take this opportunity to thank all these colleagues for their helpfulness and their valuable advice and suggestions.

I am grateful to Bayer AG for its continuing interest and assistance in the writing of this book, and to VCH Publishers for its intelligent collaboration and valuable advice.

Krefeld, November 29, 1989

Hans G. Völz



Buxbaum, G. (ed.)

# **Industrial Inorganic Pigments**

1993. XIII, 281 pages with 92 figures and 56 tables. Hardcover. DM 188.00. ISBN 3-527-28624-1

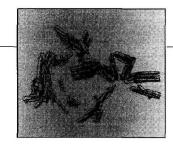
The authors, who are renowned experts in their field, ensure a concise, up-to-date presentation of the chemistry, production, properties, applications and economic importance of industrial inorganic pigments.

This book is neither a list of commercially available products nor a compilation of company product specifications but instead provides the knowledge required for the optimal selection and use of inorganic pigments. It will prove to be an indispensable guide to all chemists, material scientists and practitioners in pigment-related fields.

Date of Information: November 1994

VCH, P.O. Box 10 11 61, D-69451 Weinheim, Fax 0 62 01 - 60 61 84





Herbst, W. /Hunger, K.

# **Industrial Organic Pigments Production, Properties, Applications**

1992. XIV, 630 pages with 95 figures, 6 in color and 38 tables. Hardcover, DM 296.00. ISBN 3-527-28161-4

Currently the most comprehensive source of information on synthetic organic pigments! It treats all aspects of applications of organic pigments from chemical and physical viewpoints. Relevant test methods are covered, and toxicological and ecological properties are outlined. Readers will find the book exceptionally useful as it considers the synthesis, properties and applications of organic pigments commercially available on the world market. They will appreciate the fact that standardized methods allow test results to be compared throughout the book.

# From reviews of the German Edition:

"The volume can be recommended unreservedly to industrial and academic practitioners concerned in any way with the technological aspects of organic pigments. Presentation throughout is of the highest quality and the volume must now become the standard reference text in this important area of coloring matters."

Dyes and Pigments

"This wide-ranging reference work can be warmly recommended ..." farbe + lack

> Date of Information: November 1994

VCH, P.O. Box 10 11 61, D-69451 Weinheim, Fax 0 62 01 - 60 61 84



# **Contents**

Part I Principles 1
1 Introduction 3
<ul> <li>1.1 Coloring Materials 3</li> <li>1.2 Color Properties 9</li> <li>1.3 Summary 12</li> <li>1.4 Historical and Bibliographical Notes 12</li> </ul>
2 How Colors Depend on Spectra (Colorimetry) 15
<ul> <li>2.1 Introduction 15</li> <li>2.1.1 Concerns and Significance of Colorimetry 15</li> <li>2.1.2 Reflection and Transmission 17</li> <li>2.2 CIE Standard Colorimetric System 20</li> <li>2.2.1 Spectral Distribution and Color Stimulus 20</li> <li>2.2.2 Trichromatic Principle 21</li> <li>2.2.3 CIE System 23</li> <li>2.3 Sensation-Based Systems 26</li> <li>2.3.1 Lightness, Hue, Saturation 26</li> <li>2.3.2 Physiologically Equidistant Systems 27</li> <li>2.3.3 CIELAB System 28</li> <li>2.3.4 Color Order Systems 37</li> </ul>
<ul> <li>2.4 Mathematical Statistics of Color Coordinates 40</li> <li>2.4.1 Normal Distribution in Three Dimensions 40</li> <li>2.4.2 Standard Deviation Ellipsoid 44</li> <li>2.4.3 Standard Deviations 49</li> <li>2.4.4 Color Measurement Errors and Significance 53</li> <li>2.4.5 Acceptability 56</li> <li>2.5 List of Symbols Used in Formulas 59</li> <li>2.6 Summary 61</li> <li>2.7 Historical and Bibliographical Notes 63</li> </ul>

#### X Contents

# 3 How Spectra Depend on the Scattering and Absorption of Light (Phenomenological Theory) 67

- 3.1 Introduction 67
  - 3.1.1 Phenomenological Theory and Its Significance 67
  - 3.1.2 Many-Flux Theory 68
  - 3.1.3 Surface Phenomena 71
- 3.2 Four-Flux Theory 75
  - 3.2.1 The Differential Equations and Their Integration 75
  - 3.2.2 Transmittance and Transmission Factor 79
  - 3.2.3 Reflectance and Reflection Factor 83
  - 3.2.4 Limiting Cases of Reflection 87
  - 3.2.5 Determination of the Coefficients 90
- 3.3 Kubelka-Munk Theory 93
  - 3.3.1 Significance and Formalism 93
  - 3.3.2 Limiting Cases of Reflection 95
  - 3.3.3 Determination of the Absorption and Scattering Coefficients 99
- 3.4 Hiding Power 101
  - 3.4.1 General 101
  - 3.4.2 Achromatic Coatings 102
  - 3.4.3 Scattering and Absorption Components 105
- 3.5 Transparency 107
  - 3.5.1 Description and Definition 107
  - 3.5.2 Coloring Power 108
  - 3.5.3 Achromatic Coatings 110
- 3.6 Principle of Spectral Evaluation 112
  - 3.6.1 Description and Significance 112
  - 3.6.2 Application to Hiding Power 113
  - 3.6.3 Application to Transparency and Coloring Power 118
- 3.7 List of Symbols Used in Formulas 120
- 3.8 Summary 122
- 3.9 Historical and Bibliographical Notes 123

# 4 How Light Scattering and Absorption Depend on the Content of Coloring Material (Beer's Law, Scattering Interaction) 129

- 4.1 Introduction 129
  - 4.1.1 Description and Significance of the Concentration Dependence 129
  - 4.1.2 Pigment Particle Size 129
  - 4.1.3 Dispersing of Pigments 131
  - 4.1.4 Measures of Pigment Content 133
- 4.2 Absorption and Content of Coloring Material 137
  - 4.2.1 Dyes 137
  - 4.2.2 Pigments 137

4.3 Scattering and Pigment Content 139
4.3.1 Scattering Interaction 139
4.3.2 Experimental Test of an Empirical Formula 143
4.4 Systematic Treatment of Pigment/Achromatic Paste Mixing 145
4.4.1 Standard Methods of Pigment/Paste Mixing 145
4.4.2 Importance of the Methods 147
4.5 Kubelka-Munk Functions of Pigment/Paste Mixture 148
4.5.1 General Formula 148
4.5.2 Black Pigments Mixed with White Paste 150
4.5.3 White Pigments Mixed with Black Paste 155
4.5.4 Colored Pigments Mixed with White Paste 157
4.6 Tinting Strength 164
4.6.1 Significance and Definition 164
4.6.2 Coloristic Matching Criteria for Pigments 167
4.6.3 Color Matching Studies 172
4.6.4 Lightness Matching 181
4.6.5 Color Depth Matching 187
4.7 Special Problems 189
4.7.1 Lightening Power 189
4.7.2 Color Differences after Matching 191
4.7.3 Change in Tinting Strength 194
4.8 List of Symbols Used in Formulas 200
4.9 Summary 203
4.10 Historical and Bibliographic Notes 206
5 How Light Scattering and Absorption Depend on the Physics of the
Pigment Particle (Corpuscular Theory) 211
5.1 Introduction 211
5.1.1 Description and Significance of the Corpuscular Theory 211
5.1.2 Particle-Size Distribution 212
5.1.3 The Optical Constants: Refractive Index and Absorption Index 217
5.2 Mie Theory 222
5.2.1 Integration of the Wave Equation 222
5.2.2 Absorption and Scattering of the Particle Ensemble 224
5.2.3 Scattering Behavior of Pigments 226
5.2.4 Absorption Behavior of Pigments 229
5.3 List of Symbols Used in Formulas 231
5.4 Summary 232
5.5 Historical and Bibliographical Notes 234

#### Part II Test Methods 237

6 M	easurement	and	<b>Evaluation</b>	of	Object	Colors	239
-----	------------	-----	-------------------	----	--------	--------	-----

- 6.1 Reflection and Transmission Measurement 239
  - 6.1.1 Gloss Measurement and Assessment 239
  - 6.1,2 Measurement and Evaluation Conditions 244
- 6.2 Practical Evaluation of Color Differences 248
  - 6.2.1 Preparation of Specimens 2486.2.2 Color Measuring 249

  - 6.2.3 Full Shade 254
  - 6.2.4 Special Problems 258
- 6.3 Test Errors 262
  - 6.3.1 Calculation of the Standard Deviation Ellipsoid 262
  - 6.3.2 Visualization of the Ellipsoid 264
  - 6.3.3 Total Error and Its Components 266
- 6.4 Significance 270
  - 6.4.1 Calculation of Standard Deviations 270
  - 6.4.2 Test of Significance 272
- 6.5 Acceptability 275
  - 6.5.1 Specimen Preparation 275
  - 6.5.2 Matching and Color Measurement 277
  - 6.5.3 Evaluation and Example 279
  - 6.5.4 Acceptability and Test Errors 282

#### 7 Determination of Hiding Power and Transparency 285

- 7.1 Measurement of Film Thickness 285
  - 7.1.1 Selection of Method 285
  - 7.1,2 Gravimetric, Wedge-Cut, and Dial-Gauge/Micrometer Methods 287
  - 7.1.3 Pneumatic Method 289
- 7.2 Scattering and Absorption Coefficients 291
  - 7.2.1 Kubelka-Munk Coefficients S and K of White Pigments 291
  - 7.2.2 Kubelka-Munk Coefficients S and K of Black and Colored Pigments 296
  - 7.2.3 Four-Flux Coefficients  $s^+$ ,  $s^-$ , k' 300
- 7.3 Transparency 304
  - 7.3.1 Single-Point and Multi-Point Methods 304
  - 7.3.2 Method Based on Principle of Spectral Evaluation 307
- 7.4 Hiding Power 310
  - 7.4.1 General (Graphical Method) 310
  - 7.4.2 Achromatic Case 313
  - 7.4.3 Based on Principle of Spectral Evaluation 319
  - 7.4.4 Economic Aspects 326

#### 8 Determination of Tinting Strength and Lightening Power 331

- 8.1 Content of Coloring Material 331
  - 8.1.1 Dyes 331
  - 8.1.2 Pigments 332
- 8.2 Relative Tinting Strength 333
  - 8.2.1 Dyes 333
  - 8.2.2 Inorganic Black and Colored Pigments (Lightness Matching) 335
  - 8.2.3 Organic Pigments ("FIAF" Method Based on Principle of Spectral Evaluation) 339
  - 8.2.4 Change in Tinting Strength 348
- 8.3 Lightening Power 354
  - 8.3.1 Graphical Method 354
  - 8.3.2 Rationalized Method 357
  - 8.3.3 PVC Dependence from One Gray Mixture 360

#### Appendix: List of DIN, DIN ISO, and ISO Standards Cited 365

Subject Index 369

Name Index 375

# Part I Principles

## 1 Introduction

## 1.1 Coloring Materials

This book deals with color-imparting substances and the color phenomena which they produce. The general term for all coloring substances is "coloring materials";\* and includes, in particular, pigments and dyes.

Pigments are substances consisting of particles that are practically insoluble in the application medium. They are used chiefly as coloring materials but can also be employed for other properties in special applications (e.g., anti-corrosion or magnetic pigments). The demarcation between pigments and fillers was formerly somewhat problematic as it cannot be stated in terms of a limiting refractive index. However they can be differentiated according to their application. In contrast to pigments, a filler is not employed to impart color but to impart certain technical properties to the coating or to increase the volume of the coating material. Such a convention does not rule out the possibility that certain substances can find use as both pigments and fillers. However, there is a large group of substances that act as pigments in the great majority of cases (e.g., TiO<sub>2</sub> is never used as a filler). When we speak of pigments, we are referring to this group. This statement also applies to the present book.

Pigments can be classified according to a variety of criteria; here we generally follow the standard scheme and speak of two classes:

- Inorganic pigments
- Organic pigments

The next step in classification is according to their origin:

- Natural pigments
- Synthetic pigments

Economically, synthetic pigments are very much more significant than natural pigments, and they will therefore be our exclusive focus in the following classification.

<sup>\*</sup> For standards see "Coloring Materials, Terms" in Appendix 1.