

Industrial Inorganic Pigments

Third, Completely Revised Edition

Edited by

Gunter Buxbaum and Gerhard Pfaff



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Preface to the Third Edition

Six years have passed since the second edition of *Industrial Inorganic Pigments* was published. During this time some pigment producers have merged or vanished and new products have been developed. By including these changes, this, the third edition, gives the up to date status of the field. We have taken the opportunity to review and revise all sections to include current commercial data. The major new trends in inorganic pigments have been incorporated, for example, the increasing importance of luster pigments. An additional section on new developments has been added, but we have had to decide the criteria for qualification as an "Industrial Pigment". Similarly, sections on pigments whose industrial significance has been judged to be in decline, for example chromium dioxide, have been shortened. Finally, references have been revised and the list of the standards updated.

To meet these demands, almost every section has been completely rewritten. Some authors from the second edition have retired and acknowledged experts have revised the topics that the retired authors reported on in the past. We thank their employers for allowing these authors to contribute to this publication.

We must express our special thanks to our readers, who have made contributions or given us valued suggestions for inclusion in the new edition. Some of the previous reviewers expressed surprise that a book about pigments could be written with so few colored figures. We have made every effort to respond to these comments, but it is virtually impossible to show in a printed format the true impression of color, gloss, haze, etc. in an applied paint system. However, the named producers of the inorganic pigments are ready to deliver such information, e.g. in the form of paint shade cards, on request. So, we have again been forced to limit the color figures and those included are mainly provided to assist the text.

"*Industrial Inorganic Pigments*" is now in its third edition and has become a standard text on the subject, so, for the future continuation of this work, it seemed advisable to include a younger co-editor for this and subsequent editions. We are pleased that Gerhard Pfaff, well known as the author of Section 5.3 and extensive publications in the field, has undertaken this obligation.

Finally we thank the publishers, especially Karin Sora, for their patience and continued support.

Krefeld and Darmstadt
December 2004

*G. Buxbaum,
G. Pfaff*

Preface to the Second Edition

Inorganic pigments have a long history. Their chemistry is manifold and the information is spread over a vast number of books and articles with varying degrees of actuality. "Industrial Inorganic Pigments" covers the whole field and is written by experts in the field for all those dealing with the application of inorganic pigments.

Inorganic pigments significantly change our ambient; they are irreplaceable for the coloring of construction materials. They show good light and weather resistance and they withstand the attack of heat and chemicals. Their applications range from concrete to artist's colors, from industrial paints to toners in photocopiers, from coloring foodstuffs to their use as raw materials for catalysts.

The application properties of pigments depend not only on their chemistry but also on their physical appearance and to a greater extent on the manufacturing process. Therefore, the book places much emphasis on the description of industrial production processes. The inclusion of extensive descriptions of applications means that this book is far more than a mere list of pigments and their properties.

Since color is the most important aspect, the book opens with a basic chapter dealing with color and its measurement, incorporating the latest standards. The increasingly important environmental and health regulations are described for each separate class of pigments.

The large number of references (more than 800) will enable the reader to acquire further knowledge of this extensive field.

Preface to the Second Edition

The fact that after only five years a second edition of this book is necessary demonstrates its success. This second edition is not a mere reprint but we have used the opportunity to revise all the chapters and the commercial data. Some attention has been given to company mergers in the pigment industry, but this is something that is continually changing. The lists of the standards have been updated as well as the references. New trends in the field of inorganic pigments are described, e.g. the growing importance of luster pigments has led to the inclusion of a more detailed description of them. Sections on pigments whose importance has decreased have been shortened.

Nearly every chapter has been rewritten. Some authors of the first edition are now retired; their contributions have been revised by younger colleagues of known excellence. We express our special thanks to the readers of the first edition who made contributions or gave us valuable hints for this new edition. Finally we thank the publisher for patience and support.

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1

Introduction

1.1

General Aspects

1.1.1

History, Classification, Standards

1.1.1.1

Definition

The word “pigment” is of Latin origin (pigmentum) and originally denoted a color in the sense of a coloring matter, but was later extended to indicate colored decoration (e.g., makeup). In the late Middle Ages, the word was also used for all kinds of plant and vegetable extracts, especially those used for coloring. The word pigment is still used in this sense in biological terminology; it is taken to mean dyestuffs of plant or animal organisms that occur as very small grains inside the cells or cell membranes, as deposits in tissues, or suspended in body fluids.

The modern meaning associated with the word pigment originated in the 20th century. According to accepted standards (Table 1.1, “Coloring materials: Terms and definitions”), the word pigment means a substance consisting of small particles that is practically insoluble in the applied medium and is used on account of its coloring, protective, or magnetic properties. Both pigments and dyes are included in the general term “coloring materials”, which denotes all materials used for their coloring properties. The characteristic that distinguishes pigments from soluble organic dyes is their low solubility in solvents and binders. Pigments can be characterized by their chemical composition, and by their optical or technical properties. In this introductory section, only inorganic pigments used as coloring materials are discussed.

Extenders (fillers) are substances in powder form that are practically insoluble in the medium in which they are applied. They are usually white or slightly colored, and are used on account of their physical or chemical properties. The distinction between an extender and a pigment lies in the purpose for which it is used. An extender is not a colorant, it is employed to modify the properties or increase the bulk (volume) of a given material. Extenders are beyond the scope of this book and will not be discussed in detail.

Tab. 1.1: Listing of standards for pigments

Key words	ISO	EN	ASTM	DIN
Acidity/alkalinity	787-4		D1208	ISO 787-4
Aluminum pigments and pastes:				
Sampling and testing			D 480	55923
Specification	1247		D 962	55923
Barium chromate pigments:				
Specification	2068			
Bleeding	787-22		D 279	53775-3
Carbon black pigments (see also lampblack):				
Black value				55979
Solvent-extractable material			D 305	55968
Specification			D 561	55968
Cadmium pigments:				
Specification	4620			
Chalking degree:				
Adhesive tape method	4628-6			EN ISO 4628-6
KEMPF method			D 4214	53159
Change in Strength (see ease of dispersion and PVC)				
Chemical resistance	2812-1	ISO 2812-1		EN ISO 2812-1
Chlorides, water-soluble (see matter soluble)				
Chromium oxide pigments:				
Specification	4621		D 263	ISO 4621
Climates:				
containing evaporated water				50017
Standardized	554			50014
Open air				
SO ₂ atmosphere	6988	ISO 6988		EN ISO 6988
Coating materials:				
Terms and definitions	4618-1 to 4618-3	971-1		EN 971-1 55945
Color differences:				
CIELAB	7724-3		D 1729 D 2244 E 308	6174
Conditions/evaluation of measurements	7724-2			53236
"DIN 99"				6176
Significance				55600
Color in full-shade systems:				
Black pigments	787-1		D 3022	55985-2
Colored Pigments	787-1		D 3022	55985
White pigments	787-1		D 2805a	55983
Coloration of building materials				EN 12878
Colorimetry	7724-1 7724-2 7724-3		E 259 E 308	5033-1 to 5033-9 6174
Coloring materials:				
Classification				55944
Terms and definition	4618-1	971-1		55943 EN 971-1

Tab. 1.1: Continued

Key words	ISO	EN	ASTM	DIN
Corrosion testing:				
NaCl	9227		B 117	50021
SO ₂	6988	ISO 6988		EN ISO 6988
Density:				
Centrifuge method	787-23	ISO 787-23		EN ISO 787-23
Pycnometer method	787-10		D 153	EN ISO 787-10
Dusting behavior of pigments:				
Drop method				55992-2
Dusting value				55992-1
Ease of dispersion:				
Alkyd resin and alkyl-melamine system:				
Hardening by oxidation				53238-30 53238-33 53238-34
Stoving type				
Automatic muller	8780-5	ISO 8780-5	D 387	EN ISO 8780-5
Bead mill	8780-4	ISO 8780-4		EN ISO 8780-4
Change in gloss	8781-3	ISO 8781-3		EN ISO 8781-3
Change in tinting strength	8781-1	ISO 8781-1		EN ISO 8781-1
Fineness of grind (see below)				
High speed impeller mill	8780-3	ISO 8780-3		EN ISO 8780-3
Introduction	8780-1	ISO 8780-1		EN ISO 8780-1
Oscillatory shaking machine	8780-2	ISO 8780-2		
Triple roll mill	8780-6	ISO 8780-6		EN ISO 8780-6
Fineness of grind	1524		D 1210	EN ISO 1524
	8781-2	ISO 8781-2		EN ISO 8781-2
Heat stability (see also PVC)	787-21		D 2485	53774-5
Hiding power:				
Contrast ratio	6504-3			
Pigmented media	6504-1		D 2805a	55987
Wedge-shaped layer				55601
White and light gray media			D 2805a	55984
Hue of near-white specimens				55980
Hue relative to near-white specimens				55981
Iron blue pigments:				
Methods of analysis	2495		D 1135	
Specification	2495		D 261	EN ISO 2495
Iron, manganese oxide pigments:				
Methods of analysis	1248		D 50	ISO 1248
Natural, specification	1248		D 3722	ISO 1248
Sienna, specification	1248		D 765	ISO 1248
Umber, specification	1248		D 763	ISO 1248
Iron oxide pigments:				
Black, specification	1248		D 769	ISO 1248
Brown, specification	1248		D 3722	ISO 1248
			D 3724	
FeO content			D 3872	
Methods of analysis	1248		D 50	55913-2 ISO 1248

Tab. 1.1: Continued

Key words	ISO	EN	ASTM	DIN
Red, specification	1248		D 3721	55913-1 ISO 1248
Yellow, specification	1248		D 768	ISO 1248
Lampblack pigments: Specification			D 209	55968
Lead chromate pigments: Method of analysis	3711		D 126	ISO 3711
Specification	3711		D 211	ISO 3711
Lead chromate/phthalocyanine blue pigments: Methods of analysis			D 126	
Specification				
Lead chromate green pigments: Methods of analysis			D126	
Specification				
Lead red (see red lead)				
Lead silicochromate pigments (basic): Methods of analysis			D 1844	
Specification			D 1648	
Lead white (see white lead)				
Light stability (see also resistance to light): Short test	11341			EN ISO 11341
Lightening power of white pigments	787-17		D 2745	55982
Lightness: White pigment powders				53163
Lithopone pigments: Specification	473		D 3280	55910
Matter soluble in HCl: Content of As, Ba, Cd, Co, Cr, Cr(VI), Cu, Hg, Mn, Ni, Pb, Sb, Se, Zn	3856-1 to 3856-7		D 3718a D 3618a D 3624a D 3717a	53770-1 to 53770-15
Preparation of extract	6713			52770-1
Matter soluble in water: Chlorides	787-13			EN ISO 787-13
Cold extraction	787-8	ISO 787-8	D 2448	EN ISO 787-8
Cr(VI) content				53780
Hot extraction	787-3	ISO 787-3	D 2448	EN ISO 787-3
Nitrates: Nessler reagent	787-13			EN ISO 787-13
Salicylic acid method	787-19	ISO 787-19		EN ISO 787-19
Sulfates	787-13			EN ISO 787-13
Matter volatile	787-2	ISO 787-2	D 280	EN ISO 787-2
Molybdenum orange pigments: Methods of analysis	3711		D 2218	ISO 3711
Nitrates, water soluble (see matter soluble)				
Oil absorption	787-5	ISO 787-5	D 281 D 1483	EN ISO 787-5
Opacity: paper, cardboard	2471			53146

Tab. 1.1: Continued

Key words	ISO	EN	ASTM	DIN
Particle size analysis:				
Representation:			D 1366	53206-1
Basic terms	9276-1			66141
Logarithmic normal diagram				66144
Power function grid				66143
RRSB grid				66145
Sedimentation method:				
Balance method				66116-1
Basic standards				66111
Pipette method				66115
pH value	787-9	ISO 787-9	D 1208	EN ISO 787-9
Phtalocyanine pigments:				
Methods of analysis			D 3256	
PVC, nonplasticized:				
Basic mixture				53774-1
Heat stability				53774-5
Test specimen preparation				53774-2
PVC, plasticized:				
Basic mixture				V 53775-1
Bleeding				53775-3
Change in strength				EN 13900-2
Heat stability, in oven				EN 12877-1 + 3
Heat stability, mill aging				EN 12877-1 + 4
Test specimen preparation				53775-2
Red lead:				
Specification	510		D 49 D 83	55916
Reflectance factor; paper, cardboard:				
Fluorescent				53145-2
Nonfluorescent	2469			53145-1
Reflectometer (gloss assessment)	2813		E 430 D 523	67530
Residue on sieve:				
By water	787-7			53195
Mechanical method	787-18	ISO 787-18		EN ISO 787-18
Resistance to light	787-15	ISO 787-15		EN ISO 787-15
Resistivity, aqueous extract	787-14		D 2448	EN ISO 787-14
Sampling:				
Terms	15528		D 3925	EN ISO 15528
Solid material	15528		D 3925	EN ISO 15528
Scattering power, relative:				
Gray paste method	787-24	ISO 787-24		EN ISO 787-24
Black ground method				53164
Specific surface area:				
BET method				ISO 9277
N ₂ adsorption				66132
Permeability techniques				66126-1
Standard depth of shade:				
Specimen adjustment				53235-2

Tab. 1.1: Continued

Key words	ISO	EN	ASTM	DIN
Standards				53235-2
Strontium chromate pigments:				
Specification	2040		D 1845	55903
Sulfates, water-soluble (see matter soluble)				
SO ₂ resistance	3231			53771 EN ISO 3231
Tamped volume	787-11	ISO 787-11		EN ISO 787-11
Test evaluation:				
Scheme	4628-1			EN ISO 4628-1
Thermoplastics:				
Basic mixtures				53773-1
Heat stability				EN 12877-1 + 2
Test specimen preparation				53773-2
Tinting strength, relative:				
Change in ~	8781-1	ISO 8781-1		EN ISO 8781-1
Photometric	787-24	ISO 787-24	D 387	55986 / 55603
Visual	787-16	ISO 787-16		EN ISO 787-16
Titanium dioxide pigments:				
Methods of analysis	591-1		D 1394 D 3720 D 3946	55912-2
Specification	591-1		D 476	55912-2
Test methods	591-1		D 4563 D 4767 D 4797	55912-2
Transparency:				
Paper,cerdboard	2469			53147
Pigmented/unpigmented systems				55988
Ultramarine pigments:				
Methods of analysis			D 1135	
Specification	788		D 262	55907
Viscosity	2884-1		D 2196	53229
Weathering in apparatus	4892-1 to 4 11341			EN ISO 11341 EN ISO 4892-2
White lead:				
Methods of analysis			D 1301	
Specification			D 81	
Zink chromate pigments:				
Specification	1249			55902
Zink dust pigments:				
Methods of analysis	713 714 3549		D 521	EN ISO 3549
Specification	3549		D 520	EN ISO 3549
Zink oxide pigments:				
Methods of analysis			D 3280	55908
Specification			D 79	
Zink phosphate pigments:				
Methods of analysis	6745			ISO 6745
Specification	6745			ISO 6745

1.1.1.2

History

Natural inorganic pigments have been known since prehistoric times. Over 60,000 years ago, natural ocher was used in the Ice Age as a coloring material. The cave paintings of the Pleistocene peoples of southern France, northern Spain, and northern Africa were made with charcoal, ocher, manganese brown, and clays, and must have been produced over 30,000 years ago. About 2000 BC, natural ocher was burnt, sometimes in mixtures with manganese ores, to produce red, violet, and black pigments for pottery. Arsenic sulfide and Naples yellow (a lead antimonate) were the first clear yellow pigments. Ultramarine (lapis lazuli) and artificial lapis lazuli (Egyptian blue and cobalt aluminum spinel) were the first blue pigments. Terra verte, malachite, and a synthetically prepared copper hydroxychloride were the first green pigments. Colored glazes for bricks (i.e., ceramic pigments) were widely used by the Chaldeans. Calcite, some phases of calcium sulfate, and kaolinite were the white pigments used at that time.

Painting, enamel, glass, and dyeing techniques reached an advanced state of development in Egypt and Babylon. A synthetic lapis lazuli (a silicate of copper and calcium) is still known as Egyptian blue. Antimony sulfide and galena (lead sulfide) were commonly used as black pigments, cinnabar as a red pigment, and ground cobalt glass and cobalt aluminum oxide as blue pigments. According to Plutarch, the Greeks and Romans did not regard the art of dyeing very highly, and made very little contribution to the development of new pigments. Pliny (23–79 AD) describes the pigments orpiment, realgar, massicot, red lead, white lead, verdigris, and pigments laked with alum, as well as the pigments already listed above. Certain types of chalk and clay were used as white pigments.

From the age of the migration of the peoples (fourth to sixth century AD) to the end of the late Middle Ages, there were no notable additions to the range of coloring materials. The reinvented pigment Naples yellow and certain dyestuffs for textiles from the orient were the only innovations. New developments in the field of pigments first occurred during the early Renaissance. Carmine was introduced from Mexico by the Spanish. Smalt, safflore, and cobalt-containing blue glasses were developed in Europe.

The pigment industry started in the 18th century with products such as Berlin blue (1704), cobalt blue (1777), Scheele's green, and chrome yellow (1778).

In the 19th century, ultramarine, Guignet's green, cobalt pigments, iron oxide pigments, and cadmium pigments were developed in quick succession.

In the 20th century, pigments increasingly became the subject of scientific investigation. In the past few decades, the synthetic colored pigments cadmium red, manganese blue, molybdenum red, and mixed oxides with bismuth came onto the market. Titanium dioxide with anatase or rutile structures, and acicular zinc oxide were introduced as new synthetic white pigments and extenders, respectively. Luster pigments (metal effect, pearl/luster, and interference pigments) have assumed increasing importance.

1.1.1.3

Classification

Inorganic pigments can be classified from various points of view. The classification given in Table 1.2 (for standards see Table 1.1, “Coloring materials, terms”) follows a system recommended by ISO and DIN; it is based on coloristic and chemical considerations. Further methods for classification are shown in Section 1.2.1. As in many classification schemes, there are areas of overlap between groups so that sharp boundaries are often impossible. In this book white pigments are described in Chapter 2, colored pigments in Chapter 3, black pigments (carbon black) in Chapter 4 and specialty pigments in Chapter 5.

Tab. 1.2: Classification of inorganic pigments.

Term	Definition
White pigments	the optical effect is caused by nonselective light scattering (examples: titanium dioxide and zinc sulfide pigments, lithopone, zinc white)
Colored pigments	the optical effect is caused by selective light absorption and also to a large extent by selective light scattering (examples: iron oxide red and yellow, cadmium pigments, ultramarine pigments, chrome yellow, cobalt blue)
Black pigments	the optical effect is caused by nonselective light absorption (examples: carbon black pigment, iron oxide black)
Effect pigments	the optical effect is caused by regular reflection or interference
Metal effect pigments	regular reflection takes place on mainly flat and parallel metallic pigment particles (example: aluminum flakes)
Pearl luster pigments	regular reflection takes place on highly refractive parallel pigment platelets (example: titanium dioxide on mica)
Interference pigments	the optical effect of colored luster pigments is caused wholly or mainly by the phenomenon of interference (example: iron oxide on mica)
Luminescent pigments	the optical effect is caused by the capacity to absorb radiation and to emit it as light of a longer wavelength
Fluorescent pigments	the light of longer wavelength is emitted after excitation without a delay (example: silver-doped zinc sulfide)
Phosphorescent pigments	the light of longer wavelength is emitted within several hours after excitation (example: copper-doped zinc sulfide)

1.1.2

Economic Aspects and Uses

1.1.2.1

Economic Aspects

World production of inorganic pigments in 2000 was ca. 5.9×10^6 t. About one-third of this total is supplied by the United States, one-third by the European Community, and one-third by all the remaining countries. The German pigment industry supplied about 40% of the world consumption of inorganic colored pigments, including about

50% of the iron oxides. Estimated world consumption of inorganic pigments in 2000 can be broken down as follows:

Titanium dioxide	69%
Synthetic iron oxides	14%
Lithopone	3.5%
Zinc oxide	1%
Effect pigments	1%
Chromates	<1%
Chromium oxide	0.5%
Mixed metal oxide pigments	<0.5%
Ultramarine	<0.5%
Iron blue	<0.5%

Pigment production is still increasing, but the rate of growth has decreased. The value of inorganic pigments has diminished recent years and in 2002 totalled ca. US\$ 10 ×10⁹. The main manufacturing companies are given in the corresponding sections.

1.1.2.2

Uses

The most important areas of use of pigments are paints, varnishes, plastics, artists' colors, printing inks for paper and textiles, leather decoration, building materials (cement, renderings, concrete bricks and tiles, mostly based on iron oxide and chromium oxide pigments), imitation leather, floor coverings, rubber, paper, cosmetics, ceramic glazes, and enamels.

The paint industry uses high-quality pigments almost exclusively. An optimal, uniform particle size is important because it influences gloss, hiding power, tinting strength, and lightening power. Paint films must not be too thick; therefore pigments with good tinting strength and hiding power combined with optimum dispersing properties are needed.

White pigments are used not only for white coloring and covering, but also for reducing (lightening) colored and black pigments. They must have a minimal intrinsic color tone.

When choosing a pigment for a particular application, several points normally have to be considered. The coloring properties (e.g., color, tinting strength or lightening power, hiding power, see Section 1.3) are important in determining application efficiency and hence economics. The following properties are also important:

1. *General chemical and physical properties*: chemical composition, moisture and salt content, content of water-soluble and acid-soluble matter, particle size, density, and hardness (see Section 1.2).
2. *Stability properties*: resistance toward light, weather, heat, and chemicals, anti-corrosive properties, retention of gloss (see Section 1.4).

3. *Behavior in binders*: interaction with the binder properties, dispersibility, special properties in certain binders, compatibility, and solidifying effect (see Section 1.5).

Important pigment properties and the methods for determining them are described later.

1.1.3

New Developments

Notwithstanding that most inorganic pigments have been known for a very long time, new developments appear on the catwalk of colors. The so-called “high performance pigments” [1.1] show a lot of modern developments.

Driven by environmental laws, even some of the former important inorganic pigments have had to be replaced. For example, red lead was fully substituted in most countries in anticorrosion paint. However environmental considerations are not the only driving force in the development of new pigments. The invention of new pigments and the improvement of the already existing pigments in this class in the last decade have made new color effects available on an industrial scale (see Section 5.3). New physical effects led to the so-called “quantum effect pigments”, but these are in the very early stage of nanoscale laboratory curiosities.

The progress in multi-component mixed crystal systems shows lanthanum-tantalum oxide-nitrides as promising candidates with interesting color shades in the red to yellow range [1.2, 1.3] but the development into industrially available pigments has yet to be proven. Even the promising candidate of the last decade, cerium sulfide [1.4], presently available in technical quantities, is still waiting for its breakthrough because of stability problems, which have not yet been resolved [1.5].

The reasons for the slow introduction of new pigments may be that the regulatory hurdles for newly introduced chemicals are high, and also that customers are making more demands on the performance of new materials and the *Three Essential E's: Effectiveness, Economy and Ecology*.

There are still challenges: Brilliant, inorganic, nontoxic, stable and cheap green or blue pigments are amongst these. Probably, the mixed crystal systems are promising fields for new discoveries.

The general areas for the development of inorganic pigments that are new or already on the market can be summarized as follows [1.5]:

1. Many pigments are coated with an additional layer, having no strong influence on the color, but improving the application properties: better adjustment of pigment and binder components (pre-wetting of the pigment surface, dispersion behavior, settling behavior, etc.); improved weathering properties of the pigments in the binder system (i.e. stability against UV, humidity, etc.). These surface treatments (aftertreatments) can consist of inorganic (SiO_2 , Al_2O_3 , ZrO_2), organic (polyalcohols, siloxanes, organo-functional silanes or titanates) or combined inorganic/organic compounds.

2. The pigments are offered not only as pure, free-flowing powders, but also in the form of preparations (granulates, chips, pastes, color concentrates). These preparations contain the pigment in as high as possible concentration. In addition to the pigment, the preparations consist also of binder components or binder mixtures based on solvent and waterborne systems. Such pigment-binder combinations show certain advantages for the users of paints, printing inks or plastics (i.e. better pigment dispersibility, non-dusting introduction of the pigment in the application system, optimized wetting behavior, improved coloristic effects in the final products).
3. New approaches are being made combining the high hiding power and stability of inorganic pigments with the brilliance and saturation of organic pigments. Besides the known simple blending (e.g. “iron green” = yellow iron oxide hydroxide with phthalocyanine) new preparations of specialized titanium dioxide with high performance organic pigments show interesting properties, but the proof of merchantable quality is yet to come.

The further development of tailor-made surface treatments and pigment preparations will lead to the faster introduction of new applications for inorganic pigments in the future.

1.2

General Chemical and Physical Properties

1.2.1

Fundamental Aspects [1.6]

1.2.1.1

Chemical Composition

With few exceptions, inorganic pigments are oxides, sulfides, oxide hydroxides, silicates, sulfates, or carbonates (see Tables 1.3 and 1.4), and normally consist of single-component particles (e.g., red iron oxide, $\alpha\text{-Fe}_2\text{O}_3$ with well-defined crystal structures). However, mixed and substrate pigments consist of non-uniform or multicomponent particles.

Mixed pigments are pigments that have been mixed or ground with pigments or extenders in the dry state (e.g., chrome green pigments are mixtures of chrome yellow and iron blue). If the components differ in particle size and shape, density, reactivity, or surface tension, they may segregate during use.

In the case of *substrate pigments*, at least one additional component (pigment or extender) is deposited onto a substrate (pigment or extender), preferably by a wet method. Weak, medium, or strong attractive forces develop between these pigment components during drying or calcining. These forces prevent segregation of the components during use.

Special substrate pigments include the aftertreated pigments and the core pigments. To produce *aftertreated pigments* the inorganic pigment particles are covered

Tab. 1.3: Classification of white and black pigments

Chemical class	White pigments	Black pigments
Oxides	titanium dioxide zinc white, zinc oxide	iron oxide black iron-manganese black spinel black
Sulfides	zinc sulfide lithopone	
Carbon and carbonates	white lead	carbon black

with a thin film of inorganic or organic substances to suppress undesirable properties (e.g., catalytic or photochemical reactivity) or to improve the dispersibility of the pigments and the hydrophilic or hydrophobic character of their surfaces. The particles can be coated by precipitation (e.g., aftertreated TiO₂ pigments, see Section 2.1.3.4), by adsorption of suitable substances from solutions (usually aqueous), or by steam hydrolysis.

To produce *core pigments*, a pigment substance is deposited on an extender by precipitation or by wet mixing of the components. In the case of anticorrosive pigments (see Section 4.2.1), whose protective effect is located on their surfaces, the use of core pigments can bring about a significant saving of expensive material. Extender particles are also treated by fixing water-insoluble organic dyes on their surfaces via lake formation.

1.2.1.2

Analysis

The industrial synthesis of inorganic pigments is strictly controlled by qualitative and quantitative chemical analysis in modern, well-equipped physicochemical test laboratories. Quantitative chemical and X-ray analysis is carried out on raw materials, intermediates, and substances used for aftertreatment, but most importantly on the final products, byproducts, and waste products (wastewater and exhaust gas). This serves to fulfill not only quality requirements but also the demands of environmental protection. Quality control, carried out in specially equipped laboratories, includes testing of physical and technical application properties [1.7, 1.8]. Information on quality requirements for inorganic pigments is widely available in international (ISO), European (EN), and national standards (e.g., AFNOR, ASTM, BSI, DIN) [1.9, 1.10]. Standard analytical methods and conditions of delivery for the most important inorganic pigments are given in Table 1.1. Further information is given in later sections.