

Industrial Inorganic Pigments

Second, Completely Revised Edition

Edited by Gunter Buxbaum

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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 review 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.

Preface to the First 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.

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1. Introduction

1.1. General Aspects

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 this century. According to accepted standards (Table 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 chapter, 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.

Historical. 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 B.C., 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.

Table 1. Listing of standards for pigments

Key words	ISO	EN	ASTM	DIN
Acidity/alkalinity	787-4	ISO 787-4	D 1208	EN ISO 787-4
Aluminium 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			53223
KEMPF method			D 4214	53159
Change in Strength (see ease of dispersion and PVC)				
Chemical resistance	1812-1	ISO 2812-1		EN ISO 2812-1
Chlorides, water-soluble (see matter soluble)				
Chromium oxide pigments:				
Specification	4621		D 263	ISO 4261
Climates:				
Containing evaporated water				50017
Standardized	554			50014
Open air				50019-1
SO ₂ atmosphere	6988	ISO 6988		EN ISO 6988
Coating materials:				
Terms and definitions	4618-1 to 4618-4	971-1		EN 971-1
Color differences:				
CIELAB	7724-3		D 1729	6174
			D 2244	
			E 308	
Conditions/evaluation of measurements	7724-2			53236
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 2805	55983
Coloration of building materials				53237
Colorimetry	7724-1		E 259	5033-1 to 5033-9
	7724-2		E 308	6174
	7724-3			
Coloring materials:				
Classification				55944
Terms and definition	4618-1	971-1		55943
				EN 971-1

Table 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
Stove type				53238-31
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 21524
	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 2805	55987
Wedge-shaped layer	6504-5			55601
White and light gray media			D 2805	55984
Hue of near white specimens				55980
Hue relative of near white specimens				55981
Iron blue pigments:				
Methods of analysis	2495		D 1135	
Specification	2495		D 261	55906
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 D 3724	ISO 1248
FeO content			D 3872	
Methods of analysis	1248		D 50	55913-2 ISO 1248

Table 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	55972
Specification			D 212	55972
Lead chromate green pigments:				
Methods of analysis	3710		D 126	55973
Specification	3710			55973
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	2809			53231
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 3718 D 3618 D 3624 D 3717	53770-1 to 53770-15
Preparation of extract	6713			52770-1
Matter soluble in water:				
Chlorides	787-13			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			ISO 787-13
Salicylic acid method	787-19	ISO 787-19		EN ISO 787-19
Sulfates	787-13			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

Table 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			D 3360	66111
Pipette method				66115
pH value	787-9	ISO 787-9	D 1208	EN ISO 787-9
Phthalocyanine 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				53775-1
Bleeding				53775-3
Change in strength				53775-7
Heat stability, in oven				53775-6
Heat stability, mill aging				53775-5
Test specimen preparation				53775-2
Red lead:				
Specification	510		D 49	55916
			D 83	
Reflectance factor; paper, cardboard:				
Fluorescent				53145-2
Nonfluorescent	2469			53145-1
Reflectometer (gloss assessment)	2813		E 430	67530
			D 523	
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	ISO 787-14
Sampling:				
Terms	842		D 3925	53242-1
Solid material	842		D 3925	53242-4
Scattering power, relative:				
Gray paste method	787-24	ISO 787-24		EN ISO 787-24
Black ground method				53164
Specific surface area:				
BET method				66131
N₂ adsorption				66132
Permeability techniques				66126-1

Table 1. (continued)

Key words	ISO	EN	ASTM	DIN
Standard depth of shade:				
Specimen adjustment				53235-2
Standards				53235-2
Strontium chromate pigments:				
Specification	2040		D 1845	55903
Sulfates, water-soluble (see matter soluble)				
SO ₂ resistance	3231			53771
				ISO 3231
Tamped volume	787-11	ISO 787-11		EN ISO 787-11
Test evaluation:				
Scheme	4628-1			53230
Thermoplastics:				
Basic mixtures				53773-1
Heat stability				53772
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
Visual	787-16	ISO 787-16		EN ISO 787-16
Titanium dioxide pigments:				
Methods of analysis	591		D 1394	55912-2
			D 3720	
			D 3946	
Specification	591		D 476	55912-1
Test methods	591		D 4563	55912-1
			D 4767	
			D 4797	
Transparency:				
Paper, cardboard	2469			53147
Pigmented/unpigmented systems				55988
Ultramarine pigments:				
Methods of analysis			D 1135	
Specification	788		D 262	55907
Viscosity	2384		D 2196	53229
Weathering in apparatus	4892			53231
	11341			53387
White lead:				
Methods of analysis			D 1301	
Specification			D 81	
Zinc chromate pigments:				
Specification	1249			55902
Zinc dust pigments:				
Methods of analysis	713			
	714			
	3549		D 521	55969
Specification	3549		D 520	55969

Table 1. (continued)

Key words	ISO	EN	ASTM	DIN
Zinc oxide pigments:				
Methods of analysis			D 3280	55908
Specification			D 79	
Zinc phosphate pigments:				
Methods of analysis	6745			ISO 6745
Specification	6745			ISO 6745

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 A.D.) 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 A.D.) 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 a 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, nacreous, and interference pigments) have assumed increasing importance.

Economic Aspects. World production of pigments in 1995 was approx. 5×10^6 t. Inorganic pigments accounted for ca. 97% of this.

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 1995 can be broken down as follows [1.1]:

Titanium dioxide	66%
Iron oxides (natural and synthetic)	14%
Carbon black pigments	10%
Lithopone (incl. ZnS)	4%
Chromates	3%

Chromium oxide	1%
Zinc oxide	< 1%
Molybdates/lead chromates	< 1%
Luster pigments	< 1%
Mixed metal oxide pigments	< 0.5%
Iron blue pigments	< 0.5%
Ultramarine	< 0.5%

Pigment production is a still growth industry, but in the future the growth rate will decrease. The sales of inorganic pigments in 1995 amounted to ca. $\$13 \times 10^9$. The names of manufacturing companies are given in the corresponding sections.

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), leather imitates, 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 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.

Classification. Inorganic pigments can be classified from various points of view. The classification given in Table 2 (for standards see Table 1, "Coloring materials, terms") follows a system recommended by ISO and DIN; it is based on coloristic and chemical considerations. As in many classification schemes, there are areas of overlap between groups so that sharp boundaries are often impossible. In this article 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.

Table 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)
Luster 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)
Nacreous 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)

1.2. General Chemical and Physical Properties

1.2.1. Fundamental Aspects [1.2]

Chemical Composition. With few exceptions, inorganic pigments are oxides, sulfides, oxide hydroxides, silicates, sulfates, or carbonates (see Tables 3 and 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 nonuniform 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

Table 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

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 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 TiO_2 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 5.2), 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.

Analysis. The industrial synthesis of inorganic pigments is strictly controlled by qualitative and quantitative chemical analysis in modern, well-equipped physico-chemical 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 not only to fulfil quality requirements but also the demands of environmental protection. Quality control, carried out in specially equipped laboratories and supported by computers, includes testing of physical and technical application properties [1.3], [1.4]. Information on quality requirements for inorganic pigments is widely available in international, ISO, European (EN), and national standards (e.g., AFNOR, ASTM, BSI, DIN) [1.5], [1.6]. Standard analytical methods and conditions of delivery for the most important inorganic pigments are given in Table 1. Further information is given in later sections.

Crystallography and Spectra. The following are the most common crystal classes:

- 1) *Cubic*: zinc blende lattice (e.g., precipitated CdS), spinel lattice (e.g., Fe_3O_4 , CoAl_2O_4)
- 2) *Tetragonal*: rutile lattice (e.g., TiO_2 , SnO_2)
- 3) *Rhombic*: goethite lattice (e.g., $\alpha\text{-FeOOH}$)
- 4) *Hexagonal*: corundum lattice (e.g., $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-Cr}_2\text{O}_3$)
- 5) *Monoclinic*: monazite lattice (e.g., PbCrO_4)

Table 4. Classification of inorganic colored pigments

Chemical class	Green	Blue-green	Blue	Violet	Red	Orange	Yellow	Brown
Oxides and oxide-hydroxides								
Iron oxide pigments					iron oxide red	iron oxide orange	iron oxide yellow	iron oxide brown
Chromium oxide pigments	chromium oxide	chromium oxide hydrate green						
Mixed metal oxide pigments			cobalt green and blue			chromium rutile orange		zinc iron spinell, Mn-Fe-brown
Sulfide and sulfoselenide pigments							cadmium sulfide (Cd, Zn) S	
Chromate pigments	chrome green				molybdate red	chrome orange	chrome yellow, zinc yellow, alkaline earth chromates	
Ultramarine pigments	ultramarine green, blue, violet, and red							
Iron blue pigments			iron blue					
Others			manganese blue	cobalt, manganese violet			naples yellow, bismuth vanadate	

In ideal solid ionic compounds, the absorption spectrum is composed of the spectra of the individual ions, as is the case in ionic solutions. For metal ions with filled *s*, *p*, or *d* orbitals, the first excited energy level is so high that only ultraviolet light can be absorbed. Thus, when the ligands are oxygen or fluorine, white inorganic compounds result. The absorption spectra of the chalcogenides of transition elements with incompletely filled *d* and *f* orbitals are mainly determined by the charge-transfer spectrum of the chalcogenide ion which has a noble gas structure. For the transition metals, lanthanides, and actinides, the energy difference between the ground state and the first excited state is so small that wavelength-dependent excitations take place on absorption of visible light, leading to colored compounds [1.7].

X-ray investigation of inorganic pigments yields information on the structure, fine structure, state of stress, and lattice defects of the smallest coherent regions that are capable of existence (i.e., crystallites) and on their size. This information cannot be obtained in any other way. Crystallite size need not be identical with particle size as measured by the electron microscope, and can, for example, be closely related to the magnetic properties of the pigment.

Particle Size. The important physical data for inorganic pigments comprise not only optical constants, but also geometric data: mean particle size, particle size distribution, and particle shape [1.8]. The standards used for the terms that are used in this section are listed in Table 1 (“Particle size analysis”).

The concept of *particles and particle shape* corresponds to that used in the recommended and internationally accepted classification of pigment particles given in [1.9] (see Fig. 1 and Table 5).

The term *particle size* must be used with care, as is borne out by the large number of different “particle diameters” and other possible terms used to denote size (see Table 6). In granulometry, so-called *shape factors* are often used to convert equivalent diameters to “true” diameters. However, the determination and use of shape factors is problematic.

Table 5. Definitions of particles and associated terms (see also Fig. 1)

Term	Definition
Particle	individual unit of a pigment that can have any shape or structure
Primary or individual particles	particles recognizable as such by appropriate physical methods (e.g., by optical or electron microscopy)
Aggregate	assembly of primary particles that have grown together and are aligned side by side; the total surface area is less than the sum of the surface areas of the primary particles
Agglomerate	assembly of primary particles (e.g., joined together at the corners and edges), and/or aggregates whose total surface area does not differ appreciably from the sum of the individual surface areas
Flocculate	agglomerate present in a suspension (e.g., in pigment–binder systems), which can be disintegrated by low shear forces

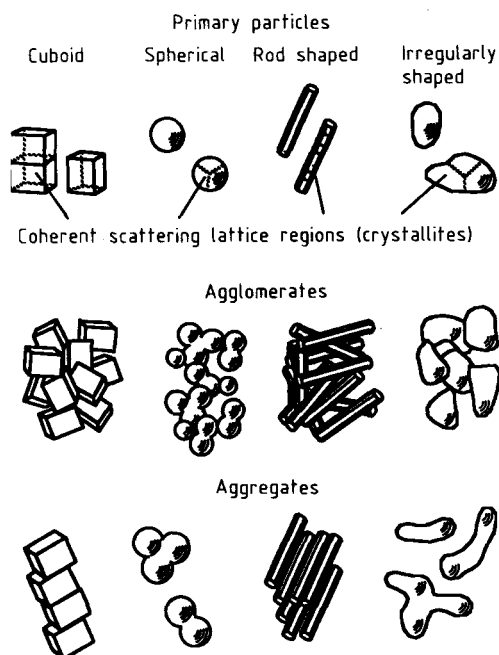


Figure 1. Primary particles, agglomerates, and aggregates

Table 6. Particle size, particle size distribution, and characteristic quantities

Term	Definition
Particle size	geometrical value characterizing the spatial state of a particle
Particle diameter D_{eff}	diameter of a spherical particle or characteristic dimension of a regularly shaped particle
Equivalent diameter D	diameter of a particle that is considered as a sphere
Particle surface area S_T	surface area of a particle: a distinction is made between the internal and external surface areas
Particle volume V_T	volume of a particle: a distinction is made between effective volume (excluding cavities) and apparent volume (including cavities)
Particle mass m_T	mass of a particle
Particle density ρ_T	density of a particle
Particle size distribution	statistical representation of the particle size of a particulate material
Distribution density	gives the relative amount of a particulate material in relation to a given particle size diameter. Density distribution functions must always be normalized
Cumulative distribution	normalized sum of particles that have a diameter less than a given particle size parameter
Fractions and class	a fraction is a group of particles that lies between two set values of the chosen particle size parameter that limits the class
Mean value and other similar parameters	the mean values of particle size parameters can be expressed in many ways, some values are used frequently in practice
Distribution spread	parameter for characterizing the nonuniformity of the particle size

In practice, empirically determined *particle size distributions* are represented by:

- 1) Tabulated results
- 2) Graphical representation in the form of a histogram (bar chart) or as a continuous curve
- 3) Approximation in the form of analytical functions

For standards see Table 1 “Particle size, representation”.

Special distribution functions are specified in some standards (e.g., power distribution, logarithmic normal distribution, and RRSB distribution). Methods of determination for pigments are rated in Section 1.2.2.

The important parameters relating to particle size distribution are the *mean particle size* and the *spread of the distribution*. The way of expressing the mean particle size depends on the test method used or on which mean value best reflects the pigment property of interest. Depending on the spread of parameter, the various mean values for a given particulate material can differ considerably. The mean particle sizes of inorganic pigments lie in the range 0.01–10 μm , and are usually between 0.1 and 1 μm .

The *specific surface area* also represents a mean of the pigment particle size distribution. It can be used to calculate the mean diameter of the surface distribution. Care must be taken that the effect of the “internal surface area” is taken into account. If the product has an internal surface area which cannot be neglected in comparison to the external surface area, then the measured specific surface area no longer gives a true measure of the mean diameter. This applies, for instance, to aftertreated pigments because the treatment material is often very porous.

For anisometric particles (e.g., needle- or platelet-shaped particles) mathematical statistics may likewise be applied [1.10]. The two-dimensional logarithmic normal distribution of the length L and breadth B of the particles also allows the representation and calculation of the characteristic parameters and mean values. The eccentricity of the calculated standard deviation ellipse (Fig. 2) is a measure of the correlation between the length and breadth of the particle. By using more than two

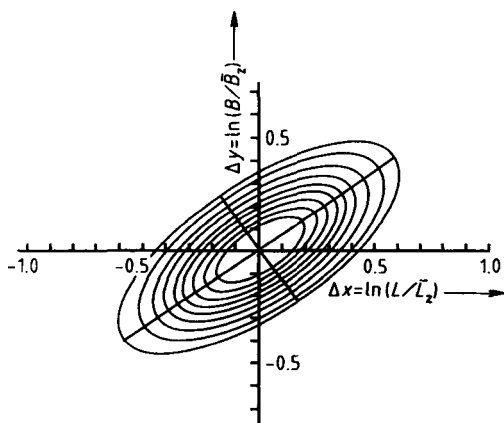


Figure 2. Standard deviation ellipses of a logarithmic normal distribution (yellow iron oxide pigment)
 \bar{L}_z, \bar{B}_z = median of L, B