1
Introduction

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General Aspects

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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.

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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
Stoving type				53238-34
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	55912-2
			D 3720	
			D 3946	
Specification	591-1		D 476	55912-2
Test methods	591-1		D 4563	55912-2
			D 4767	
			D 4797	
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			EN ISO 11341
	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 orpigment, 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$ 10×10^9. 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, anticorrosive 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, α-Fe_2O_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 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 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.

Tab. 1.4: 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	nickel rutile yellow, chromium rutile yellow	zinc iron spinel, Mn–Fe brown
Sulfide and sulfoselenide pigments					cadmium sulfoselenide cerium sulfide	cadmium sulfide, (Cd, Zn)S		
Chromate pigments	chrome green	molybdate red	chrome orange	chrome yellow, zinc yellow				
Ultramarine pigments	ultramarine green, blue, violet, and red							
Iron blue pigments			iron blue					
Others			manganese blue	cobalt manganese violet	$(Ca,La)Ta(O,N)_3$		naples yellow, bismuth vanadate	

1.2.1.3
Crystallography and Spectra

The following are the most common crystal classes:

1. *Cubic*: zinc blend 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., α-FeOOH)
4. *Hexagonal*: corundum lattice (e.g., α-Fe_2O_3, α-Cr_2O_3)
5. *Monoclinic*: monazite lattice (e.g., $PbCrO_4$)

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 [1.11].

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.

1.2.1.4
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 [1.12]. The standards used for the terms that are used in this section are listed in Table 1.1 (“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 Ref. [1.13] (see Figure 1.1 and Table 1.5).

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 1.6). In granulometry, so-called *shape factors* are sometimes used to convert equivalent diameters to “true” diameters. However, the determination and use of shape factors is problematic.

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

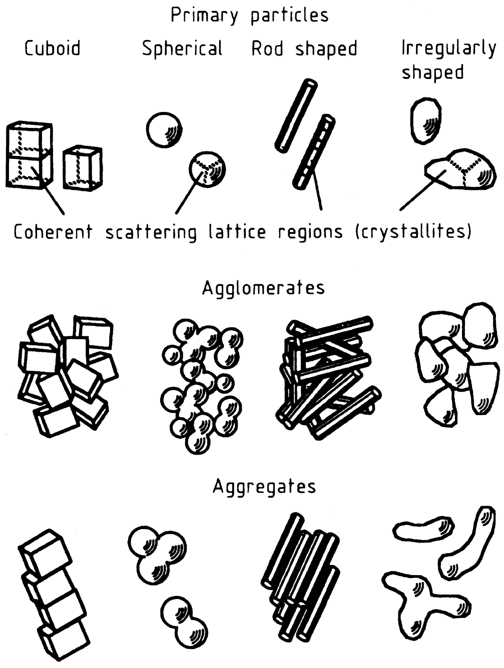

Fig. 1.1 Primary particles, agglomerates, and aggregates.

Tab. 1.5: Definitions of particles and associated terms (see also Fig. 1.1)

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

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

Tab. 1.6: 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 Q_{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

For standards see Table 1.1 “Particle size, representation”. Special distribution functions are specified in some standards (e.g., power distribution, logarithmic normal distribution, and RRSB distribution). The representation of particle size distributions and methods for their determination are described elsewhere. 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 anisomeric particles (e.g., needle- or platelet-shaped particles) mathematical statistics may likewise be applied [1.14]. 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 (Figure 1.2) is a measure of the correlation between the length and breadth of the particle. By using more than two particle fineness parameters, this principle can be further extended in a similar manner. The effect of particle size on optical properties of pigments is described in Section 1.3.

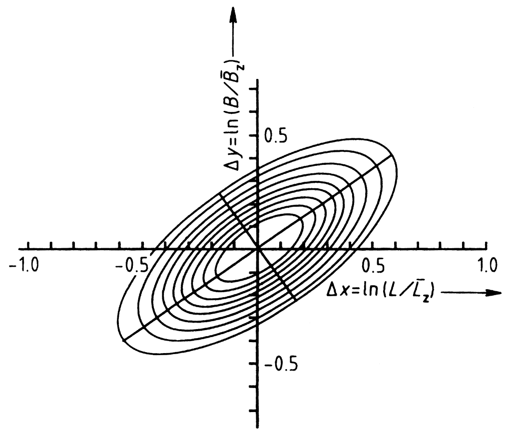

Fig. 1.2 Standard deviation ellipses of a logarithmic normal distribution (yellow iron oxide pigment). $\bar{L}_z$, $\bar{B}_z$ = median of L, B.

1.2.2
Methods of Determination

1.2.2.1
General Methods

Sampling with a suitable device (beaker, sampling scoop) is applicable for solid materials, especially pigments, fillers, and resins in powder, granular, or lump form. For standards, see Table 1.1 (“Sampling”).

Standard climates are constant artificial climatic conditions with a defined temperature and humidity and limited ranges of air pressure and flow velocity. They can be set up in “clima” cabinets, closets, or rooms. The standard climate 23/50 (23°C and 50% relative humidity) is recommended. For standards, see Table 1.1 (“Climates”).

Evaluation Methods. In testing paint materials, paints, and other coating materials, the properties or variations in properties often cannot be described quantitatively but must be assessed subjectively. A uniform system of evaluation has been established in the form of a numerical scale to facilitate the assessment of results and mutual understanding. This system should only be used if a result cannot be obtained as a directly measured value. For standards, see Table 1.1 (“Test evaluation”).

1.2.2.2
Matter Volatile and Loss on Ignition

The content of *matter volatile* in a pigment is determined by drying a sample in an oven at 105 ± 2 °C. This normally gives a measure of the moisture content. For standards, see Table 1.1 (“Matter volatile”).

Loss on ignition is determined by various means, depending on the pigment. The principle is the same in all the methods: a weighed sample is heated to a predetermined temperature, cooled in a desiccator, and reweighed. Special standard procedures are specified for iron oxide pigments and carbon black. For standards, see Table 1.1 (“Iron oxide pigments: Specifications” and “Carbon black pigments: Specifications”).

1.2.2.3
Aqueous Extracts

The content of *matter soluble in water* in pigments is determined by hot or cold extraction of the pigments under prescribed testing conditions. For standards, see Table 1.1 (“Matter soluble in water”). The decision whether to use hot or cold extraction depends on the properties of the pigment and should be agreed between the interested parties unless otherwise prescribed.

The *pH value* of a pigment denotes the pH of an aqueous suspension of the pigment prepared in a prescribed manner. For standards, see Table 1.1 (“pH value”). Apparatus: pH meter.

The *electrical conductivity* (or resistivity) of an aqueous pigment extract is determined from the electrical conductance (or resistance). For standards, see Table 1.1 (“Resistivity”). Apparatus: centrifuge with glass containers, resistance measurement bridge, electrolytic cell.

The *acidity* or *alkalinity* is measured as the quantity of cubic centimeters of 0.1 N alkali (NaOH or KOH) or acid solution that are required to neutralize an aqueous extract of 100 g pigment under prescribed conditions. Unless otherwise agreed, the pigment is extracted with hot water. If cold water is used, this must be specifically stated. For standards, see Table 1.1 (“Acidity/alkalinity”). Test reagents: 0.5 N HCl or H_2SO_4, 0.5 N NaOH or KOH, indicators (by agreement).

Water-soluble Sulfates, Chlorides and Nitrates. The procedures are applicable to pigments and extenders. The choice of hot or cold extraction depends on the properties of the pigment and should be agreed. The anions are determined by the usual analytical methods. For standards, see Table 1.1 (“Sulfates”, “Chlorides”, and “Nitrates”). Apparatus: Nessler tubes or spectrophotometer, equipment for pH measurement.

Water-Soluble Chromium(VI). Chromium(VI) is determined photometrically in an aqueous extract obtained by hot or cold extraction using the color produced with diphenylcarbazide, or directly as chromate. For standards, see Table 1.1 (“Matter soluble in water”). Apparatus: equipment for shaking conical flasks, photometer with glass cells, pH meter.

Matter Soluble in HCl. The pigment is extracted with 0.1 M hydrochloric acid under prescribed conditions to determine the content of As, Ba, Cd, Co, Cr, Cr(VI), Cu, Hg, Mn, Ni, Pb, Sb, Se, and Zn. For standards, see Table 1.1 (“Matter soluble in HCl”). Apparatus: shaker for conical flasks.

1.2.2.4
Particle Size Distribution

The particle sizes relevant for inorganic pigments stretch between several tens of nanometers for transparent pigment types to approximately two micrometers. For practical applications it is very desirable to determine not only the mean particle size but also the whole distribution. These parameters must not be confused with the crystal size determined by X-ray diffraction, as pigment particles usually are not monocrystals.

The determination of the particle size distribution is a complex issue and the subject of voluminous monographs [1.15] so only an introduction to the questions relevant for applications concerning inorganic pigments can be given.

Measuring and counting the particles shown on a suitable electron micrograph is the most straightforward means of determination of the particle size distribution of inorganic pigments. The necessary number of particles (2500–10000) renders this method too costly and time consuming for day-to-day business, although the process can be automated to a certain degree. Another disadvantage is the length of time for the process, which makes it impossible to apply this method for production control. An advantage is of course that additional information about particle shape and morphology can be obtained in this way.

Two methods are mainly used for the determination of particle size of inorganic pigments: Sedimentation methods (centrifuges) and Fraunhofer diffraction with additional correction due to Mie scattering.

When evaluating the results of these measurements one has to remember that a property of the particles (light scattering or the velocity of sedimentation) is determined. With models relying on a number of assumptions (for example that all particles are spherical) and further input (for example the complex index of refraction or the density) the particle size distribution is calculated in the final step. Applying the results of the measurement this and other deviations from the model have to be taken into account. Different measurement techniques usually result in different results for the measurements of particle size distributions.

The main advantage of centrifuges is the high resolution these instruments usually deliver, making it possible to differentiate between particle sizes that are very closely spaced. Instruments using Fraunhofer diffraction with Mie correction have found wide use in the industry during the last decade. They can make fast and very reproducible measurements while being able to determine particle sizes between 0.05 and 1500 μm, although it seems that the lower range cannot be reached with all substances. An advantage is that these instruments can also be used with fluidized samples and can determine the particle size distribution of dry powders.

While using a dilute suspension in a pump-through cell there is the possibility to determine even particles far from the main distribution, present only in minor amounts, with high precision. This makes it possible to catch the particles several times, resulting in good reproducibility of the measurement result.

As stated above these instruments need the complex index of refraction at all the wavelengths used by the instrument. Most types apply only a single wavelength but there are also instruments available which make use of four different wavelengths. While this can be advantageous with respect to the resolution of the instrument it should be ascertained that the index of refraction is known with sufficient certainty for the materials to be measured.

Furthermore it should be proven in every case and for every instrument that the results are independent of the remnant error in this and every other input parameter. One of the most important topics regarding the particle size distribution is sample preparation and dispersion. The dispersion process typically generates most of the particles determined in the measurement.

The dispersion procedure must reflect the conditions that the particles are subjected to in the application considered for the substances. In practice the task is often not to determine the mean particle size of a pigment, but to analyze problems occurring in an application.

As pigments are most often used in paints and varnishes a dispersion with a high energetic input should be used if not otherwise stated. This can conceal effects occurring at lower energy levels as, for example, more agglomerates can be broken up. A common feature of both instrument types mentioned above is the use of a very dilute solution. The exact concentration is dependent on the specific type of instrument used, as well as on the material and particle size to be measured, but is nearly always below 1% (weight).

Although the effect of the concentration of suspension on the results of the measurement of pigments has never been proven, the development of techniques able to cope with concentrations closer to the applications if of interest. These would make it possible, for example, to determine the particle size distribution in a dispersion paint or in a reaction vessel where a pigment is produced by the precipitation process. A measurement technique having no problems, in principle, with high concentration dispersions is the scattering of ultrasonic waves. Nevertheless the instruments on the market have up to now failed to realize the great expectations of this technique.

Sieve Analysis. The sieving residue can be determined by two methods:

1. *Wet Sieving by Hand.* In the utilization of pigments, it is important to know the content of pigment particles that are appreciably larger than the mean particle size. This material can consist of coarse impurities, pigment aggregates (agglomerates), or large primary particles. The dried pigment is washed with water through a sieve of the appropriate mesh size, and the retained material is determined gravimetrically after drying. For standards, see Table 1.1 ("Residue on sieve: By water").

2. *Wet Sieving by a Mechanical Flushing Procedure.* The sieve residue is the portion of coarse particles that cannot be washed through a specified test sieve with water. The result depends on the mesh size of the sieve. For standards, see Table 1.1 ("Residue on sieve: Mechanical method"). Apparatus: Mocker's apparatus.

Additionally, wet sieving down to a mesh size of 5 μm can be realized by applying special sieves of pure nickel membranes. The material is fluidized in an ultrasonic bath.

The *specific surface* is usually understood to mean the area per unit mass of the solid material, but it is sometimes useful to relate the surface area to the volume of the solid (see Section 1.2.1). The specific surface area can only be determined indirectly owing to the small size of the pigment particles:

1. *Gas Adsorption by the Brunauer, Emmett, and Teller (BET) Method.* The specific surface area of porous or finely divided solids is measured. The method is limited to solids that do not react with the gas used (e.g., while the gas is adsorbed), and nonmicroporous materials. For standards, see Table 1.1 ("Specific Surface, BET Method" and "N_2 Adsorption").
2. *Carman's Gas Permeability Method.* A gas or a wetting liquid is made to flow through the porous material in a tube by applying vacuum or pressure. The pressure drop or flow rate is measured. For pigments, a modified procedure is used in which mainly nonlaminar flow takes place [1.16]. For standards, see Table 1.1 ("Specific surface: Permeability techniques").

1.2.2.5
Pigment Density

Density is determined by pyknometry at a standard temperature of 25°C. For standards, see Table 1.1 ("Density"). Apparatus: pyknometer, vacuum pump or centrifuge.

The *apparent density* of a powdered or granulated material after tamping is the mass (g) of 1 cm^3 of the material after tamping in a tamping volumeter under prescribed conditions. The *tamped volume* is the volume (cm^3) of 1 g of the material. Tamped volume and apparent density after tamping depend mainly on the true density, shape, and size of the particles. Knowledge of these parameters allows decisions to be made regarding dimensions of packing materials and product uniformity. For standards, see Table 1.1 ("Tamped volume"). Apparatus: tamping volumeter.

1.2.2.6
Hardness and Abrasiveness

The abrasiveness of a pigment is not identical to its intrinsic hardness, i.e., the hardness of its primary particles. In practice the Mohs hardness is therefore not a useful indication of the abrasiveness of a pigment. Abrasion rather depends on pigment particle size and shape and is usually caused by the sharp edges of the particles. A standard test procedure for determining abrasiveness does not exist. A method based on the abrasion of steel balls by the pigment is described in Ref. [1.17].

1.3
Color Properties

1.3.1
Fundamental Aspects [1.18–1.22]

When a photon enters a pigmented film, one of three events may occur:

1. It may be absorbed by a pigment particle
2. It may be scattered by a pigment particle
3. It may simply pass through the film (the binder being assumed to be nonabsorbent)

The important physical-optical properties of pigments are therefore their light-absorption and light-scattering properties. If absorption is very small compared with scattering, the pigment is a white pigment. If absorption is much higher than scattering over the entire visible region, the pigment is a black pigment. In a colored pigment, absorption (and usually scattering) is selective (i.e., dependent on wavelength).

Pigments and coatings may be unambiguously characterized by their spectral reflectance curves $\rho(\lambda)$ or spectral reflectance factor curves $R(\lambda)$ (Figure 1.3). The reflectance spectrum $\rho(\lambda)$ or $R(\lambda)$ and hence the color properties can be almost completely derived from physical quantities [1.21] (Figure 1.4):

1. *Colorimetry* relates the perceived color quality to the color stimulus, which in turn is based on the reflectance spectrum $\rho(\lambda)$.
2. The *Kubelka–Munk theory* relates $\rho(\lambda)$ to scattering, absorption, and film thickness (scattering coefficient S, absorption coefficient K, film thickness h).
3. The *theory of multiple scattering* (scattering interaction) relates the scattering coefficient S to the pigment volume concentration σ and to the scattering diameter Q_S of the individual particle. The absorption coefficient K is directly proportional to the absorption diameter Q_A and the concentration σ.
4. In *Mie's theory*, the scattering diameter Q_S and the absorption diameter Q_A are related to the particle size D, the wavelength λ, and the optical constants of the material (refractive index n and absorption index κ).

1.3.1.1
Colorimetry [1.23–1.25]

The principles of colorimetry are based on the fact that all color stimuli can be simulated by additively mixing only three selected color stimuli (trichromatic principle). A color stimulus can, however, also be produced by mixing the spectral colors. Thus, it has a spectral distribution, which in the case of nonluminous, perceived colors is

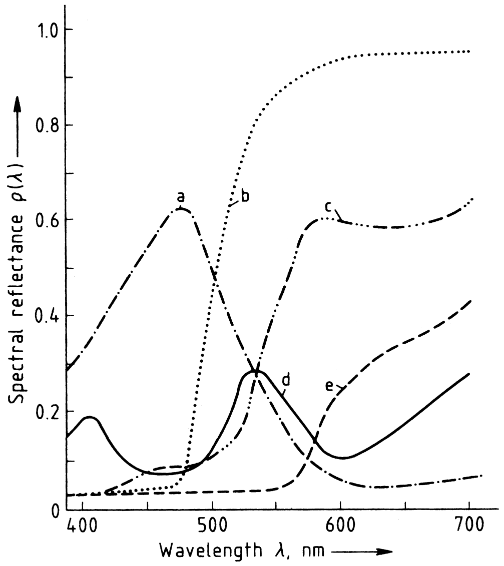

Fig. 1.3 **Figure 1.3** Spectral reflectance curves of some inorganic pigments in paints. (a) Manganese blue; (b) CdS; (c) α-FeOOH; (d) α-Cr_2O_3; (e) α-Fe_2O_3.

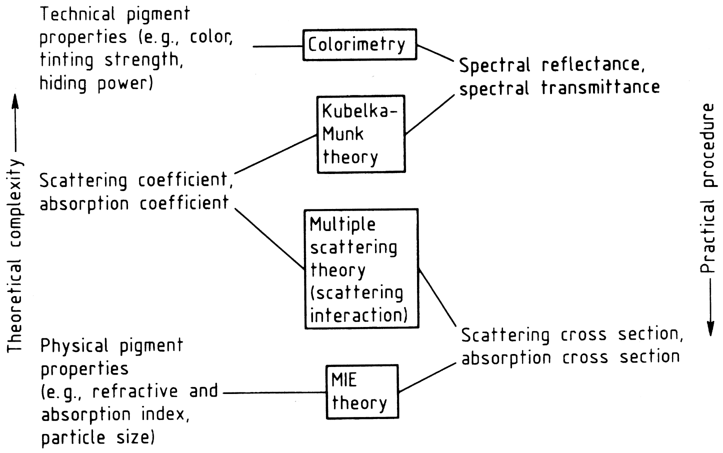

Fig. 1.4 The relationships between the optical properties of pigments and their theoretical basis.

called the spectral reflectance $\rho(\lambda)$. After defining three reference stimuli, the trichromatic principle allows a three-dimensional color space to be built up in which the color coordinates (tristimulus values) can be interpreted as components of a vector (CIE system; for standards, see Table 1.1, “Colorimetry”; CIE = Commission Internationale de l’Éclairage). The three CIE tristimulus values depend on the spectral reflectance $\rho(\lambda)$ and the spectrum of the illuminant $S(\lambda)$ as follows:

$$X = \int_{700}^{400} \overline{x}(\lambda)\rho(\lambda)S(\lambda)d\lambda$$

$$Y = \int_{700}^{400} \overline{y}(\lambda)\rho(\lambda)S(\lambda)d\lambda$$

$$Z = \int_{700}^{400} \overline{z}(\lambda)\rho(\lambda)S(\lambda)d\lambda$$

where $\overline{x}(\lambda)$, $\overline{y}(\lambda)$, and $\overline{z}(\lambda)$ are the CIE tristimulus values of the spectral colors and are called the CIE spectral tristimulus values (color matching function). The CIE chromaticity coordinates (x,y, and z) are given by

$$x = \frac{X}{X+Y+Z};$$

$$y = \frac{Y}{X+Y+Z};$$

$$z = 1 - x - y$$

They are represented as coordinates in a color plane. The chromaticity coordinates x and y are used to specify the saturation and hue of any color in the CIE chromaticity diagram. See Figure 1.5 for illumination D 65. The CIE spectral tristimulus value $y(\lambda)$ corresponds to the lightness sensitivity curve of the human eye. Therefore, a third color variable is specified in addition to x and y, namely the CIE tristimulus value Y, which is a measure of lightness.

This system allows exact measurement of color with worldwide agreement. For pigment testing, however, this is not sufficient because small color differences usually have to be determined and evaluated (e.g., between test and reference pigment). Using the CIE system, it is certainly possible to say which spectral distributions are visually identical, but this is not suitable for determining color differences. To establish color differences an "absolute color space" must be used. Here, colors are arranged three-dimensionally such that the distance between two colors in any direction in space corresponds to the perceived difference. Such a type of color space can be based on the color qualities lightness, hue, and saturation. Several such systems exist. The most widespread color system is probably the Munsell system, which is available in the form of an atlas.

For the quantitative determination of color differences, the transformation relationships between the CIE system (which has to be used for color measurement) and the physiologically equidistant color system must be established. Color differences can then be calculated in the latter system. A large number of color difference systems have been developed, mainly as needed for industrial color testing. The

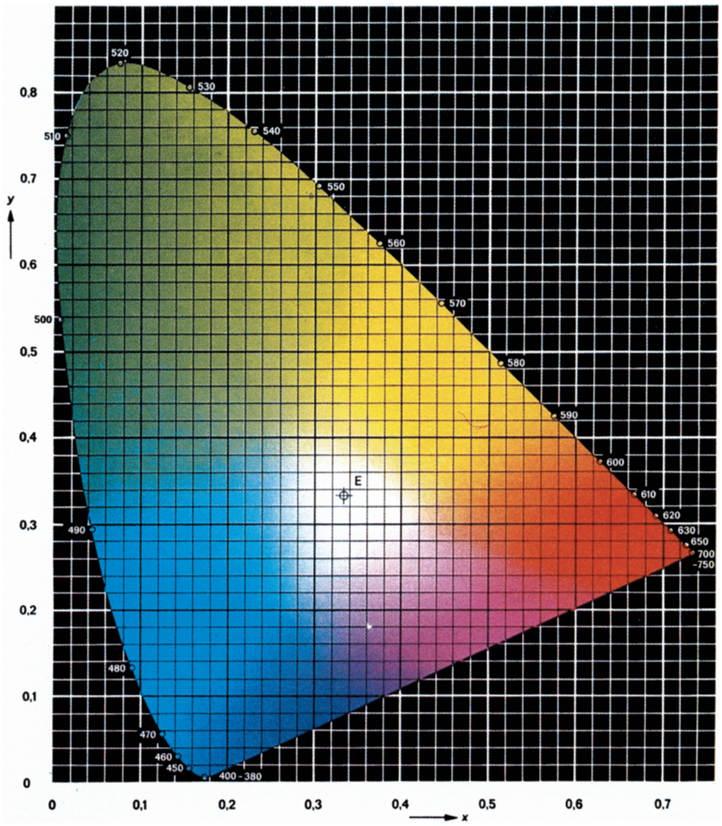

Fig. 1.5 CIE 1931 *xy* – chromaticity diagram for illuminant D 65.

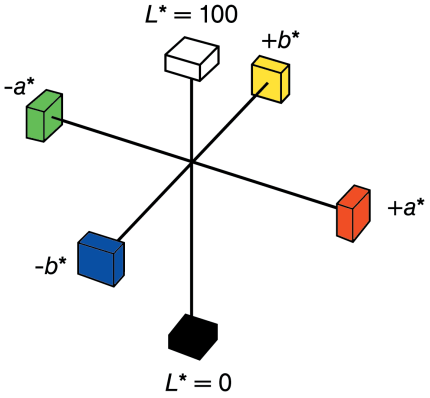

Fig. 1.6 Representation of the CIELAB system.

Adams–Nickerson (AN) system, well known for many decades and derived from the Munsell system, was recommended for pigment testing by DIN (German Standards

Institute) and later worldwide by the CIE ("CIELAB"; for standards, see Table 1.1, "Color differences"). The three coordinates are denoted by a^* (the red–green axis), b^* (the yellow–blue axis), and L^* (the lightness axis). See Figure 1.6 for a simple representation of the CIELAB system. To calculate the CIELAB coordinates, X, Y, and Z are first converted into the functions X^*, Y^*, and Z^* by using a relationship that approximately takes account of the physiologically equidistant lightness steps:

$$X^* = \sqrt[3]{X/X_\mathrm{n}};$$

$$Y^* = \sqrt[3]{Y/Y_\mathrm{n}};$$

$$Z^* = \sqrt[3]{Z/Z_\mathrm{n}}$$

where X_n, Y_n, and Z_n are the CIE tristimulus values of the illuminant, especially a standard illuminant. For radicands $\leqq 0.008856$, these equations become:

$$X^* = (7.787X/X_\mathrm{n}) + 0.138$$

$$Y^* = (7.787Y/Y_\mathrm{n}) + 0.138$$

$$Z^* = (7.787Z/Z_\mathrm{n}) + 0.138$$

Values of a^*, b^*, and L^* are obtained from the values of X^*, Y^*, and Z^*:

$$a^* = 500\,(X^* - Y^*)$$

$$b^* = 200\,(Y^* - Z^*)$$

$$L^* = 116\,Y^* - 16$$

The components of the color difference are obtained as differences between the test sample (T) and the reference pigment (R):
$\Delta a^* = a_\mathrm{T}^* - a_\mathrm{R}^*$; $\Delta b^* = b_\mathrm{T}^* - b_\mathrm{R}^*$; $\Delta L^* = L_\mathrm{T}^* - L_\mathrm{R}^*$

The color difference is finally calculated as the geometrical distance between the two positions in the CIELAB color space:

$$\Delta E_{ab}^* = \sqrt{\Delta a^{*2} + \Delta b^{*2} + \Delta L^{*2}}$$

An important advantage of the CIELAB system is that the resulting color difference can be split into component contributions, namely lightness, saturation, and hue, corresponding to the arrangement of the color space:

Lightness difference

$$\Delta L^* = L_\mathrm{T}^* - L_\mathrm{R}^*$$

Chroma difference (saturation difference)

$$\Delta C_{ab}^* = \sqrt{a_\mathrm{T}^{*2} + b_\mathrm{T}^{*2}} - \sqrt{a_\mathrm{R}^{*2} + b_\mathrm{R}^{*2}}$$

Hue difference

$$\Delta H_{ab}^* = \sqrt{\Delta E_{ab}^{*2} - \Delta L^{*2} - \Delta C_{ab}^{*2}}$$

In 1994 the CIE proposed a modified formula called “CIE94”. This formula is to be tested by interested laboratories [1.26].

1.3.1.2
Kubelka–Munk Theory

The Kubelka–Munk theory [1.25, 1.27, 1.28] is based on the fact that the optical properties of a film which absorbs and scatters light may be described by two constants: the absorption coefficient K and the scattering coefficient S. In a simplification, the flux of the diffuse incident light is represented by a single beam L^+, and the flux of the light scattered in the opposite direction by a beam L^-. Each beam is attenuated by absorption and scattering losses, but is reinforced by the scattering losses of the respectively opposite beam. The absorption and scattering losses are determined quantitatively by the two coefficients K and S. A simple system of two linked differential equations can be written. These can be integrated for the valid boundary conditions at the incident light side, and at the opposite side. Solutions for the transmittance τ and the reflectance ρ are obtained from these integrals as a function of the absorption coefficient K, the scattering coefficient S, the film thickness h, and in special cases of the reflectance ρ_0 of a given substrate.

The most important and widely used quantity derived from the Kubelka–Munk theory is the reflectance of an opaque (infinitely thick) film that is described by a very simple equation:

$$K/S \;=\; (1-\rho_\infty)^2/(2\rho_\infty)$$

From this expression (Kubelka–Munk function) it follows that, within the range of validity of the theory, ρ_∞ depends only on the ratio of the absorption coefficient to the scattering coefficient, and not on their individual values. The equation has been most useful where reflectance measurements are used to obtain information about absorption and scattering (e.g., in textile dyeing, thin layer chromatography, and IR spectroscopy).

This theory is especially useful for computer color matching of pigmented systems [1.25, 1.29–1.31]: absorption and scattering coefficients are combined additively using the specific coefficients of the components multiplied by their concentrations.

1.3.1.3
Multiple Scattering

The absorption coefficient K obeys Beer’s law, even at high pigment volume concentrations σ, and is therefore proportional to σ (Figure 1.7). The relationship between the scattering coefficient S and the concentration gives rise to problems, however. The distance between the pigment particles decreases with increasing concentration; consequently there is interaction and hindrance between the light scattered by individual particles, and their scattering power usually falls. The scattering coefficient S is therefore linearly related to concentration only at low concentrations (the Beer’s law region), at higher concentrations it remains below the linear value (Figure 1.8). The concentration dependence of the scattering coefficient can be quantitatively repre-

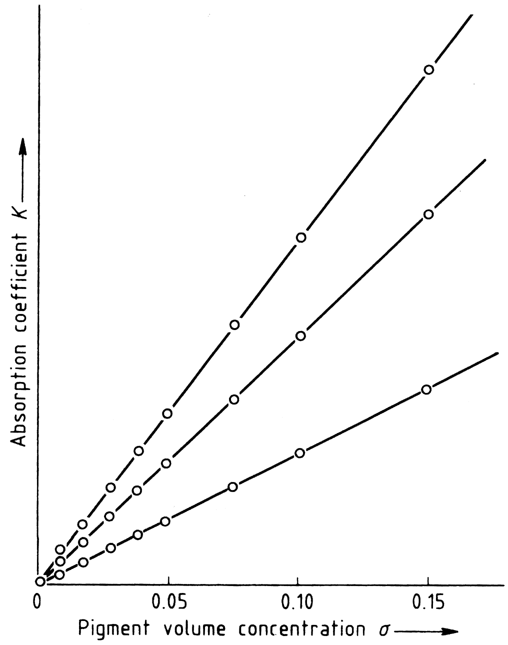

Fig. 1.7 Absorption coefficient *K* for diffuse illumination as a function of the pigment volume concentration for three red iron oxide pigments.

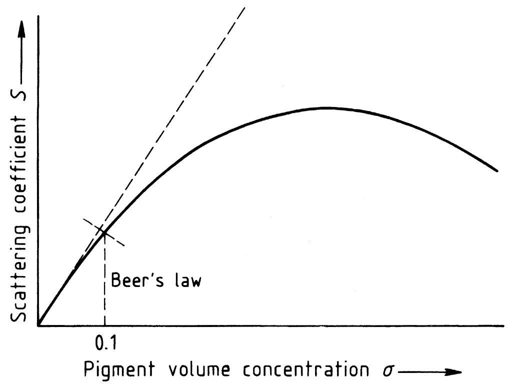

Fig. 1.8 Scattering coefficients as a function of pigment volume concentration.

sented by using empirical formulae [1.32], e.g., there is a linear relationship between S/σ and $\sigma^{2/3}$.

1.3.1.4
Mie's Theory

Mie applied the Maxwell equations to a model in which a plane wave front meets an optically isotropic sphere with refractive index n and absorption index κ [1.33–1.36]. Integration gives the values of the absorption cross section Q_A and the scattering cross section Q_S; these dimensionless numbers relate the proportion of absorption and scattering to the geometric diameter of the particle. The theory has provided useful insights into the effect of particle size on the color properties of pigments.

Scattering is considered first. Here, the crucial parameter α in the Q_A and Q_S formulae is a relative measure of particle size because it is proportional to the particle diameter D and is inversely proportional to the wavelength λ. At a constant wavelength λ and for various relative refractive indices n (i.e., relative to the binder, $n = n_P/n_B$ where n_P and n_B are the refractive indices of the particle and binder, respectively), it gives the relationship between scattering and particle size (Figure 1.9) [1.34]. If, on the other hand, the particle size D is kept constant, α denotes the relationship between the scattering and the wavelength ($1/\lambda$ replaces D on the abscissa of Figure 1.9). The well-marked maxima are typical, and their existence signifies

1. that an optimum particle size must exist with respect to lightening power [1.37], and
2. that for a given particle size, there must be a particular wavelength for maximum light scattering [1.38].

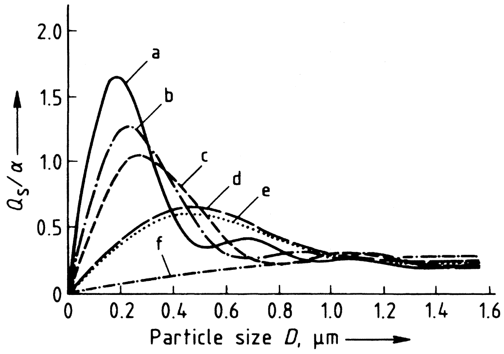

Fig. 1.9 Scattering of white pigments as a function of particle size (λ = 550 nm). (a) Rutile; (b) anatase; (c) zinc sulfide; (d) zinc oxide; (e) white lead; (f) barium sulfate.

The first relationship can be used to predict the optimum particle size of white pigments (Table 1.7). The second relationship explains, for example, how white pigments in gray color mixtures can produce colored undertones as a result of selective light scattering (see Section 1.3.2).

The consequences of Mie's theory for *absorption* (i.e., for tinting strength) are now considered. Calculations from Mie's theory, using the relative refractive index n and the absorption index κ, are given in Figure 1.10 [1.39]. The parameter α on the abscissa can once more be taken as a relative measure of the particle size. The following conclusions may be drawn:

1. For very small particles, the absorption is independent of the particle size, and hence any further reduction in particle size does not produce additional absorption.
2. With increasing absorption index κ, the absorption of very small particles increases.

Tab. 1.7: Refractive indices and optimal particle sizes of some white pigments (λ = 550 nm) calculated according to the van de Hulst formula [1.27]

Pigment	Formula	Mean refractive index		Optimal particle size (relative to binder) D_{opt}, µm
		Vacuum	Binder	
Rutile	TiO_2	2.80	1.89	0.19
Anatase	TiO_2	2.55	1.72	0.24
Zinc blende	α-ZnS	2.37	1.60	0.29
Baddeleyite	ZrO_2	2.17	1.47	0.37
Zincite	ZnO	2.01	1.36	0.48
Basic lead carbonate		2.01	1.36	0.48
Basic lead sulfate		1.93	1.30	0.57

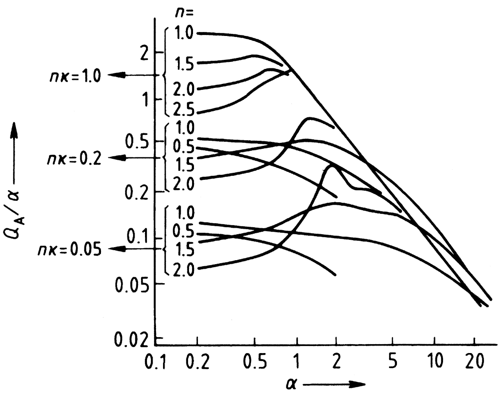

Fig. 1.10 Absorption as a function of particle size.

3. Absorption values for large particles are approximately equal for all relative refractive indices n and absorption indices κ, and decrease hyperbolically.

4. The top curve in Figure 1.10 applies to pigments with a high absorption index κ and low refractive index n (e.g., carbon black) and shows that the optimal particle size lies below a given limit.

5. The lowest curve applies to pigments with a small absorption index κ and high relative refractive index n, as is usually the case with inorganic pigments (e.g., red iron oxide). Here, there is a distinct maximum [1.16, 1.22].

The above relationships (Figure 1.10) show that the optical pigment properties depend on the particle size D and the complex refractive index $n^* = n\,(1 - i\kappa)$, which incorporates the real refractive index n and the absorption index κ. As a result, the reflectance spectrum, and hence the color properties, of a pigment can be calculated if its complex refractive index, concentration, and particle size distribution are known [1.40]. Unfortunately, reliable values for the necessary optical constants (refractive index n and absorption index κ) are often lacking. These two parameters generally depend on the wavelength and, owing to the optical anisotropy of most pigments, on the illuminant and viewing direction. In pigments with a high absorption, the refractive index shows “anomalous dispersion”. Selected values of material of interest are given in Refs. [1.41, 1.42]. Applying these values it has to be remembered that they have been obtained from natural minerals found in the size necessary to make a measurement by ellipsometry possible. The results do not necessarily match the exact values in pigments. Unfortunately, no direct methods exist for determining n and κ in colored inorganic pigments. A good review of the problems occurring when trying to simulate the behavior of pigments in paints with Mie-scattering can be found in e.g. Ref. [1.43]. Refractive indices of inorganic pigment materials are given at selected wavelengths in Tables 1.7 and 1.8. However, these values were measured on large crystals, and not on pigment particles.

Tab. 1.8: Refractive indices of important colored inorganic pigments [1.31a]

Mineral	**Formula**	**Wavelength λ, nm**	**Refractive index**		
			n_ω	n_ε	
			n_α	n_β	n_γ
Bismuth vanadate	$BiVO_4$	670	2.45[a]		
Cobalt blue	$CoAl_2O_4$	(blue)	1.74		
Eskolaite	α-Cr_2O_3	671	2.5[a]		
Greenockite	CdS	589	2.506	2.529	
Goethite	α-FeOOH	589	2.275	2.409	2.415
Hematite	α-Fe_2O_3	686	2.988	2.759	
Carbon[b]	C	578	1.97		
Crocoite	$PbCrO_4$	671	2.31	2.37	2.66
Magnetite	Fe_3O_4	589	2.42		
Red lead	Pb_3O_4	671	2.42		
Ultramarine[c]			1.50		

a) Mean refractive index. **b)** For carbon arc lamps. **c)** Formula see Section 3.5.1.

1.3.2
Color Measurement

1.3.2.1
General

The instruments used for color measurements are nowadays spectrophotometers determining the reflectance of a sample. Three-filter colorimeters, trying to mimic the spectral response of the human eye are now next to obsolete. For applications in the field of uni-pigments photometer illuminating/viewing geometries are standardized as methods A and B, and are designed to suit the individual application (see Section 1.4.2). For standards, see Table 1.1 (“Color Differences, Conditions/ Evaluation...”).

Method A. The geometry d/8 (diffuse illumination, viewing from an angle of 8°) or 8/d (illumination from an angle of 8°, diffuse viewing), including specular reflection, enables total surface reflection and reflection from the interior of a sample to be measured. An amount representing the surface reflection has to be subtracted from the measured value. Thus, measured color variations can be ascribed to differences or changes of the colorants in the interior of the sample.

Method B. Here, color differences in samples are evaluated in almost the same way as in visual evaluation by exclusion of gloss effects. Suitable geometries are d/8, d/0, 8/d, and 0/d with a gloss trap, and 45/0 and 0/45.

After the color of the sample and reference pigments has been measured, color differences are usually calculated by transformation of the $X, Y,$ and Z values into the CIELAB system to calculate color differences. Color measurement results of black and white pigments can be expressed more simply because they only amount to a determination of the relative color undertone. For this, the environment of the reference pigment is divided into eight sectors, these being filled with color names from "red" to "violet". The octant in which the CIELAB color position of the sample is located is found by calculation.

When colored or black systems are reduced with white pigments, an undertone is observed, which is a particle-size effect of the white pigment (see Section 1.3.1). These undertones can be conveniently expressed as CIELAB color differences. The effects can, however, also be measured by using the difference R_Z-R_X between the values obtained with the blue and red reflectometer values. The undertone measured in this way depends on the lightness, and has a maximum at $Y = 41.4$. The lightness of a gray paste should therefore have this value to ensure that undertone differences between white pigments are comparable [1.44, 1.45].

Measured color differences are only true (i.e., significant) when they are not falsified by measuring errors. A *significance* test standard (see Table 1.1, "Color differences, significance") has been developed to check this [1.45]. The numerical value of a color difference must be higher than a critical value, which is statistically calculated using the standard deviation.

Problems concerning the *acceptance* (tolerance) of color differences (e.g., in production quality control or in computer color matching) should also be solved by mathematical statistics [1.22].

The *gloss* of pigmented coatings is not a true pigment property. The pigment can, however, influence the luster quality, mainly via its dispersing properties (see Section 1.5.2). The degree of gloss of a coating can range from high gloss (specular reflection) to an ideally matt surface (complete scattering). *Gloss haze* is due to a disturbance of specular reflection: the reflected objects appear as if seen through a veil, this is caused by halation effects. Gloss retention is discussed in Section 1.4.1; a method of gloss measurement is described in Section 1.4.2. Special problems arise in the measurement of black [1.46] and fluorescent pigments [1.47].

1.3.2.2
Methods of Determination

Lightness. The white pigment powder is compressed in a suitable powder press to give an even, matt surface. The CIE tristimulus value Y is measured with color measuring

Tab. 1.9: CIELAB color differences between two yellow oxide pigments

Full shade (CIELAB, C/2°)	R_x	R_y	R_z	L^*	a^*	b^*	C	h_{ab}
Reference	37.27	29.07	7.95	60.8	8.3	46.5	47.2	79.9°
Test	36.83	28.23	7.93	60.1	10.3	45.3	46.5	77.2°
Color difference:								
test minus reference		$\Delta E_{ab}{}^*$	ΔL^*	Δa^*	Δb^*	$\Delta C_{ab}{}^*$	$\Delta H_{ab}{}^*$	Δh_{ab}
		2.4	−0.7	2.0	−1.2	−0.7	−2.2	−2.7

equipment. For standards, see Table 1.1 (“Lightness”). Apparatus: spectrophotometer, powder press, white standard.

Full Shade. Full-shade systems are media that contain only a single pigment. The color of the full-shade system in an optically infinitely thick (opaque) coating is referred to as full shade. The *mass tone* denotes the color obtained when the pigmented medium is applied as a layer that does not hide the substrate completely (e.g., on a white substrate). Evaluation can be carried out visually or by color measurement. For standards, see Table 1.1 (“Color in full-shade systems”). Apparatus: spectrophotometer.

Color Difference. Figure 1.11 shows the CIELAB color positions of a reference pigment and a test sample: the color difference $\Delta E^*{}_{ab}$, and the derived differences (Section 1.3.1), i.e., lightness difference ΔL^*, chroma difference $\Delta C^*{}_{ab}$, and hue difference $\Delta H^*{}_{ab}$. The color difference of colored pigments in reduction can be similarly determined, including the “color difference after color reduction” which arises when tinting strength matching is carried out (see Section 1.3.3). A number of color difference formulas have been published recently. They typically introduce weighting factors giving the lightness, chroma and hue difference values depending on the location in color space:

- CIE 94, chroma and hue difference depend on the chroma values [1.22].
- CMC (British Standard BS 6923) additionally take into account the dependence on the hue angle.
- CIEDE 2000, (CIE-report 142), extending the color difference formulas by introducing a fourth factor [1.48, 1.49].
- DIN99, trying a different approach: In contrast to the formulas stated above this formula tries to keep the calculation of the color difference as simple as in the CIELAB system while changing the color space to give a better conformance to the visual impression.

The future will tell the acceptance of the new formulas. All formulas can be transformed to give equivalent values in a Euclidean color space [1.50].

Undertone of Near-White Samples and Gray Undertones. The undertone of an almost uncolored sample is the small amount of color by which the color of a sample differs from ideal white or achromatic material. It is described by hue and chroma. The distance and direction of the CIELAB color position of the test sample (a_T^*, b_T^*) from the achromatic position (0, 0) are used to characterize the hue. The *relative undertone* is expressed by the distance and direction between the CIELAB color position of the test sample (a_T^*, b_T^*) and that of the reference pigment (a_R^*, b_R^*). In both cases, the distance is expressed by a figure and the direction by a color name. For standards, see Table 1.1 ("Hue relative to near white specimens"). Apparatus: spectrophotometer for determining the CIE tristimulus values X, Y and Z with standard illuminants D 65 or C. If a computer is available, the color name can be printed out instead of the number of the octant (for example, see Figure 1.12).

Tab. 1.10: Undertone of two nearly white samples (TiO_2 pigments)

	Reflectometer coordinates			**CIELAB color differences**		**Undertone**	
	R_x	R_y	R_z	ΔE_{ab}^*	ΔL^*	Color	Distance, Δs
Reference	94.38	93.62	91.09				
Test	94.34	93.95	92.05	0.55	0.13	blue-green	0.54

1.3.3
Tinting Strength, Lightening Power, and Scattering Power

The *tinting strength* is a measure of the ability of a colorant to confer color to a light-scattering material by virtue of its absorption properties. The *lightening power* can be considered as the tinting strength of a white pigment, and is a measure of its ability to increase the reflectance of an absorbing (black or colored) medium by virtue of its scattering power. Tinting strength is expressed as the mass ratio in which the reference pigment (mass, m_R) can be replaced by the test pigment (mass, m_T) to give the same color quality in a white system. Analogously, lightening power is the mass ratio in which the reference pigment can be replaced by the test pigment to give the same lightness in a colored system. Thus, the same equation defines tinting strength and lightening power:

$$P = (m_R/m_T)_{\Delta Q=\text{const}}$$

where ΔQ = const expresses the tinting strength matching. Both parameters are yield properties; if, for example, tinting strength is doubled, only half the weight of pigment is required. Optical properties can therefore provide information about the economic performance of a colored pigment ("value for money"). Testing of tinting strength and lightening power can be rationalized by means of the Kubelka–Munk theory (see Section 1.3.1).

1.3.3.1
Tinting Strength

Within certain limits, relative tinting strength can be interpreted as the ratio of the absorption coefficients of equal masses of test and reference pigments. This procedure avoids visual matching of the test and reference pigments employed in a previously used method (tinting strength matching). For standards, see Table 1.1 ("Tinting strength, relative"). Materials and apparatus: white paste, spectrophotometer.

In the determination of the tinting strength, specification of the matching between the test and the reference pigments is extremely important [1.51]. Since the criterion used for matching greatly influences the value of the tinting strength, it is not permissible to speak of tinting strength purely and simply. There are as many tinting strength values as there are matching criteria. In the German Standard, the following criteria are permitted:

1. The lowest of the three CIE tristimulus values X, Y and Z.
2. The CIE tristimulus value Y.
3. The depth of shade (see Section 1.4.2.1).

When using commercial colorimeter software it has to be ascertained which formula is used to calculate the tinting strength. As there is no universally accepted definition and the formulas in use result in divergent results under certain circumstances only values with a known tinting strength criteria can be applied. When determining the tinting strength of inorganic pigments, the tristimulus value Y (lightness) is usually used [1.51].

Another standard method uses depth of shade as the matching criterion, but it is employed almost exclusively for testing organic pigments. This method can be applied by means of the "principle of spectral evaluation" (see Section 1.3.4 [1.52], which uses the wavelength-dependent Kubelka–Munk coefficients $S(\lambda)$, $K(\lambda)$ to calculate the match [1.53]. The tinting strength for all other matching criteria can be determined by applying the principle of spectral evaluation. (For tinting strength in cement, see Section 1.5.2.3; for change in tinting strength, see Section 1.5.2.2).

1.3.3.2
Lightening Power

If the gray paste method is used to determine the lightening power (for standards, see Table 1.1, "Lightening power of white pigments"), the concentration at which the white pigment should be assessed has to be agreed between the intended parties in accordance with the type of application [1.54]. This process is especially recommended for the routine testing of pigments because the lightening power, the relative scattering power (see below), and the undertone can be determined with the same gray milling paste of the test pigment.

The method can be rationalized by means of the Kubelka–Munk theory. For standards, see Table 1.1 ("Tinting strength, relative: Photometric").

1.3.3.3
Relative Scattering Power

For standards, see Table 1.1 ("Scattering power, relative"). The relative scattering power S is the ratio of the scattering power S_T of the test white pigment to the scattering power of a white reference pigment S_R [1.55]. It can be determined in two ways:

1. *Black-Ground Method.* The relative scattering power is determined from the tristimulus values Y of the pigmented medium applied in various film thicknesses to black substrates. Compared with the gray paste method, the black-ground method has the advantage that it is not restricted to any particular test medium. Apparatus: spectrophotometer.

2. *Gray Paste Method.* The relative scattering power is determined from the tristimulus values Y of gray pastes. The method has the advantage of being less time consuming than the black-ground method. The results of the two methods are not, however, generally in agreement. Materials and apparatus: black paste, spectrophotometer.

1.3.4
Hiding Power and Transparency

The definition of hiding power is based on a black and white contrasting support upon which the film of coating is applied. The thickness h of the applied film is determined at the point at which the contrasting surface just disappears, as judged by eye. The film thickness (mm), which fulfills this condition, is called the *hiding thickness*. Its reciprocal, the *hiding power* ($\text{mm}^{-1} = \text{m}^2\ \text{L}^{-1}$) is, like tinting strength, an indicator of yield because it gives the area (m^2) that can be covered with 1 L of applied paint. This traditional visual testing method has been improved by the use of a photometer and a colorimetric criterion to evaluate the hiding film thickness, e.g., $\Delta E^*_{ab} = 1$ for equally thick films applied to black and white backgrounds. The method can, however, be further rationalized. In this method only a single coating has to be prepared. The total reflectance spectrum is measured and after measuring the film thickness, the spectral scattering and absorption coefficients $S(\lambda)$ and $K(\lambda)$ are calculated at selected wavelengths (e.g., at intervals of 20 nm) by the Kubelka–Munk method. Once these values are known, the expected reflectance over black and white at the chosen wavelengths of the spectrum can be calculated for a given film thickness. Using the CIE and CIELAB systems, the CIELAB position of a color, which would have this spectrum, is calculated. This provides an iteration method for determining the film thickness at which the hiding power criterion $\Delta E^*_{ab} = 1$ is satisfied [1.52, 1.56, 1.57]. This principle of spectral evaluation [1.52] is the key to handling test methods based on the visual matching of two color samples (see also "Transparency" and "Tinting Strength", Section 1.3.3).

The *transparency* of a pigmented system denotes its ability to scatter light as little as possible. The color change of a transparent pigmented system when applied to a black substrate has to be very small; the lower the color change, the higher is the transparency [1.58]. Measurement of transparency is important for assessing transparent varnishes and printing inks.

1.3.4.1
Hiding Power

The hiding criterion is an agreed color difference between two contrasting areas of a coated contrast substrate. The hiding power can be determined and expressed as D_v (m^2 L^{-1}) or D_m (m^2 kg^{-1}), which give the area (m^2) of the contrasting substrate that can be coated with 1 L or 1 kg, respectively, of the pigmented medium when the hiding criterion is satisfied. Layers of various thicknesses or mass-to-area ratios of the test material are applied to the contrast background. The color difference ΔE^*_{ab} between the two contrasting areas is determined by color measurement on each of the layers. The color difference is plotted against the reciprocal of the film thickness (mm^{-1}) or the reciprocal of the mass to area ratio (m^2 kg^{-1}). The hiding power D_v (m^2 L^{-1}) or D_m (m^2 kg^{-1}) at the hiding criterion (e.g., $\Delta E^*_{ab} = 1$) is then obtained from the diagram (Figure 1.11). For standards, see Table 1.1 ("Hiding power"). Apparatus: spectrophotometer, film thickness measuring equipment.

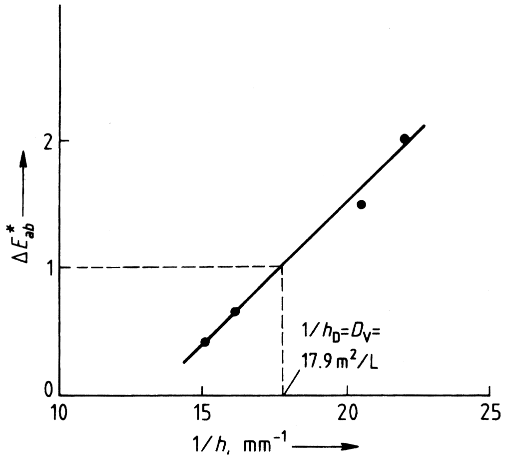

Fig. 1.11 Determination of the hiding power of a yellow iron oxide pigment.

A modern well-equipped color measurement laboratory can use the "principle of spectral evaluation" described above [1.52] to simulate this procedure with a computer. The thickness of the hiding film can then be calculated in advance from the reflectance curves of a single film on a black/white substrate at a known film thickness.

Hiding Power of Achromatic Coatings. Equally thick coatings of the pigmented coating material are applied to a black and white background, and their reflectance measured with a photometer after drying. The hiding power is then calculated from the reflection on black and white substrates and the film thickness. The hiding criterion is $\Delta L^* = 1$, in analogy with that for colored pigments [1.19]. The use of hiding power as a basis for assessing the economy and effectiveness of pigments is described in [1.59]. Apparatus: spectrophotometer, black and white glass plates.

1.3.4.2
Transparency

Transparency is expressed quantitatively as the transparency number. This is defined as the reciprocal of the increase in color difference $\Delta E^*_{ab} = 1$ on a black substrate obtained on increasing the film thickness h of the pigmented medium. The transparency number has the unit mm (= L m^{-2}). It indicates the number of liters of pigmented medium needed to coat 1 m^2 of a black substrate in order to obtain a color difference of $\Delta E^*_{ab} = 1$ relative to this substrate. In a simplified method the transparency number can be determined by evaluating one or two points on the straight part of the ΔE^*_{ab} (h) curve. A computer method is more exact; furthermore, calculations can be made using the spectral "principle of spectral evaluation." For standards, see Table 1.1 ("Transparency").

1.4
Stability Towards Light, Weather, Heat, and Chemicals

1.4.1
Fundamental Aspects [1.60]

Many pigmented systems show typical color or structural changes when subjected to intense radiation or weathering [1.61]. The best known of these are yellowing [1.62], chalking, and loss of gloss. These processes involve photochemical reactions in which the pigment can act as a catalyst or in which the pigment itself undergoes chemical changes.

Inorganic pigments are chemically very stable and are classed as one of the most stable coloring matters. This is especially true for oxide pigments, which often have a highly protective effect on the substrate [1.63]. Apart from the purely mechanical stabilization imparted by the pigment, this protective effect can give a coating an increased economic advantage. On the other hand, sulfide pigments can be oxidized by the atmosphere to form sulfates, which can be washed away by rain [1.64].

The photochemical processes that take place when TiO_2-containing coatings undergo chalking have been elucidated [1.65]. The shorter wavelength radiation of sunlight acts on rainwater and atmospheric oxygen to form extremely reactive radicals ($\bullet OH$, $HO_2\bullet$) that cause deterioration of the coating matrix by oxidative attack. Titanium dioxide pigments may be stabilized by reducing the number of radical-producing hydroxy groups on the surface of the TiO_2 particles (e.g., by doping with zinc oxide). Alternatively, coatings of oxide hydrates are produced by aftertreatment of the pigment surface to give "reaction walls" on which the radicals are destroyed [1.66].

Continuous breakdown of the binder leads to the loss of gloss. Surface gloss gives an attractive appearance and is usually desired, it is obtained by ensuring that the pigment particles are well dispersed. The stability of gloss to weathering is therefore of great importance. If breakdown of the binder is so extensive that the pigment may be loosened, *chalking* takes place. Chalking is defined as loosening of pigment or

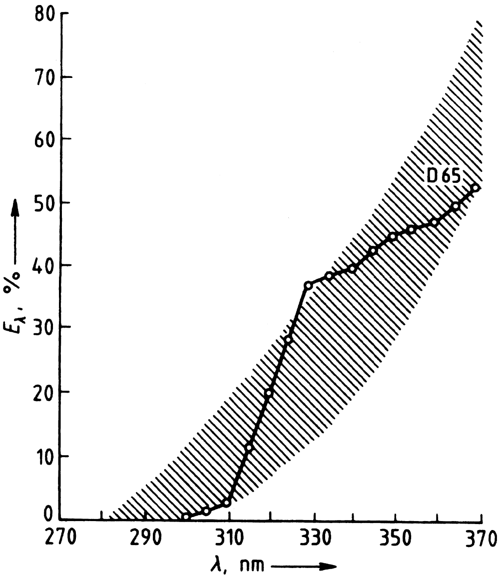

Fig. 1.12 Spectral energy distribution of daylight phase D 65 with permitted range of deviation (shading).

extender particles following destruction of the binder at the surface. For standards, see Table 1.1 ("Coating materials").

Resistance to light and weather generally depend on the chemical composition, structure, defects, particle shape and size, and concentration of the pigment [1.67]. However, these properties also depend on the medium in which the pigment is used. Testing is carried out by open-air weathering, accelerated weathering, and chemical test methods.

Accelerated weathering is carried out in special weathering devices (e.g., Weatherometer, Xenotest), which simulate exposure to sunlight and periods of rain. The spectral composition of the light used (Figure 1.12) should match the "global radiation" in temperate latitudes (global radiation denotes the sum of the direct solar radiation and indirect radiation from the sky). However, accelerated tests only allow limited conclusions to be drawn about light and weather resistances because it is not possible to accurately simulate all climatic conditions, their combinations and sequences, or sudden changes. Even so, natural weathering tests are not without problems: weather cannot be standardized, and a "uniform" weather therefore does not exist [1.68, 1.69]. Weathering results, even from successive years, can thus vary considerably [1.70]. Weather also varies with the geographical coordinates. For standards, see Table 1.1 ("Climates: Normalized"); the earth is classified into climatic regions and weathering adjustment scales exist [1.71].

None of the chemical methods (e.g., mandelic acid or methanol test) gives a perfect indication of weather resistance. Most of them only measure partial qualities of the photochemical reactivity [1.72].

The oxide pigments have the highest *heat stability*, followed by the sulfide pigments, which can even be used in enamels, and glass melts (e.g., cadmium pigments). The oxide hydroxides and carbonates are less heat stable. Thermal stability is of great importance for modern coating techniques (e.g., for stoving finishes and other products requiring high temperatures). The heat resistance of a pigment primarily depends on the binder and the duration of heating. It is conveniently determined by observing hue changes in the pigmented coating system after a defined heat treatment, e.g., with white coatings yellowing occurs. For standards, see Table 1.1 ("PVC"). The *chemical resistance* of inorganic pigments, especially oxide pigments, is in general very high [1.73]. Other fastness properties such as overspray fastness, fastness to blooming, and fastness to plasticizers are of more relevance to organic pigments. For corrosion inhibiting (anticorrosive) pigments, see Section 5.2.

1.4.2
Test Methods

1.4.2.1
Light Stability

Accelerated Tests

Light stability is a material property. It is defined as the resistance of coatings towards changes caused by the action of global radiation (daylight phase: standard illuminant D 65), possibly in the presence of moisture. In coatings, light and moisture can lead to chalking and changes in gloss and color. For standards, see Table 1.1 ("Light stability"). Apparatus: testing cabinets, equipment for wetting the test plates, equipment for producing airflow.

Evaluation of Color Changes (see Section 1.3.2)

Color changes are differences in lightness, chroma, and hue such as exist between identical samples with different histories. Evaluation methods are particularly suitable for the determination and evaluation of color changes that occur following physical and chemical stresses on pigmented materials. The CIE tristimulus values X, Y, and Z of the samples or of different test locations on a sample are determined with a colorimeter. The CIELAB color difference is calculated for each sample or test location from the tristimulus values before and after the stress (see Section 1.3.2). Apparatus: spectrophotometer.

Standard Depth of Shade

The depth of shade is a measure of the intensity of a color sensation. It increases with increasing chroma and generally decreases with increasing lightness. The colorfastness of colorations (e.g., textile dyeing) is dependent on depth of shade; the fastness properties of pigments or pigmented systems must therefore be tested at a predetermined depth of shade. This standard method therefore ensures that samples with standard depths of shade are used to determine the fastness properties of pigments or pigmented systems [1.74, 1.75]. For standards, see Table 1.1 ("Standard depth of shade"). Apparatus: spectrophotometer with gloss trap. (For light stability in cement, see Section 1.5.2.3).

1.4.2.2
Weather Resistance

The empirical tests described below determine the chalking and weathering differences between two pigments, but do not always give the true differences. Other test methods have therefore been developed, e.g., determination of mass losses on weathering (gravimetric test) [1.65].

Accelerated Tests

Weather resistance in an accelerated test is defined as the resistance of plastics towards changes caused by simulated open-air weathering (simulation of global radiation by means of filtered xenon arc radiation and periodic rain). After the weathering (measured by the product of intensity and duration), defined properties of the test sample are compared with those of an identical unweathered sample. Properties should be considered which are of practical importance, such as color or surface properties. For standards, see Table 1.1 ("Weathering in apparatus"). Apparatus: test chamber, rain and air humidification equipment, airflow equipment, radiation measuring equipment.

Degree of Chalking

The degree of chalking of a coating is measured by the quantity of loose pigment particles. It may be determined by three methods:

1. *Kempf Method.* For standards, see Table 1.1 ("Chalking degree: Kempf method"). Water-treated photographic paper is applied to the coating (with the humid gelatin side facing the coating surface) and pressed by means of a special stamp device. The gelatin coating picks up loose pigment particles that are not attached to the binder. The degree of chalking is judged visually (for scale of measurement see Table 1.1, "Test evaluation"). See also Section 1.2.2. Apparatus: Kempf stamp equipment.

2. *Adhesive Tape Method.* For standards, see Table 1.1 ("Chalking degree; Adhesive tape method"). Loose pigment particles are picked up by transparent adhesive tape. The degree of chalking is determined from a reference scale (see Table 1.1, "Test Evaluation" and Section 1.2.2) or by using a comparative scale that is agreed upon by the interested parties.

3. *Photographic Methods.* For standards, see Table 1.1 ("Chalking degree: Photographic method"). Chalking prints on paper are compared with photographic standards.

Assessment of Gloss

Gloss is not a purely physical quantity; it is also dependent on physiological and psychological factors. The usefulness of measured reflectance values lies in the possibility of detecting surface changes of the test sample and observing them over a long period. These changes can be produced by weathering, abrasion, and similar causes of surface wear, or by the method used to produce the surface. For standards, see Table 1.1 (“Reflectometer”). Apparatus: reflectometer with incident light angles of 2°, 6°, or 8°.

Effects of Humid Climates

The specimen is exposed to warm air saturated with water vapor, with or without intermittent cooling to room temperature. The test is very suitable for assessing the corrosion resistance of metals, protective coatings, and composite materials in buildings. For standards, see Table 1.1 (“Climates: Containing evaporated water”). Apparatus: Kesternich condensation equipment.

1.4.2.3
Heat Stability [1.76]

Measured values of the heat stability of pigments depend on the type and duration of the heat applied, and also on the binder used. Low thermal stability in white coatings leads to yellowing, even when the unpigmented binder is resistant to yellowing. With colored coatings, changes in the hue of the pigmented binder can be measured colorimetrically (see Section 1.3.2). Standards only exist for special systems (e.g., hard and soft PVC; and cement, see Section 1.5.2.3). Thermal resistances of pigments are customarily quoted at two temperatures: 1. the maximum temperature at which the hue remains stable, and 2. the temperature at which a defined hue change is observed. For standards, see Table 1.1 (“Heat stability” and “Coloration of building materials”).

1.4.2.4
Fastness to Chemicals [1.76]

General Chemical Resistance

This can be classified as short-, medium-, or long-time resistance. Changes in the coating are assessed visually. For standards, see Table 1.1 (“Chemical resistance”). Apparatus: film thickness measuring equipment.

Resistance to Water in Sulfur Dioxide-Containing Atmospheres

For standards, see Table 1.1 (“Corrosion testing; SO_2” and “SO_2 resistance”). General conditions are standardized for exposing samples to a varying climate where water condenses in the presence of sulfur dioxide, so that tests in different laboratories give comparable results. The test allows rapid detection of defects in corrosion-inhibiting systems. Furthermore, a method for determining the colorfastness of pigments in binders in the presence of sulfur dioxide is also prescribed. The test is carried out simultaneously on ten identical samples and consists of three cycles. Apparatus: condensation equipment.

Salt Spray Fog Test with Sodium Chloride Solutions

The sample is sprayed continuously with a 5% aqueous sodium chloride solution. There are three variations of the test: the salt spray fog test, the acetic acid salt spray test, and the copper chloride-acetic acid salt spray test. For standards, see Table 1.1

("Corrosion testing: NaCl"). Materials and apparatus: spray chamber, test solutions (5% NaCl solutions).

Resistance to Spittle and Sweat

This test indicates whether a pigment on a child's colored toy is likely to be transferred to the mouth, mucous membranes, or skin during use. Strips of filter paper are wetted with $NaHCO_3$ and NaCl solutions and pressed against the test samples. The discoloration of the paper is judged visually. For standards, see Table 1.1 ("Spittle/sweat resistance").

1.5

Behavior of Pigments in Binders

1.5.1

Fundamental Aspects [1.77, 1.78]

A pigment–binder dispersion is a suspension before it is dried; after drying it is a solid sol. In pigment-binder systems, the concepts and laws of colloid chemistry therefore apply. The dispersing of pigments and extenders in binders is an extremely complex process consisting of a series of steps that can be interlinked [1.77]. Dispersing involves the following steps:

1. *Wetting.* Removal of the air from the surface of the pigment particles and formation of a solvate layer [1.79, 1.80].
2. *Disintegration.* Breaking up of pigment agglomerates with external energy (e.g., by dispersing equipment).
3. *Stabilization.* Maintenance of the disperse state by creating repulsive forces between the particles (e.g., by coating them with solvate layers). These forces must be greater than the van der Waals attraction forces [1.81] that cause flocculation [1.82, 1.83].

The degree of dispersing usually has a large influence on the properties of the coating system [1.84, 1.85]. Some of these properties depend strongly on the degree of dispersing, and are therefore used to measure dispersibility. For standards, see Table 1.1 ("Ease of dispersion"). Examples are viscosity (pigment-binder dispersions always show non-Newtonian behavior properties before drying) and color properties, especially hue, tinting strength, gloss, and gloss haze [1.86] (see Sections 1.3 and 1.4).

In many systems, tinting strength depends so highly on the degree of dispersing that the rate of tinting strength development can be taken as a direct measure of dispersibility [1.87–1.90] (see Section 1.5.2.2). The numerical values of the half-life times (characterizing the dispersibility) and of the increases in strength (characterizing the strength potential) depend on the binder and the dispersing equipment used.

In systems where different pigments are combined (e.g., white and colored pigments), segregation effects can occur which change the optical appearance (flooding

[1.91]). Flooding can be counteracted by preflocculation of the pigments with suitable gelling agents, and in some cases by addition of extenders. In solvent-containing systems with several pigments, but also in full-shade systems, color changes (rub-out effect) can take place due to flocculation, especially if the systems are subjected to mechanical stress during application and drying. The flocculation tendency can be determined by means of the "rub-out test".

1.5.2
Test Methods

1.5.2.1
Pigment–Binder Interaction

Oil Absorption

The oil absorption gives the mass or volume of linseed oil required to form a coherent putty-like mass with 100 g pigment under specified conditions. The mixture should just not smear on a glass plate. For standards, see Table 1.1 ("Oil absorption"). Materials and apparatus: rough glass plate, spatula with steel blade, raw linseed oil.

Binder Absorption, Smear Point, and Yield Point

[1.92] Smear point and yield point are used to determine the binder needed to formulate a suitable millbase for grinding by dissolvers, roll mills, ball mills, attritors, sand mills, and pearl mills. The amount of binder is given in volume or mass units. Apparatus: rough glass plate, spatula with steel blade.

Viscosity

Viscosity is a useful parameter for coatings applied by brushing. It is determined by measuring the torque applied to a rotating cylinder or disk in or on the surface of a suspension. This method is applicable to Newtonian and non-Newtonian systems. In non-Newtonian suspensions, the apparent viscosity is obtained by dividing the shear stress by the shear rate. The viscosities provide information about the force required in the initial brushing phase of a coating. For standards, see Table 1.1 ("Viscosity"). Apparatus: cone/plate or rotating cylinder viscometer.

Fineness of Grind

fineness of grind The grind gauge (grindometer) consists of a steel block with a groove. The depth of the groove at one end is approximately twice the diameter of the largest pigment particle, and decreases continuously to zero at the other end. The sample is placed at the deep end of the groove and drawn to the other end with a scraper. The depth at which a large number of particles become visible as pinholes or scratches on the surface of the pigment–binder system is read off from a scale graduated in micrometers. For standards, see Table 1.1 ("Fineness of grind"). Apparatus: Hegman's grindometer gauge (block and scraper).

1.5.2.2
Dispersing Behavior in Paint Systems

Low-Viscosity Media

The time that is required to produce a homogeneous suspension of particles in the dispersion medium using an oscillatory shaking machine equipped with several containers is measured. Not only can small quantities of the millbase with the same composition be tested (as with other types of apparatus), but various millbases can also be tested under the same conditions. A low-viscosity alkyd resin system of the stoving or oxidatively drying type can be used as a test medium. For standards, see Table 1.1 ("Ease of dispersion: Oscillatory shaking machine").

High-Viscosity Media (Pastes)

The dispersion properties are determined with an automatic muller. The advantage is that small amounts of material can be simply tested under reproducible conditions. For standards, see Table 1.1 ("Ease of dispersion: Automatic muller").

Development of Fineness of Grind

The quantity measured is the dispersing effect needed to achieve a given fineness of grind. Samples of the product are taken at various stages of the dispersion process and the fineness of grind is determined with a grindometer gauge. The method is used to compare diverse millbase material types of dispersing equipment, or dispersing methods used with the same pigment. For standards, see Table 1.1 ("Fineness of grind").

Change in Tinting Strength, Half-Life Times, and Increase in Strength

For standards see Table 1.1 ("Change in strength"). Dispersibilities of pigments may be compared by means of their dispersing resistance; dispersing equipment may be characterized by means of dispersing effects. Measurement can be based on the determination of half-life times in relation to the final tinting strength. The increase in strength, however, only gives the difference between the initial and final tinting strength [1.90]. Half-life times are functions of the dispersing rate. They are only valid for a given combination of dispersing equipment, dispersing process, and medium. Samples are taken from the millbase at specified stages in the dispersing process and mixed with a white paint based on the same binder material, or with a compatible white paste. The tinting strength is then determined (see Section 1.3.3) and a graph is drawn; development of tinting strength is plotted against the dispersion stages (Figure 1.13) [1.93].

Making use of equations used in the description of the kinetics of chemical reactions a quantitative description of the dispersion process can even be achieved [1.22] by defining three types of size reduction of large particles:

- against themselves (2nd order reaction)
- against the vessel walls and grinding bodies (1st order reaction)
- against the small particles already produced (interaction).

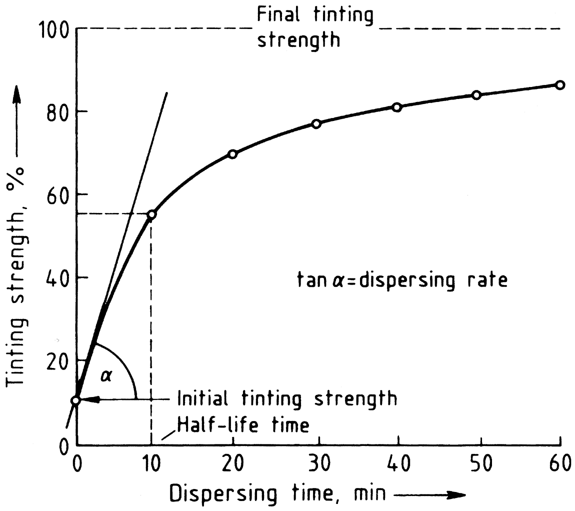

Fig. 1.13 Change in tinting strength as a function of dispersing time.

Pigment Volume Concentration (PVC) and Critical Pigment Volume Concentration (CPVC)
The pigment volume concentration (σ) is the fractional volume of pigment in the total solids volume of the dry paint film:

$$\sigma = \frac{V_\mathrm{P}}{V_\mathrm{P} + V_\mathrm{b}}$$

where V_P is the pigment volume and V_b the binder volume. The *PVC* [1.94] is determined by separating the pigment fraction from a weighed paint sample by, for example, extracting the (liquid) binder with suitable organic solvents or solvent mixtures (sometimes using a centrifuge) or using combustion methods (sometimes including fuming with sulfuric acid) and analysis of the residue [1.95].

Under *CPVC* conditions, the pigment particles are at a maximum packing density, and the interstices are completely filled with binder. With smaller amounts of binder, the interstices are incompletely filled. The *CPVC* thus represents a pigment concentration boundary at which abrupt changes in the properties of the film occur.

The methods of determining the *CPVC* [1.96] are divided into two groups:

1. Methods based on the observation of a sudden change in properties in a series of *PVC*s (e.g., ion permeability, permeability to water vapor, color, gloss stability after coating with a silk-luster paint).
2. Methods based on the experimental production of the dense pigment packing typical of *CPVC*, e.g., by means of oil absorption, filtration, vacuum filtration, or by measuring the volume of the supercritical film.

Measurement of Deposit

Common methods used to measure sediments are manual testing, sedimentation balance, radioactive methods, dipping of bodies, and probe tools.

The special measuring equipment known as the Bayer system [1.97] can test for deposits with great accuracy and good reproducibility. The force acting on a needle probe which penetrates into the coating material from above is measured.

1.5.2.3
Miscellaneous Pigment–Binder Systems

Plastics

Specifications for thermoplastics are given in Table 1.1 (“Thermoplastics”). Specifications for poly(vinyl chloride) are also listed (“PVC”). These specifications include methods for producing basic mixtures for testing pigments in PVC and for specimen preparation. A method is described for determining bleeding, i.e., the migration of coloring matter into a material in contact with the sampling equipment. Special procedures are also included for the determination of heat stability and increase in strength caused by cold rolling.

Building Materials For standards, see Table 1.1 (“Coloration of building materials”). The following tests are prescribed for assessing the suitability of a pigment for coloring cement and lime-bonded building materials:

- Relative tinting strength
- Colorfastness in cement
- Colorfastness in lime
- Lightfastness
- Heat stability
- Influence of the pigment on the hardness of the building material
- Influence of the pigment on setting properties

Paper and Board

For standards, see Table 1.1 (“Opacity” and “Transparency”). Methods of measurement are specified for the reflectance of paper and board (nonfluorescent), and the opacity or transparency of paper (to measure the transmitted light).

References

1 Smith, H. M. (Ed.), *High Performance Pigments*, Wiley-VCH, Weinheim, **2002**

2 Jansen, M., Letschert, H. P., *Nature* 404 (**2000**), p. 980

3 Jansen, M., Letschert, H. P., Speer, D. (Cerdec AG) EP 0627382 (**1994**)

4 Berte, J. N., in *High Performance Pigments* (Ed.: H. M.Smith), Wiley-VCH, Weinheim, **2002**, p. 27

5 Pfaff, G., *Phänomen Farbe* 22 (**2002**), p. 19

6 *Kirk-Othmer*, 3rd edn., 17, 788. Kittel, J., Spille, J., Lehrbuch der Lacke und Beschichtungen, Band 5: Pigmente, Füllstoffe und Farbmetrik, S. Hirzel Verlag, Stuttgart, **2003**

7 Rechmann, H., Sutter, G., *Farbe + Lack* 82 (**1976**), p. 793

8 Gall, L., *Farbe + Lack* 81 (**1975**), p. 1015

9 Fritzsche, E., *Farbe + Lack* 80 (**1974**), p. 731

10 Völz, H. G., *DEFAZET – Dtsch. Farben Z.* 28 (**1974**), p. 559

11 Hund, F., *Farbe + Lack* 73 (**1967**), p. 111

12 Kämpf, G., *Farbe + Lack* 71 (**1965**), p. 353.

13 Honigmann, B., Stabenow, J., in: *Congress FATIPEC VI, 1962*, Verlag Chemie, Weinheim, **1963**, p. 89

14 Völz, H. G., *Farbe + Lack* 90 (**1984**), pp. 642, 752

15 Allen, T., *Particle Size Measurement*, Vol. 1 and 2, 5th edn., Kluwer, Dordrecht, **1997**

16 Kindervater, F., in *Congress FATIPEC XII*, 1974, Verlag Chemie, Weinheim, **1974**, p. 399

17 Keifer, S., Wingen, A., *Farbe + Lack* 79 (**1973**), p. 886

18 Judd, D. B., Wyszecki, G., *Color in Business, Science and Industry*, J. Wiley & Sons, New York, **1975**

19 Völz, H. G. *Prog. Org. Coat.* 1 (**1973**), p. 1

20 Berns, R. S., *Billmeyer and Saltzman's Principles of Color Technology*, Wiley Interscience, New York, **2000**

21 Völz, H. G., *Angew. Chem., Int. Ed. Eng.* 14 (**1975**), p. 655

22 Völz, H. G., *Industrial Color Testing. Fundamentals and Techniques*, Wiley-VCH, Weinheim, **2001**

23 Berger-Schunn, A., *Practical Color Measurement: A Primer for the Beginner, a Reminder for the Expert*, Wiley Interscience, New York, **1994**

24 Wyszecki, G., Stiles, W. S. *Color Science*, Wiley Interscience, New York, **2000**

25 *Colour Physics for Industry*, (Ed.: R. McDonald) Society of Dyers and Colourists, **1997**

26 *CIE Technical Report* 116 (**1995**)

27 Kubelka, P., Munk, F., *Z. Tech. Phys.* 12 (**1931**), p. 539

28 Kubelka, P., *J. Opt. Soc. Am.* 38 (**1948**), p. 448

29 Gall, L., *Farbe + Lack* 80 (**1974**), p. 297

30 Hoffmann, K., *Farbe + Lack* 80 (**1974**), pp. 118, 221

31 Billmeyer, Jr., F. W., Abrams, R. L., Phillips, D. G., *J. Paint Technol.* 45

(**1973**) pp. 23, 31; 46 (**1974**), p. 36; 48 (**1976**), p. 30

32 Völz, H. G., *Ber. Bunsen-Ges. Phys. Chem.* 71 (**1967**), p. 326

33 Mie, G. *Ann. Phys.* 25 (**1908**), p. 377

34 van de Hulst, H. C., *Light Scattering by Small Particles,* J. Wiley & Sons, New York, **1957**

35 Kerker, M., *The Scattering of Light and other Electromagnetic Radiation,* Academic Press, New York, **1969**

36 Bohren, C. F., *Absorption and Light Scattering by Small Particles,* J. Wiley & Sons, New York, **1983**

37 Jaenicke, W., *Z. Elektrochem.* 60 (**1956**), p. 163

38 Völz, H. G., *DEFAZET – Dtsch. Farben Z.* 31 (**1977**), p. 469

39 Brockes, A., *Optik (Stuttgart)* 21 (**1964**), p. 550

40 Brossmann, R., in *Internationale Farbtagung "Color 69",* vol. II, Verlag Musterschmidt, Göttingen, **1969**, p. 890

41 *Handbook of Optical Constants of Solids* (Ed.: E. D. Palik), Academic Press, Boston, **1985**

42 Querry M. R., *Optical Constants,* Government Report, CRDC-CR-85034, Kansas City, Missouri, MO64110

43 Bohren, C. F., Saltzman, G. C., Palmer, B. R., Stamatakis, P., A Multiple Scattering Model for Opacifying Particles in Polymer Films, *J. Coat. Technol.* 61, 779 (**1989**), p. 41

44 Völz, H. G., *Farbe + Lack* 76 (**1970**), p. 9; Keifer, S., *Farbe + Lack* 81 (**1975**) p. 289

45 Völz, H. G., *Farbe + Lack* 88 (**1982**), pp. 264, 443

46 Schumacher, W., in *Congress FATIPEC XIII. 1976,* EREC, Paris, **1977**, p. 582

47 Finus, F., *DEFAZET – Dtsch. Farben Z.* 28 (**1974**), p. 494

48 Cui, G., Luo, M. R., Rigg, B., *Col. Res. Appl.* 26 (**2001**), No. 5, p. 340

49 Fairchild, M. D., Johnson, G. M., *Col. Res. Appl.* 28 (**2003**), No. 6, p. 425

50 Völz, H. G., *DIE FARBE* 44 (1998), H. 1–3, 1 and H. 4–6, 97, 45 (**1999/2000**), H. 1–3, 1 and 4–6, 187; *Col. Res. Appl.*, in press

51 Keifer, S., Völz, H. G., *Farbe + Lack* 83 (**1977**), pp. 180, 278

52 Völz, H. G., *Progr. Org. Coat.* 15 (**1987**), p. 99

53 Gall, L., in *Congress FATIPEC IX, 1968,* Chimie des Peintures, Brussels, **1969**, p. 34

54 Keifer, S., *Farbe + Lack* 82 (**1976**), p. 811

55 Vial, F., in *Congress FATIPEC XII, 1974,* Verlag Chemie, Weinheim, **1975**, p. 159

56 Gall, L., *Farbe + Lack* 72 (**1966**), p. 955

57 Gall, L., *Farbe + Lack* 72 (**1966**), p. 1073

58 Völz, H. G., *DEFAZET – Dtsch. Farben Z.* 30 (**1976**), pp. 392, 454

59 Keifer, S., Deckvermögen, in *Anorganische Pigmente für Anstrich- und Beschichtungsstoffe,* Bayer, Leverkusen, **1973**, Section 3.3.2

60 Völz, H. G., in *Lehrbuch der Lacke und Beschichtungen,* Ed. H. Kittel, Vol. II, Verlag W. A. Colomb, Berlin, **1974**, p. 22

61 Brugger, K., Jehle, N., in *Congress FATIPEC XIII, 1976,* EREC, Paris, **1977**, p. 15

62 Epple, R., Englisch, A., in *Congress FATIPEC XII.* 1974, Verlag Chemie, Weinheim, **1975**, p. 241

63 Kämpf, G., Papenroth, W., *Farbe + Lack* 83 (**1977**), p. 18

64 Grassmann, W., *Farbe + Lack* 66 (**1960**), p. 67

65 Völz, H. G., Kämpf, G., Fitzky, H. G., Klaeren, A., *ACS Symp. Ser.* 151 (**1981**) p. 163

66 Völz, H. G., Kämpf, G., Fitzky, H. G., *Farbe + Lack* 78 (**1972**), p. 1037

67 Bohmann, Th., in *Congress FATIPEC X, 1970,* Verlag Chemie, Weinheim, **1971**, p. 123

68 Papenroth, W., Koxholt, P. *Farbe + Lack* 82 (**1976**), p. 1011

69 Freier, H. J., *Farbe + Lack* 72 (**1967**), p. 1127

70 Rechmann H. et al., in *Congress FATIPEC X,* 1970, Verlag Chemie, Weinheim, **1971**, p. 3

71 Sadowski, F., *Farbe + Lack* 80 (**1974**), p. 29

72 Keifer, S., in *Congress FATIPEC XII,* 1974, Verlag Chemie, Weinheim, **1975**, p. 517

73 Kresse, P., in *Congress FATIPEC XIII,* 1976, EREC, Paris, **1977**, p. 346

74 Gall, L., *DEFAZET – Dtsch. Farben Z.* 30 (**1976**), p. 127

75 Finus, F., Fleck, W., *DEFAZET – Dtsch. Farben Z.* 28 (**1974**), p. 153

76 Lincke, G., *Einfärben Kunststoffe,* VDI-Verlag, Düsseldorf, **1975**, p. 135

77 Bialas, D., in *Lehrbuch der Lacke und Beschichtungen,* Ed. H. Kittel, Vol. II, Verlag W. A. Colomb, Berlin, **1974**, p. 486

78 Kämpf, G., *DEFAZET – Dtsch. Farben Z.* 31 (**1977**), p. 347

79 Joppien, G. R., *Farbe + Lack* 81 (**1975**), p. 1102

80 Marwedel, G., *Farbe + Lack* 82 (**1976**), p. 789

81 Herrmann, E., *DEFAZET – Dtsch. Farben Z.* 29 (**1975**), p. 116

82 Keifer, S., *Farbe + Lack* 79 (**1973**), p. 1161

83 Kresse, P., *DEFAZET – Dtsch. Farben Z.* 28 (**1974**), p. 459

84 Miele, M., *Farbe + Lack* 81 (**1975**), p. 495

85 Zosel, A., in *Congress FATIPEC XIII,* 1976, EREC, Paris, **1977**, p. 653

86 Bohmann, Th., in *Congress FATIPEC IX,* 1968, Chimie des Peintures, Brussels, **1969**, p. 47

87 Schmitz, O. J., in *Congress FATIPEC XII,* 1974, Verlag Chemie, Weinheim, **1975**, p. 511

88 Gall, L., Kaluza, U., *DEFAZET – Dtsch. Farben Z.* 29 (**1975**), p. 102

89 Klaeren, A., Völz, H. G. *Farbe + Lack* 81 (**1975**), p. 709

90 Völz, H. G., *Farbe + Lack* 96 (**1990**), p. 19

91 Kaluza, U., *DEFAZET – Dtsch. Farben Z.* 27 (**1973**), pp. 427–439; 28 (**1974**), p. 449

92 Gardner, H. A., Sward, G. G., *Paints, Varnishes, Lacquers and Colors,* Gardner Laboratory, Inc., 12th edn., Bethesda, **1962**, p. 251

93 Kaluza, U., *Farbe + Lack* 80 (**1974**), p. 404

94 Gardner, H. A., Sward G. G., in Ref. [1.92], p. 501

95 Stock, E.. *Analyse der Körperfarben,* Wissenschaftl. Verlags GmbH, Stuttgart, **1953**

96 Kresse, P., *Farbe + Lack* 71 (**1965**), p. 178

97 Papenroth, W., Kox, K. *DEFAZET – Dtsch. Farben Z.* 28 (**1974**), p. 311