Industrial Inorganic Pigments
Edited by G. Buxbaum and G. Pfaff

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Third, Completely Revised Edition

Edited by
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Contents

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Preface to the Third Edition

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

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

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

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

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

Krefeld and Darmstadt — *G. Buxbaum,*
December 2004 — *G. Pfaff*

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Preface to the Second Edition

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

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

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

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

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

Preface to the Second Edition

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

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

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1
Introduction

1.1
General Aspects

1.1.1
History, Classification, Standards

1.1.1.1
Definition

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

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

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

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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 ϱ_{T}	density of a particle
Particle size distribution	statistical representation of the particle size of a particulate material
Distribution density	gives the relative amount of a particulate material in relation to a given particle size diameter. Density distribution functions must always be normalized
Cumulative distribution	normalized sum of particles that have a diameter less than a given particle size parameter
Fractions and class	a fraction is a group of particles that lies between two set values of the chosen particle size parameter that limits the class
Mean value and other similar parameters	the mean values of particle size parameters can be expressed in many ways, some values are used frequently in practice
Distribution spread	parameter for characterizing the nonuniformity of the particle size

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.

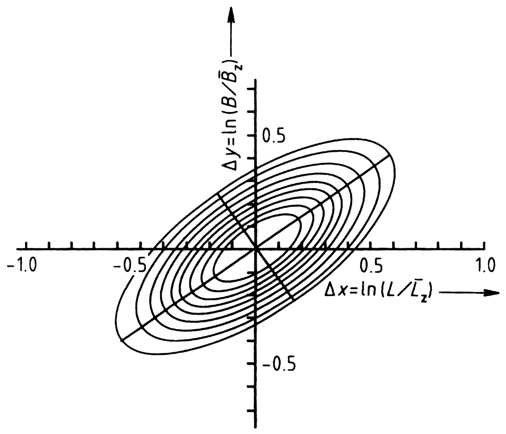

Fig. 1.2 Standard deviation ellipses of a logarithmic normal distribution (yellow iron oxide pigment). $\bar{L}_z$, $\bar{B}_z$ = median of *L*, *B*.

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

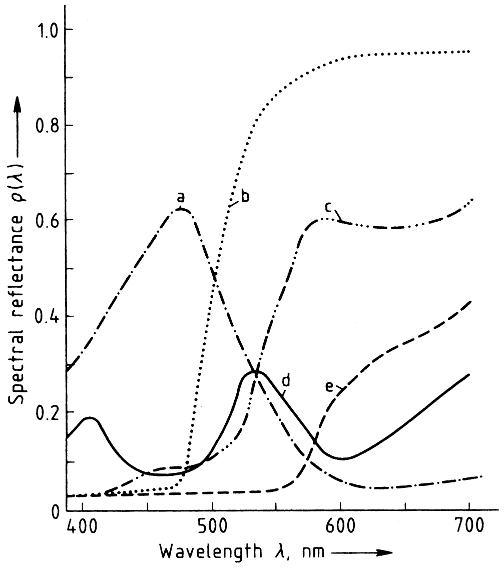

Fig. 1.3 **Figure 1.3** Spectral reflectance curves of some inorganic pigments in paints. (a) Manganese blue; (b) CdS; (c) α-FeOOH; (d) α-Cr_2O_3; (e) α-Fe_2O_3.

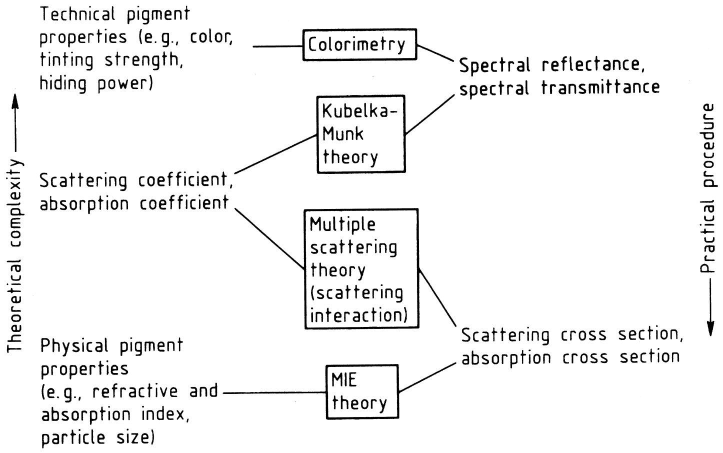

Fig. 1.4 The relationships between the optical properties of pigments and their theoretical basis.

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

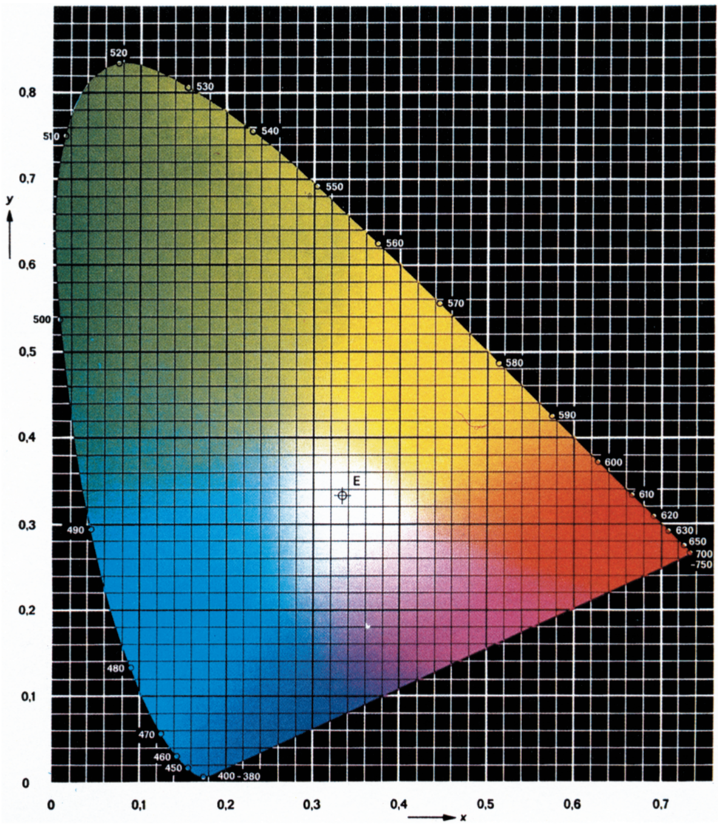

Fig. 1.5 CIE 1931 *xy* – chromaticity diagram for illuminant D 65.

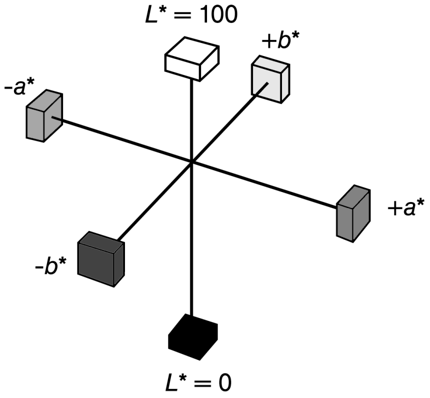

Fig. 1.6 Representation of the CIELAB system.

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^*:

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

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

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

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-

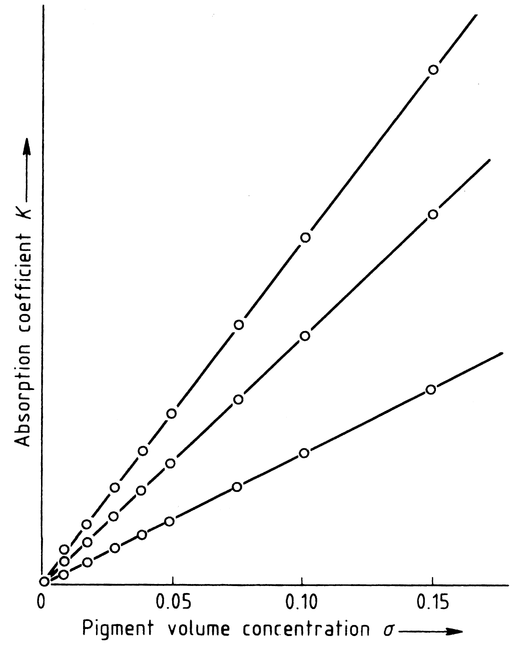

Fig. 1.7 Absorption coefficient *K* for diffuse illumination as a function of the pigment volume concentration for three red iron oxide pigments.

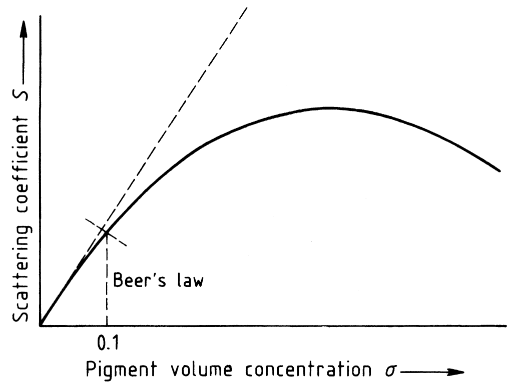

Fig. 1.8 Scattering coefficients as a function of pigment volume concentration.

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 (l/λ 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].

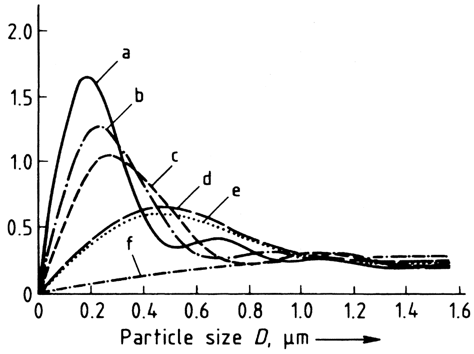

Fig. 1.9 Scattering of white pigments as a function of particle size (λ = 550 nm). (a) Rutile; (b) anatase; (c) zinc sulfide; (d) zinc oxide; (e) white lead; (f) barium sulfate.

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

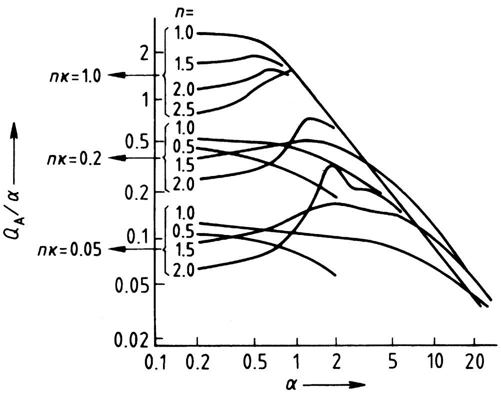

Fig. 1.10 Absorption as a function of particle size.

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 ΔE^*_{ab}, and the derived differences (Section 1.3.1), i.e., lightness difference ΔL^*, chroma difference ΔC^*_{ab}, and hue difference ΔH^*_{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.

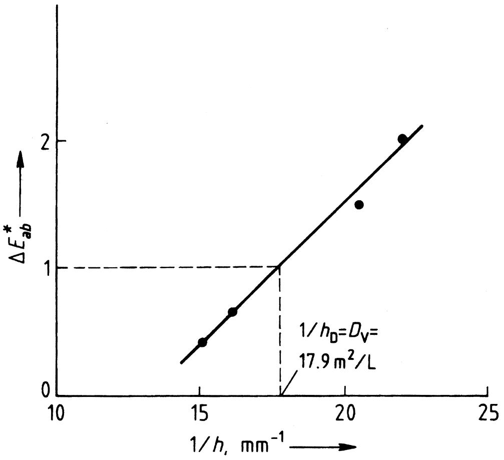

Fig. 1.11 Determination of the hiding power of a yellow iron oxide pigment.

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 (•OH, HO_2•) 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

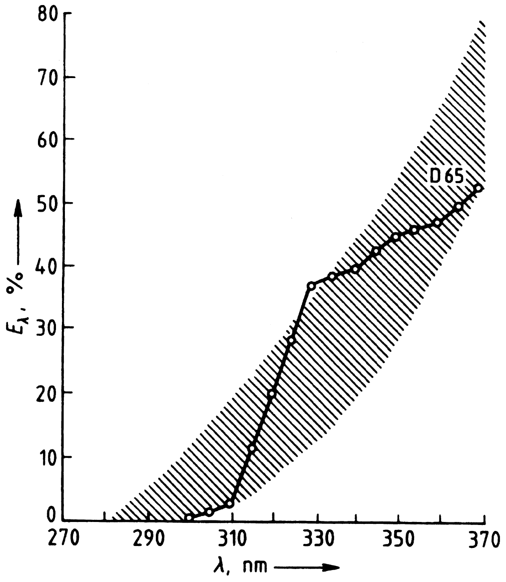

Fig. 1.12 Spectral energy distribution of daylight phase D 65 with permitted range of deviation (shading).

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).

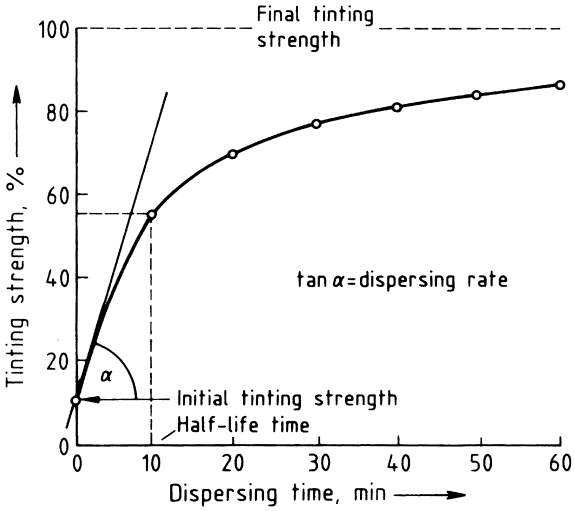

Fig. 1.13 Change in tinting strength as a function of dispersing time.

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:

$$\sigma = \frac{V_P}{V_P + V_b}$$

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).

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2
White Pigments

White pigments include TiO_2, zinc white (ZnO), zinc sulfide and lithopone (a mixed pigment produced from zinc sulfide and barium sulfate). Historical white pigments like white lead (basic lead carbonate) and chalk are of no industrial importance. White fillers are outside the scope of this book. The optical properties of white pigments are a result of their low light absorption in the visible range and their strong, mainly nonselective, scattering of light.

2.1
Titanium Dioxide

Titanium dioxide [*13463-67-7*], TiO_2, M_r 79.90, occurs in nature in the modifications rutile, anatase, and brookite. Rutile and anatase are produced industrially in large quantities and are used as pigments and catalysts, and in the production of ceramic materials.

Titanium dioxide is of outstanding importance as a white pigment because of its scattering properties (which are superior to those of all other white pigments), its chemical stability, and lack of toxicity. Titanium dioxide is the most important pigment in terms of quantity and value, with about 4.2×10^6 t being produced in 2003. World production of titanium dioxide pigment is shown in Table 2.1 [2.1–2.4].

2.1.1
Properties [2.5, 2.6]

2.1.1.1
Physical Properties

Of the three modifications of TiO_2, rutile is the thermodynamically most stable one. Nevertheless, the lattice energies of the other phases are similar and hence are stable over long periods. Above 700 °C, the monotropic conversion of anatase to rutile takes place rapidly. Brookite is difficult to produce, and therefore has no value in the TiO_2 pigment industry.

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Tab. 2.1: World production of TiO_2 pigment.

Year	Sulfate process		Chloride process		Total
	1000 t a^{-1}	%	1000 t a^{-1}	%	1000 t a^{-1}
1965	1254	90.3	135	9.7	1389
1970	1499	77.4	437	222.6	1936
1977	1873	72.3	716	27.7	2589
1988	1781	60.2	1178	39.8	2959
1995	1481	46.0	1739	54.0	3220
2000	1640	42.0	2260	58.0	3900
2001	1590	42.0	2190	58.0	3780
2002	1640	41.0	2360	59.0	4000
2003	1720	41.0	2480	59.0	4200

In all three TiO_2 modifications, one titanium atom in the lattice is surrounded octahedrally by six oxygen atoms, and each oxygen atom is surrounded by three titanium atoms in a trigonal arrangement. The three modifications correspond to different ways of linking the octahedra at their corners and edges. Crystal lattice constants and densities are given in Table 2.2.

Tab. 2.2: Crystallographic data for TiO_2 modifications

Phase	CAS registry no.	Crystal system	Lattice constants, nm			Density, g/cm³
			a	*b*	*c*	
Rutile	*[131-80-2]*	tetragonal	0.4594		0.2958	4.21
Anatase	*[1317-70-0]*	tetragonal	0.3785		0.9514	4.06
Brookite	*[12188-41-9]*	rhombic	0.9184	0.5447	0.5145	4.13

Rutile and anatase crystallize in the tetragonal system, brookite in the rhombic system. The melting point of TiO_2 is at about 1800 °C. Above 1000 °C, the oxygen partial pressure increases continuously as oxygen is liberated and lower oxides of titanium are formed. This is accompanied by changes in color and electrical conductivity. Above 400 °C, a significant yellow color develops, caused by thermal expansion of the lattice; this is reversible. Rutile has the highest density and the most compact atomic structure, and is thus the hardest modification (Mohs hardness 6.5–7.0). Anatase is considerably softer (Mohs hardness 5.5).

Titanium dioxide is a light-sensitive semiconductor, and absorbs electromagnetic radiation in the near-UV region. The energy difference between the valence and the conductivity bands in the solid state is 3.05 eV for rutile and 3.29 eV for anatase, corresponding to an absorption band at <415 nm for rutile and <385 nm for anatase.

Absorption of light energy causes an electron to be excited from the valence band to the conductivity band. This electron and the electron hole are mobile, and can move on the surface of the solid where they take part in redox reactions.

2.1.1.2
Chemical Properties

Titanium dioxide is amphoteric with very weak acidic and basic character. Accordingly, alkali metal titanates and free titanic acids are unstable in water, forming amorphous titanium oxide hydroxides on hydrolysis.

Titanium dioxide is chemically very stable, and is not attacked by most organic and inorganic reagents. It dissolves in concentrated sulfuric acid and in hydrofluoric acid, and is attacked and dissolved by molten alkaline and acidic materials.

At high temperature, TiO_2 reacts with reducing agents such as carbon monoxide, hydrogen, and ammonia to form titanium oxides of lower valency; metallic titanium is not formed. Titanium dioxide reacts with chlorine in the presence of carbon above 500 °C to form titanium tetrachloride.

2.1.1.3
Surface Properties of TiO_2 Pigments

The specific surface area of commercial TiO_2 products can vary between 0.5 and $>300\ m^2\ g^{-1}$ depending on its intended use. The surface of TiO_2 is saturated by coordinatively bonded water, which forms hydroxyl ions. Depending on the type of bonding of the hydroxyl groups to the titanium, these groups possess acidic or basic character [2.7, 2.8]. The surface of TiO_2 is thus always polar. The surface covering of hydroxyl groups has a decisive influence on pigment properties such as dispersibility and weather resistance.

The presence of the hydroxyl groups makes photochemically induced reactions possible, e.g., the decomposition of water into hydrogen and oxygen and the reduction of nitrogen to ammonia and hydrazine (see also Section 2.1.5) [2.9].

2.1.2
Raw Materials [2.10, 2.11]

The raw materials for TiO_2 production include natural products such as ilmenite, leucoxene, and rutile, and some very important synthetic materials such as titanium slag and synthetic rutile. Production figures for the most important titanium-containing raw materials are listed in Table 2.3 [2.4]. Total production of titanoferous raw materials, grew in 2000 to about 4.6 millions tons (as TiO_2) [2.4]. Australia was the largest producer, followed by South Africa, Norway, and Canada.

2.1.2.1
Natural Raw Materials

Titanium is the ninth most abundant element in the earth's crust, and it is always found in combination with oxygen. The most important titanium minerals are shown in Table 2.4. From the natural titanium minerals, only ilmenite, leucoxene and rutile are of economic importance. Leucoxene is a weathering product of ilmenite.

The largest titanium reserves in the world are in the form of anatase and titanomagnetite, but these cannot be worked economically at the present time. About 95%

Tab. 2.3: Production of titanium-containing raw materials (2000).

Product	**Process**	**t a^{-1} (as TiO_2 units)**
Ilmenite	Sulfate	1,005,000
Ilmenite and leucoxene	Chloride	649,000
Rutile	Chloride	390,000
Total mineral feedstock		*2,044,000*
Synthetic rutile	Chloride	821,000
Slag	Sulfate	738,000
Slag	Chloride	832,000
Upgraded slag	Chloride	143,000
Total upgraded feedstock		*2,534,000*
Total feedstock		*4,578,000*

Tab. 2.4: Titanium minerals

Mineral	Formula	TiO_2 content (wt%)
Rutile	TiO_2	92–98
Anatase	TiO,	90–95
Brookite	Ti02	90–100
Ilmenite	$FeTiO_3$	35–60
Leucoxene	$Fe_2O_3TiO_2$	60-90
Perovskite	$CaTiO_3$	40–60
Sphene (titanite)	$CaTiSiO_5$	30–42
Titanomagnetite	$Fe(Ti)Fe_2O_4$	2–20

of the world's production of ilmenite and rutile is used to produce TiO_2 pigments, the remainder for the manufacture of titanium metal and for welding electrodes.

Ilmenite and Leucoxene

Ilmenite is found worldwide in primary massive ore deposits or as secondary alluvial deposits (sands) that contain heavy minerals. In the massive ores, the ilmenite is frequently associated with intermediary intrusions (Tellnes in Norway and Lake Allard in Canada). The concentrates obtained from these massive ores often have high iron contents in the form of segregated hematite or magnetite in the ilmenite. These reduce the TiO_2 content of the concentrates (Table 2.5). Direct use of these ilmenites has decreased owing to their high iron content.

The enrichment of ilmenite in beach sand in existing or fossil coastlines is important for TiO_2 production. The action of surf, currents, and/or wind results in concentration of the ilmenite and other heavy minerals such as rutile, zircon, monazite, and other silicates in the dunes or beaches. This concentration process frequently leads to layering of the minerals. Attack by seawater and air over geological periods of time leads to corrosion of the ilmenite. Iron is removed from the ilmenite lattice, resulting in enrichment of the TiO_2 in the remaining material. The lattice is stable with TiO_2 content up to ca. 65%, but further removal of iron leads to the formation of a submicroscopic mixture of minerals, which may include anatase, rutile, and amorphous phases. Mixtures with TiO_2 contents as high as 90% are referred to as *leucoxene*. Leucoxene is present in corroded ilmenite and in some deposits is recovered and treated separately. However, the quantities produced are small in comparison to those of ilmenite.

The concentrates obtained from ilmenite sand, being depleted in iron, are generally richer in TiO_2 than those from the massive deposits. Other elements in these concentrates include magnesium, manganese, and vanadium (present in the ilmenite) and aluminum, calcium, chromium, and silicon that originate from mineral intrusions.

Tab. 2.5: Composition of ilmenite deposits (wt%)

Component	Tellnes (Norway)	Richard's Bay (Republic of South Africa)	Capel (Western Australia)	Quilon (India)
TiO_2	43.8	46.5	54.8	60.3
Fe_2O_3	14.0	11.4	16.0	24.8
FeO	34.4	34.2	23.8	9.7
Al_2O_3	0.6	1.3	1.0	1.0
SiO_2	2.2	1.6	0.8	1.4
MnO	0.3	n.d.	1.5	0.4
Cr_2O_3	n.d.	0.1	0.1	0.1
V_2O_5	0.3	0.3	0.2	0.2
MgO	3.7	0.9	0.15	0.9

More than 70% of the known ilmenite reserves of about 350×10^6 t that can be used economically are in Australia, South Africa, Norway, Canada and India. On the basis of current production capacities, these countries could supply all demand for ca. 150 years. The countries with the largest outputs are Australia (sands), Canada (massive ore), and the Republic of South Africa (sands). Other producers are the United States (sands, Florida), India (sands, Quilon), the former Soviet Union (sands, massive ore), Sri Lanka (sands), and Brazil (rutilo e ilmenita do Brasil). In 2000 the production of ilmenite was ca. 1.6×10^6 t of contained TiO_2 [2.4].

Rutile

Rutile is formed primarily by the crystallization of magma with high titanium and low iron contents, or by the metamorphosis of titanium-bearing sediments or magmatites. The rutile concentrations in primary rocks are too low for commercial use, therefore, only sands in which rutile is accompanied by zircon and/or ilmenite and other heavy minerals can be regarded as reserves. The world reserves of rutile are estimated to be 45×10^6 t [2.4].

As in the case of ilmenite, the largest producers are in Australia, the Republic of South Africa, and Sierra Leone. There is not enough natural rutile to meet demand, and it is therefore gradually being replaced by the synthetic variety. In 2000 the worldwide production of rutile was about 390,000 t (as TiO_2). Compositions of some rutile concentrates are given in Table 2.6.

Tab. 2.6: Composition of rutile deposits

Rutile component	Content (wt%)		
	Eastern Australia	Sierra Leone	Republic of South Africa
TiO_2	96.00	95.70	95.40
Fe_2O_3	0.70	0.90	0.70
Cr_2O_3	0.27	0.23	0.10
MnO	0.02	n.d.	n.d.
Nb_2O_5	0.45	0.21	0.32
V_2O_5	0.50	1.00	0.65
ZrO_2	0.50	0.67	0.46
Al_2O3	0.15	0.20	0.65
CaO	0.02	n.d.	0.05
P_2O_5	0.02	0.04	0.02
SiO_2	1.00	0.70	1.75

Ore Preparation

Most of the world's titanium ore production starts from heavy mineral sands. Figure 2.1 shows a scheme of the production process. The ilmenite is usually associated with rutile and zircon, so that ilmenite production is linked to the recovery of these minerals. If geological and hydrological conditions permit, the raw sand (usually containing 3–10% heavy minerals) is obtained by wet dredging (a). After a sieve test (b), the raw sand is subjected to gravity concentration in several stages with Reichert cones (d) and/or spirals (e) to give a product containing 90–98% heavy minerals. This equipment separates the heavy minerals from the light ones (densities: 4.2–4.8 g cm^{-3} and <3 g cm^{-3} respectively) [2.12].

The magnetic minerals (ilmenite) are then separated from the nonmagnetic (rutile, zircon, and silicates) by dry or wet magnetic separation (f). If the ores are from unweathered deposits, the magnetite must first be removed. An electrostatic separation stage (h) allows separation of harmful nonconducting mineral impurities such as granite, silicates, and phosphates from the ilmenite, which is a good conductor. The nonmagnetic fraction (leucoxene, rutile, and zircon) then experiences further hydromechanical processing (i) (shaking table, spirals) to remove the remaining low-density minerals (mostly quartz). Recovery of the weakly magnetic weathered ilmenites and leucoxenes is by high-intensity magnetic separation (j) in a final dry stage. The conducting rutile is then separated from the nonconducting zircon electrostatically in several stages (l). Residual quartz is removed by an air blast.

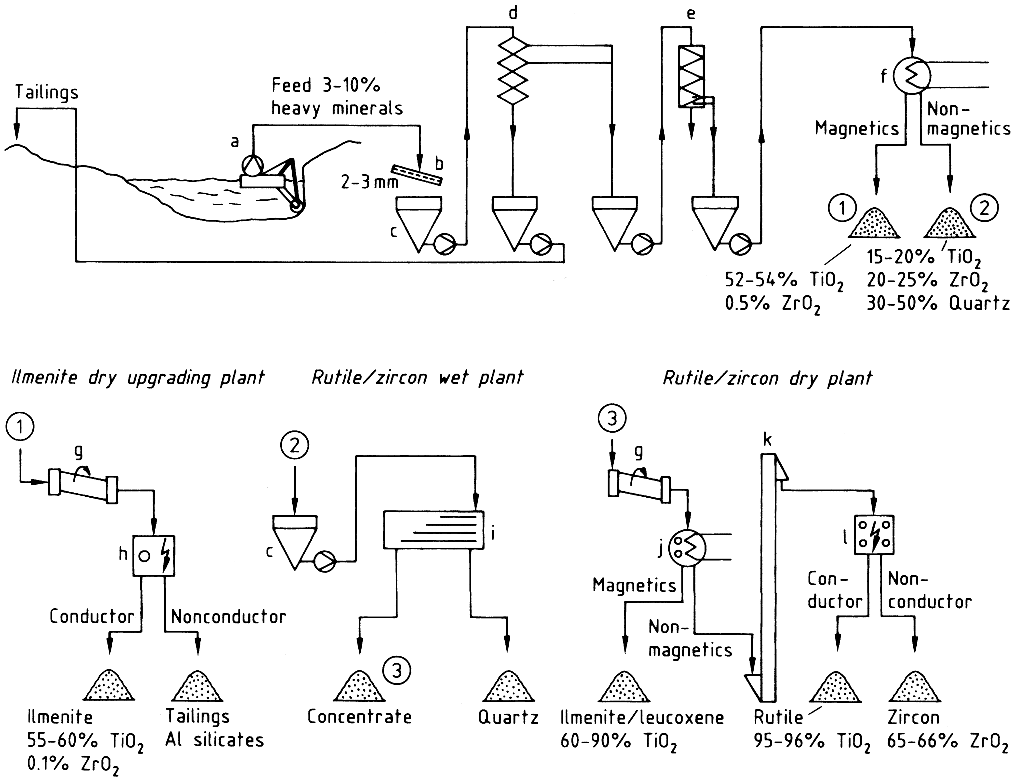

Fig. 2.1 The processing of heavy mineral sands. a) Dredger; b) Sieve; c) Bunker; d) Reichert cones; e) Spirals; f) Magnetic separator; g) Dryer; h) Electrostatic separator; i) Shaking table; j) Dry magnetic separator; k) Vertical belt conveyer; l) Electrostatic separator.

2.1.2.2
Synthetic Raw Materials

Increasing demand for raw materials with high TiO_2 contents has led to the development of synthetic TiO_2 raw materials. In all production processes, iron is removed from ilmenites or titanomagnetites.

Titanium Slag

The metallurgical process for removing iron from ilmenite is based on slag formation in which the iron is reduced by anthracite or coke to metal at 1200–1600 °C in an electric arc furnace and then separated. Titanium-free pig iron is produced together with slag containing 70–85% TiO_2 (depending on the ore used) that can be digested with sulfuric acid because they are high in Ti^{3+} and low in carbon. Raw materials of this type are produced in Canada by the Quebec Iron and Titanium Corporation (QIT), in the Republic of South Africa by Richard's Bay Minerals (RBM), and to a smaller extent by Tinfos Titan and Iron K.S. (Tyssedal, Norway). Total slag production grew in 2000 to 1.7 ×10^6 t of contained TiO_2, with 0.7 ×10^6 t being slag for the sulfate process and 1.0 ×10 ^{6} t being slag for the chloride process.

Synthetic Rutile

In contrast to ilmenite, only a small number of rutile deposits can be mined economically, and the price of natural rutile is therefore high. Consequently, many different processes have been developed to remove the iron from ilmenite concentrates without changing the grain size of the mineral because this is highly suitable for the subsequent fluidized-bed chlorination process. All industrial processes involve reduction of Fe^{3+} with carbon or hydrogen, sometimes after preliminary activation of the ilmenite by oxidation. Depending on the reducing conditions, either Fe^{2+} is formed in an activated ilmenite lattice, or metallic iron is produced.

The activated Fe^{2+}-containing ilmenite can be treated with hydrochloric or dilute sulfuric acid (preferably under pressure), and a "synthetic rutile" with a TiO_2 content of 85–96% is obtained [2.13]. The solutions containing iron(II) salts are concentrated and then thermally decomposed to form iron oxide and hydrochloric acid, which can be used again in the digestion process [2.14].

Metallic iron can be removed in various ways. The following processes are described in the patent literature:

1. Size reduction followed by physical processes such as magnetic separation of flotation.
2. Dissolution in iron(III) chloride solutions [2.15], the resulting iron(II) salt is oxidized with air to give iron oxide hydroxides and iron(III) salts.
3. Dissolution in acid.
4. Oxidation with air in the presence of electrolytes. Various iron oxide or iron oxide hydroxide phases are formed depending on the electrolyte used. Possible electrolytes include iron(II) chloride solutions [2.16], ammonium chloride [2.17], or ammonium carbonate–carbonic acid [2.18].
5. Oxidation with the iron(III) sulfate from ilmenite digestion, followed by crystallization of the iron(II) sulfate (see Section 2.1.3.1) [2.19].
6. Chlorination to form iron(III) chloride [2.20].
7. Reaction with carbon monoxide to form iron carbonyls [2.21] which can be decomposed to give high-purity iron.

Another possible method of increasing the TiO_2 content of ilmenite is by partial chlorination of the iron in the presence of carbon. This is operated on a large scale by several companies [2.22, 2.23]. The most important

companies producing synthetic rutile are located in Australia (Renison Goldfields Consolidated, Tiwest, Westralien Sands), India (Kerala Minerals and Metals, DCW, Bene-Chlor Chemicals), and Malaysia (Hitox). In 2000 production of synthetic rutile was ca. 0.8 ×10^6 t (as TiO_2).

2.1.3
Production

Titanium dioxide pigments are produced commercially using two different processes. The older *sulfate process* starts with a digestion reaction of the titanium-containing raw material (ilmenite or titanium slag) with concentrated sulfuric acid at 150–220 °C resulting in the „black liquor“. Relatively pure TiO_2 dihydrate is precipitated by hydrolysis of this sulfate solution, which contains colored heavy metal sulfates, sometimes in high concentration. Impurities are largely removed in further purification stages. The titanium oxyhydrate is then calcined, ground, and coated with inorganic compounds.

In the *chloride process,* the titanium-containing raw materials ilmenite, leucoxene, rutile, titanium slag, or anatase are chlorinated at 700–1200 °C. The $TiCl_4$ is oxidized at temperatures of 900–1400 °C to form TiO_2. This raw pigment is ground and coated with inorganic compounds.

2.1.3.1
Sulfate Method

The sulfate method is summarized in Figure 2.2.

Grinding

The titanium-bearing raw materials are dried to a moisture content of < 0.1%. Drying is mainly intended to prevent heating and premature reaction on mixing with sulfuric acid. The raw materials are ground in ball mills to give a mean particle size of <40 μm.

Digestion

Batch digestion is usually employed. The ground raw materials (ilmenite, titanium slag, or mixtures of the two) are mixed with 80–98% H_2SO_4. It is possible to use 80% sulfuric acid and start the reaction by the addition of oleum. or the reaction can be started by adding water to a suspension of the raw materials in concentrated sulfuric acid. In either case the mixing enthalpy initiates the process, resulting in a vigorous digestion reaction with a maximum temperature of about 200 °C or even more.

The ratio of H_2SO_4 to raw material is chosen so that the weight ratio of free H_2SO_4 to TiO_2 in the suspension produced by the hydrolysis is between 1.8 and 2.2 (the so-called “acid number”). The reaction in the digestion vessel (f) is started by adding water, dilute sulfuric acid, oleum, or sometimes steam. The temperature initially increases to 50–70 °C due to the heat of hydration of the acid. The exothermic sulfate formation then increases the temperature to 170–220 °C. If dilute acid or sparingly soluble raw materials are used, external heating is required.

After the maximum temperature has been reached, the reaction mixture must be left to mature for 1–12 h, depending on the raw material, so that the titanium-containing components become as soluble as possible. Digestion can be accelerated by blowing air through the mass while the temperature is increasing and also during the maturing period.

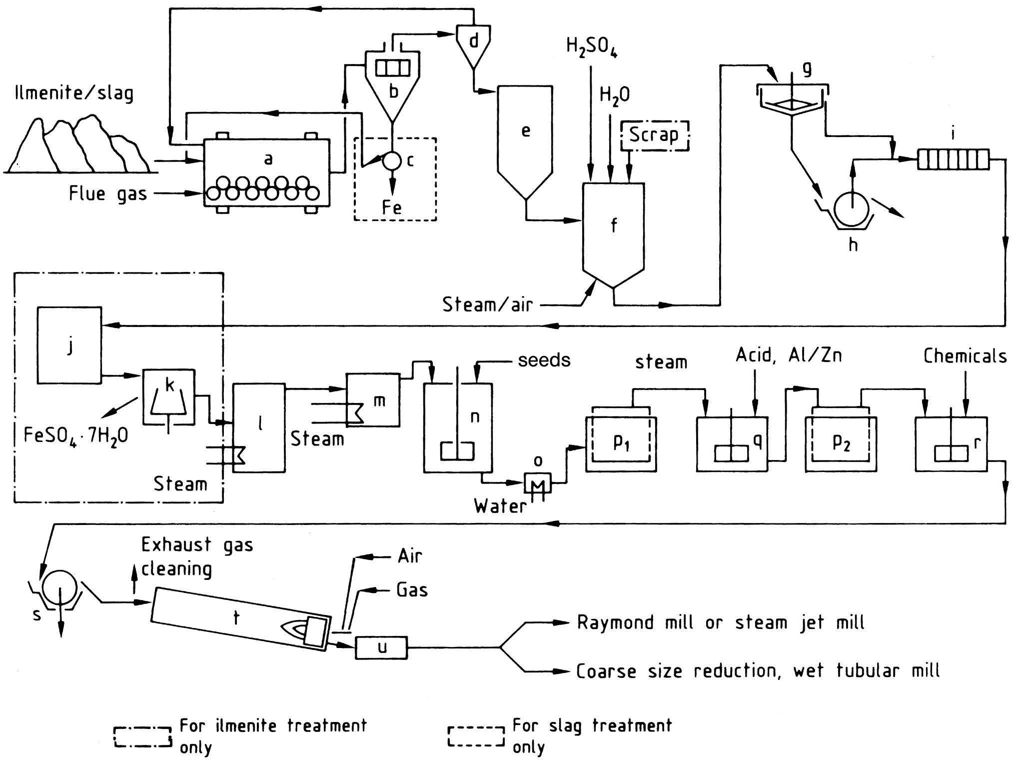

Fig. 2.2 Production of TiO_2 by the sulfate process. a) Ball mill/dryer; b) Screen; c) Magnetic separator (optionally); d) Cyclone; e) Silo; f) Digestion vessel; g) Thickener; h) Rotary filter; i) Filter press; j) Crystallizer; k) Centrifuge; l) Vacuum evaporator; m) Preheater; n) Stirred tank for hydrolysis; o) Cooler; p) Moore filters; q) Stirred tank for bleaching; r) Stirred tank for doping; s) Rotary filter for dewatering; t) Rotary kiln; u) Cooler.

Several *continuous digestion processes* have been proposed [2.24]. A proven method is to continuously feed a mixture of ilmenite and water together with the acid into a double-paddle screw conveyor. After a relatively short dwell time (<1 h), a crumbly cake is produced [2.25]. This process utilizes a more limited range of raw materials than the batch process because they need to be very reactive.

Due to the high cost of the titaniferous raw materials there have been numerous attempts to re-use the solid residue from digestion (with about 40-65% of TiO_2) as raw material. Due to sophisticated and expensive equipment and/or processing conditions none of these developments have found large-scale realization [2.26]. Recently, however, there a redigestion process using the standard equipment and the standard processing technology has been found [2.27].

Redigestion: Dissolution and Reduction

The cake obtained by digestion is dissolved in cold water or in dilute acid recycled from the process. A low temperature must be maintained (<85 °C) to avoid premature hydrolysis, especially with the product from ilmenite. Air is blown in to agitate the mixture during dissolution. With the ilmenite product, the TiO_2 concentration of the solution is 8–12 wt.%, and with the slag product 13–18 wt.%.

The trivalent iron is hydrolyzed together with the titanium compounds, and adheres to the titanium oxide hydrate. Therefore, all of the Fe^{3+} has to be reduced to Fe^{2+} by scrap iron during dissolution of the ilmenite product, or immediately afterwards. Reoxidation of the iron during subsequent processing is prevented with a small amount of Ti^{3+} being present until the end of the hydrolysis. Alternatively, reduction of Ti^{4+} to Ti^{3+} can be carried out in part of the solution under optimized conditions; this concentrated Ti^{3+} solution is then added in a controlled manner to the reaction solution [2.28]. In solutions obtained from titanium slag, the Ti^{3+} content of the solution must be decreased by oxidation with atmospheric oxygen so that no loss of yield occurs during hydrolysis.

With both ilmenite and titanium slag, mixed digestion can be carried out in which the Ti^{3+} content of the slag reduces all the Fe^{3+} to Fe^{2+}. The dissolved products obtained from the separate digestion of ilmenite and titanium slag can also be mixed [2.29, 2.30].

Clarification

All undissolved solid material must be removed as completely as possible from the solution. The most economical method is to employ preliminary settling in a thickener (g), followed by filtration of the sediment with a rotary vacuum drum filter (h) or a filter press. The filtrate and the supernatant from the thickener are passed through filter presses (i) to remove fines. Owing to the poor filtering properties of the solution, the rotary filter must be operated as a precoat filter. Preliminary separation in the thickener must be assisted by adding chemicals to promote sedimentation. Attempts to carry out the entire clarification process in a single stage using automated filter presses have been reported [2.31].

Crystallization

The solutions from slag digestion contain 5–6 wt.% $FeSO_4$, and those from ilmenite digestion 16–20 wt.% $FeSO_4$ after reduction of the Fe^{3+}. The ilmenite solution is cooled under vacuum to crystallize and separate $FeSO_4 \cdot 7\ H_2O$ (j) and reduce the quantity of $FeSO_4$ discharged with the waste acid. The concentration of the TiO_2 in the solution is thereby increased by ca. 25%. The copper salt is separated by filtration or centrifugation (k).

The iron sulfate is used in water purification, and as a raw material for the production of iron oxide pigments. Alternatively, it can be dehydrated and thermally decomposed to give iron(III) oxide and sulfur dioxide.

Due to the recent legislation in the European Union [2.32], from 2005 there will be a huge demand (ca. 1 million tons per year) for $FeSO_4$ as chromate reducing agent for cement. This will have an enormous impact for the titanium dioxide industry, as $FeSO_4$, that formerly has been a waste material, will then become a commercial product.

Hydrolysis

Titanium oxide hydrate is precipitated by hydrolysis at 94–110 °C. Other sulfuric-acid-soluble components of the raw material are precipitated simultaneously, mainly niobium as its oxide hydrate.

Hydrolysis is carried out in brick-lined, stirred tanks (n) into which steam is passed. The hydrolyzate does not have any pigment properties. The properties of the hydrolyzate are strongly influenced by the particle size and degree of flocculation of the hydrolyzate (mean primary particle size of hydrolyzate is ca. 5 nm, and the particle size of TiO_2 pigments is 200–300 nm).

The properties of the hydrolyzate depend on several factors:

1. The hydrolysis of concentrated solutions of titanium sulfate (170–230 $gTiO_2$ L^{-1}) proceeds very sluggishly and incompletely (even if boiled) unless suitable nuclei are added or formed to accelerate hydrolysis. The nuclei are usually produced by two methods. In the Mecklenburg method, colloidal titanium oxide hydrate is precipitated with sodium hydroxide at 100 °C, 1% of this hydrate is sufficient. In the Blumenfeld method a small part of the sulfate solution is hydrolyzed in boiling water and then added to the bulk solution [2.33]. The particle size of the hydrolyzate depends on the number of nuclei.

2. The particle size and degree of flocculation of the hydrolyzate depend on the intensity of agitation during the nuclei formation by the Blumenfeld method and also during the initial stage of the hydrolysis.

3. The titanium sulfate concentration has a great influence on the flocculation of the hydrolyzate. It is adjusted, if necessary by vacuum evaporation, to give a TiO_2 content of 170–230 g L^{-1} during hydrolysis. Lower concentrations result in a coarser particle size.

4. The acid number should be between 1.8 and 2.2. It has a considerable effect on the TiO_2 yield and on the particle size of the hydrolyzate. For a normal hydrolysis period (3–6 h) the TiO_2 yield is 93–96%.

5. The properties of the hydrolyzate are affected by the concentrations of other salts present, especially $FeSO_4$. High concentrations lead to finely divided hydrolyzates.

6. The temperature regime mainly affects the volume–time yield and hence the purity of the hydrolyzate.

Purification of the Hydrolyzate

After hydrolysis, the liquid phase of the titanium oxide hydrate suspension contains 20–28% H_2SO_4 and various amounts of dissolved sulfates, depending on the raw material. The hydrate is filtered off from the solution (p_1) (weak acid), and washed with water or dilute acid. Even with acid washing, too many heavy metal ions are adsorbed on the hydrate for it to be directly usable in the production of white pigment. Most of the impurities can be removed by reduction (bleaching), whereby the filter cake is slurried with dilute acid (3–10%) at 50–90 °C and mixed with zinc or aluminum powder (q). Bleaching can also be carried out with powerful nonmetallic reducing agents (e.g., $HOCH_2–SO_2Na$). After a second filtration and washing process (p_2), the hydrate only has low concentrations (ppm) of colored impurities but still contains chemisorbed 5–10% H_2SO_4. This cannot be removed by washing and is driven off by heating to a high temperature.

Doping of the Hydrate

When producing titanium dioxide of maximum purity, the hydrate is heated (calcined) without any further additions. This gives a fairly coarse grade of TiO_2 with a rutile content that depends on the heating temperature. However, to produce specific pigment grades, the hydrate must be treated with alkali metal compounds and phosphoric acid as mineralizers (<1%) prior to calcination (r). Anatase pigments contain more phosphoric acid than rutile pigments. To produce rutile pigments, rutile nuclei (<10%) must be added; ZnO, Al_2O_3, and/or Sb_2O_3 (<3%) are sometimes also added to stabilize the crystal structure.

Nuclei are produced by converting the purified titanium oxide hydrate to sodium titanate, which is washed free of sulfate and then treated with hydrochloric acid to produce the rutile nuclei. Rutile nuclei can also be prepared by precipitation from titanium tetrachloride solutions with sodium hydroxide solution.

Calcination

The doped hydrate is filtered with rotary vacuum filters (s) to remove water until a TiO_2 content of ca. 30–40% is reached. Pressure rotary filters or automatic filter presses can also be used to obtain a TiO_2 content of ca. 50%. Some of the water-soluble dopants are lost in the filtrate and can be replaced by adding them to the filter cake before it is charged into the kiln. Calcination is performed in rotary kilns (t) directly heated with gas or oil in countercurrent flow. Approximately two-thirds of the residence time (7–20 h in total) is needed to dry the material. Above ca. 500 °C, sulfur trioxide is driven off and partially decomposes to sulfur dioxide and oxygen at higher temperatures. The product reaches a maximum temperature of 800–1100 °C depending on pigment type, throughput, and temperature profile of the kiln. Rutile content, particle size, size distribution, and aggregate formation are extremely dependent on the operating regime of the kiln. After leaving the kiln, the clinker can be indirectly cooled or directly air-cooled in drum coolers (u).

The exhaust gas must have a temperature of >300 °C at the exit of the kiln to prevent condensation of sulfuric acid in the ducting. Energy can be saved by recirculating some of the gas to the combustion chamber of the kiln and mixing it with the fuel gases as a partial replacement for air. Alternatively, it can be used for concentrating the dilute acid (see Section 2.1.3.5.). The gas then goes to the waste-gas purification system.

Grinding

The agglomerates and aggregates in the clinker can be reduced to pigment fineness by wet or dry grinding. Coarse size reduction should be carried out in hammer mills prior to wet grinding in tube mills (with addition of dispersion agents). The coarse fraction can be removed from the suspension by centrifugation, and recycled to the mills. Another established technology with very low maintenance cost is roller milling with subsequent deagglomeration by wet milling. Hammer mills, cross-beater mills, roller mills, and particularly pendular and steam-jet mills are suitable for dry grinding. Special grinding additives can be used that act as wetting agents during subsequent pigment treatment or improve the dispersibility of untreated pigments.

2.1.3.2

The Chloride Process

The chloride process is summarized in Figure 2.3.

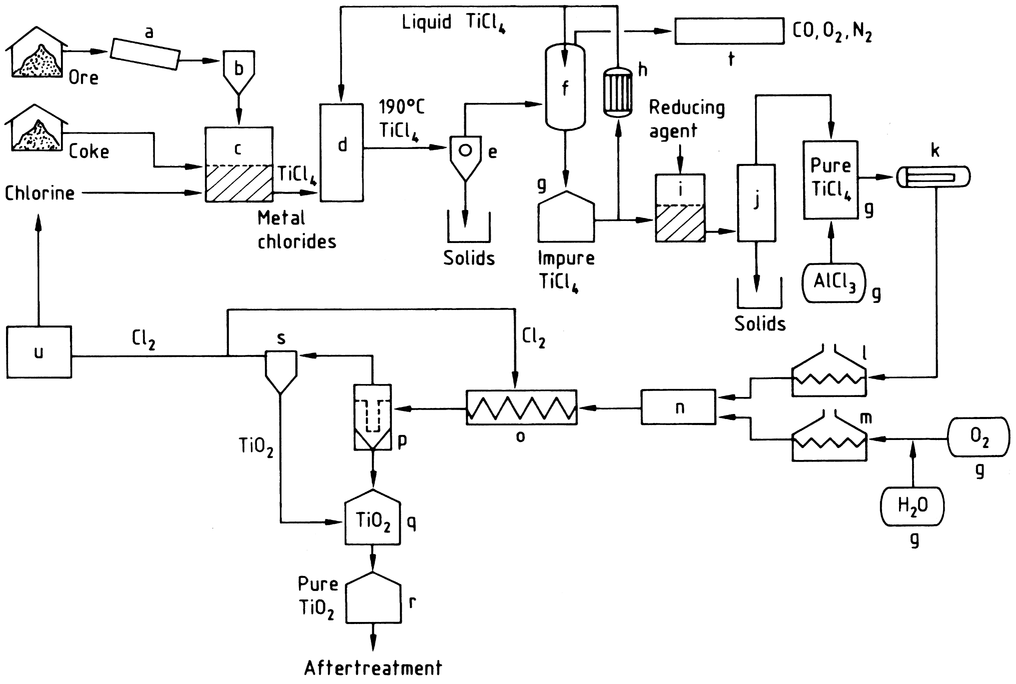

Fig. 2.3 Flow diagram of TiO_2 production by the chloride process. a) Mill; b) Silo; c) Fluidized-bed reactor; d) Cooling tower; e) Separation of metal chlorides; f) $TiCl_4$ condensation; g) Tank; h) Cooler; i) Vanadium reduction; j) Distillation; k) Evaporator; l) $TiCl_4$ superheater; m) O_2 superheater; n) Burner; o) Cooling coil; p) Filter; q) TiO_2 purification; r) Silo; s) Gas purification; t) Waste-gas cleaning; u) Cl_2 liquefaction.

Chlorination

The titanium in the raw material is converted to titanium tetrachloride in a reducing atmosphere. Calcined petroleum coke is used as the reducing agent because it has an extremely low ash content and, due to its low volatiles content, very little HCl is formed. The titanium dioxide reacts exothermically as follows:

$$TiO_2 + 2Cl_2 + C \rightarrow TiCl_4 + CO_2$$

As the temperature rises, an endothermic reaction in which carbon monoxide is formed from the carbon dioxide and carbon also occurs to an increasing extent. Therefore, oxygen must be blown in with the chlorine to maintain the reaction temperature between 800 and 1200 °C. The coke consumption per tonne of TiO_2 is 250–300 kg. If CO_2-containing chlorine from the combustion of $TiCl_4$ is used, the coke consumption increases to 350–450 kg.

The older *fixed-bed chlorination method* is hardly used today. In this process, the ground titanium-containing raw material is mixed with petroleum coke and a binder, and formed into briquettes. Chlorination is carried out at 700–900 °C in brick-lined reactors.

Fluidized-bed chlorination was started in 1950. The titanium raw material (with a particle size similar to that of sand) and petroleum coke (with a mean particle size ca. five times that of the TiO_2) are reacted with chlorine and oxygen in a brick-lined fluidized-bed reactor (c) at 800–1200 °C. The raw materials must be as dry as possible to avoid HCl formation. Since the only losses are those due to dust entrainment the chlorine is 98–100% reacted, and the titanium in the raw material is 95–100% reacted, depending on the reactor design and the gas velocity. Magnesium chloride and calcium chloride can accumulate in the fluidized-bed reactor due to their low volatility. Zirconium silicate also accumulates because it is chlorinated only very slowly at the temperatures used. All the other constituents of the raw materials are volatilized as chlorides in the reaction gases.

The ceramic cladding of the fluidized-bed reactor is rather rapidly destroyed by abrasion and corrosion. If chlorination is interrupted, there is a further danger that the raw materials may sinter and eventually cannot be fluidized.

Gas Cooling

The reaction gases are cooled with liquid $TiCl_4$ either indirectly or directly (d). Crystallization of the chlorides of the other components causes problems because they tend to build up on the cooling surfaces, especially the large quantities of iron(II) and iron(III) chlorides formed on chlorination of ilmenite [2.34]. In this first stage, the reaction gases are cooled down only to a temperature (<300 °C) at which the accompanying chlorides can be satisfactorily separated from the $TiCl_4$ by condensation or sublimation (e).

The gas then consists mainly of $TiCl_4$, and is cooled below 0 °C, causing most of the $TiCl_4$ to condense (f). The small amounts of $TiCl_4$ and Cl_2 remaining in the exhaust gas (CO_2, CO, and N_2) are removed by scrubbing with alkali (t).

Purification of $TiCl_4$

The chlorides that are solid at room temperature and the entrained dust can be separated from the $TiCl_4$ by simply evaporating (distilling) this off (j). Dissolved chlorine can be removed by heating or reduction with metal powders (Fe, Cu, or Sn).

Removal of vanadium tetrachloride (VCl_4) and vanadium oxychloride ($VOCl_3$) from the $TiCl_4$ by distillation is more challenging owing to the closeness of their boiling points. They are therefore reduced to form solid, low-valence vanadium chlorides (i). An enormous number of reducing agents have been recommended; important examples are copper, titanium trichloride, hydrogen sulfide, hydrocarbons, soaps, fatty acids, and amines. After subsequent evaporation (j) the titanium chloride should contain <5 ppm vanadium. If organic reducing agents are used, the residues may cause problems by baking onto the surfaces of the heat exchanger.

Phosgene and $SiCl_4$ can be removed by fractional distillation.

Oxidation of $TiCl_4$ and Recovery of TiO_2

Titanium tetrachloride is reacted with oxygen at 900–1400 °C to form TiO_2 pigment and chlorine (n). The purified $TiCl_4$ is vaporized (k) and the vapor is indirectly heated to ca. 500 – 1000 °C (l). The reaction

$$TiCl_4 + O_2 \rightarrow 2Cl_2 + TiO_2$$

is moderately exothermic, and requires a high reaction temperature, so that the oxygen must also be heated to >1000 °C (m). This can be achieved with an electric plasma flame, by reacting part of the oxygen with carbon monoxide, or by indirect heating. Hot $TiCl_4$ and oxygen (110–150% of the stoichiometric amount) are fed separately into a reaction chamber where they must be mixed as rapidly and completely as possible to give a high reaction rate. For this reason, and also because the TiO_2 has a strong tendency to cake onto the walls [2.35–2.37], many different reactor designs have been proposed and used. The same considerations apply to the cooling unit (o) where the pigment is very rapidly cooled to below 600 °C. Cooling zones of various geometries are used. Usually, the material is prevented from sticking to the walls by introducing abrasive particles like sand, coarse TiO_2 particles, sodium chloride or other materials [2.38, 2.39].

The mixture of gases (Cl_2, O_2, CO_2) and pigment can be further cooled during dry separation of the pigment either indirectly or directly by solid particles, e.g., sand. The pigment is separated from the gas by filtration (p). The gas stream is recycled to the cooling zone (o) of the combustion reactor and to the chlorination process as oxygen-containing chlorine via the liquefaction unit (u). The chlorine adsorbed on the pigment can be removed by heating or by flushing with nitrogen or air.

The wet separation process, in which the pigment-containing gas mixture (Cl_2, O_2, and CO_2) is quenched in water, has not found application.

2.1.3.3
Pigment Quality

The quality of the TiO_2 pigment is influenced by various factors. Reaction temperature, excess oxygen, and rheologic conditions in the reactor affect particle size and size distribution. Therefore, sophisticated conditions must be established for every reactor. Caking of the TiO_2 on the walls of the reactor leads to deterioration of quality and reduced on-stream time.

The presence of water and/or alkali compounds during combustion of the $TiCl_4$ results in the generation of nuclei, which promote the controlled formation of finely divided pigment particles with high scattering power [2.40]. Additives may be added directly to the oxygen or can be produced by the combustion of hydrogen-containing materials.

The presence of $AlCl_3$ promotes the formation of rutile and a more finely divided pigment. It is added in amounts of up to 5 mol%. Many methods have been proposed for rapidly generating and directly introducing the $AlCl_3$ vapor into the $TiCl_4$ vapor. Addition of PCl_3 and $SiCl_4$ suppresses rutile formation, so that anatase pigment is obtained [2.41]. However, pigments of this type have not appeared in the market.

2.1.3.4
Aftertreatment

Aftertreatment or coating of the pigment particles improves the weather resistance and lightfastness of the pigmented organic matrix, and improves dispersibility of the pigments in this matrix. The treatment consists of coating the individual pigment particles with colorless inorganic compounds of low solubility by precipitating them onto the surface. However, this reduces the optical performance of the pigment approximately in proportion to the decrease in the TiO_2 content. The surface coatings prevent direct contact between the binder matrix and the reactive surface of the TiO_2. The effect of these coatings largely depends on their composition and method of application, which may give porous or dense coatings. The treatment process also affects the dispersibility of the pigment, and therefore a compromise often has to be made. High weather resistance and good dispersibility of the pigment in the binder or matrix are usually desired. These effects are controlled using different coating densities and porosities. In addition organic substances can be added during the final milling of the dried pigment.

Several types of treatment can be used:

1. Deposition from the gas phase by hydrolysis or decomposition of volatile substances such as chlorides or organometallic compounds. Precipitation onto the pigment surface is brought about by adding water vapor. This method is especially applicable to chloride pigments, which are formed under dry conditions.

2. Addition of oxides, hydroxides, or substances that can be adsorbed onto the surface during pigment grinding. This can produce partial coating of the pigment surface.

3. Precipitation of the coating from aqueous solutions onto the suspended TiO_2 particles. Batch processes in stirred tanks are most common; various compounds are deposited one after another under specific conditions. There are hundreds of patents on this subject. Continuous precipitation is sometimes

used in mixing lines or cascades of stirred tanks. Coatings of widely varying compounds are produced in a variety of sequences. The most common are oxides, oxide hydrates, silicates, and/or phosphates of titanium, zirconium, silicon, and aluminum. For special applications, boron, tin, zinc, cerium, manganese, antimony, or vanadium compounds can be used [2.42], [2.43].

Typical groups of inorganic coatings are:

1. Pigments with dense surface coatings for paints or plastics made by:
   - Homogeneous precipitation of SiO_2 with precise control of temperature, pH, and precipitation rate [2.44].
   - Aftertreatments, with tempering at 500–800 °C in between or at the end of the aftertreatment [2.45].
   - Aftertreatment with Zr, Ti, Al, and Si compounds [2.46].
   - Aftertreatment with merely 1–3% of alumina.
2. Pigments with porous coatings for use in emulsion paints obtained by simple treatment with Ti, Al, and Si compounds, giving a silica content of 10% and a TiO_2 content of 80–85%
3. Lightfast pigments with dense surface coatings for the paper laminate industry that have a highly stabilized lattice and a surface coating based on silicates or phosphates of titanium, zirconium, and aluminum: ca. 90% TiO_2

Coprecipitation of special cations such as antimony or cerium can improve lightfastness further [2.47].

For coloring of plastics usually smaller TiO_2 particles are used with typically less than 3% of inorganic coating (TiO_2 typically >95%).

After treatment in aqueous media, the pigments are washed on a rotary vacuum filter or filter press until they are free of salt, and then dried in, e.g., belt, spray, or fluidized-bed dryers.

Before micronizing the pigment in air-jet or steam-jet mills, and sometimes also before drying, the pigment surface is further modified by adding organic substances to improve dispersibility and facilitate further processing. The nature of the compounds used depends on the intended use of the pigment. The pigment surface can be made either hydrophobic (e.g., using silicones, organophosphates, and alkyl phthalates) or hydrophilic (e.g., using alcohols, esters, ethers and their polymers, amines, organic acids). Also combinations of hydrophobic and hydrophilic substances may be used for obtaining tailor-made surface properties [2.48].

Problems arising from the temperature (>>100 °C) of the micronized pigments (packaging problems, low pouring weight, decomposition of organic additives) can be overcome by indirect or direct cooling of the pigments prior to packaging, especially when using PE or PP packaging materials [2.49].

Chloride or Sulfate Pigments?

Pigments produced by the chloride process (chloride pigments) typically have better brightness and a more neutral hue than pigments produced by the sulfate process (sulfate pigments). Often chloride pigments show better scattering power and better durability.

For a wide range of applications, however, chloride and sulfate pigments are exchangeable; and for various applications sulfate pigments may offer superior properties (e. g. for printing inks due to the less abrasive character of sulfate pigments).

Pigments used in demanding applications are almost always subjected to inorganic aftertreatment.

2.1.3.5
Waste Management

Aqueous Waste

In the *sulfate process*, 2.4–3.5 t concentrated H_2SO_4 are used per tonne of TiO_2 produced, depending on the raw material. During processing, some of this sulfuric acid is converted to sulfate, primarily iron(II) sulfate, the rest is obtained as free sulfuric acid (weak acid). Filtration of the hydrolyzate suspension can be carried out to give 70–95 wt.% of the SO_4^{2-} in a weak acid fraction containing ca. 20–25% free acid, the remaining sulfate (5–30%) is highly diluted with wash-water.

In the past it was common practice to discharge acid directly into the open sea or coastal waters. For a long time the weak-acid problem was the subject of controversy. As a result the European Community decided to stop the discharge of weak acid into open waters by 1993.

The European TiO_2 producers developed various effluent-treatment processes to meet the environmental requirements [2.50]. The most important processes are the precipitation of gypsum from the weak acid [2.51] and the concentration and recovery of the free and bound acid. Another outlet for the metal sulfate solution is the production of iron oxide pigments (see Section 3.1.1.2).

In the gypsum process, the acid effluent is treated in a first stage with finely divided $CaCO_3$ to precipitate white gypsum. After filtering off, washing, and drying, the white gypsum is used for the manufacturing of plasterboard. In a second stage, the residual metal sulfates in the filtrate are precipitated as metal hydroxides and further gypsum by adding calcium hydroxide. This mixture, the so-called red gypsum, can be used for landfill. It has also been suggested to produce iron oxide pigments from the iron sulfate solution obtained after (partial) neutralization of the weak acid with $CaCO_3$ or metallic iron [2.52].

In the recycling process, both the free and the bound sulfuric acid (as metal sulfates) can be recovered from the weak acid in the calcination furnace (Figure 2.4, k) and in metal sulfate calcination (Figure 2.5). The process consists of two stages:

1. Concentration and recovery of the free acid by evaporation
2. Thermal decomposition of the metal sulfates and production of sulfuric acid from the resulting sulfur dioxide.

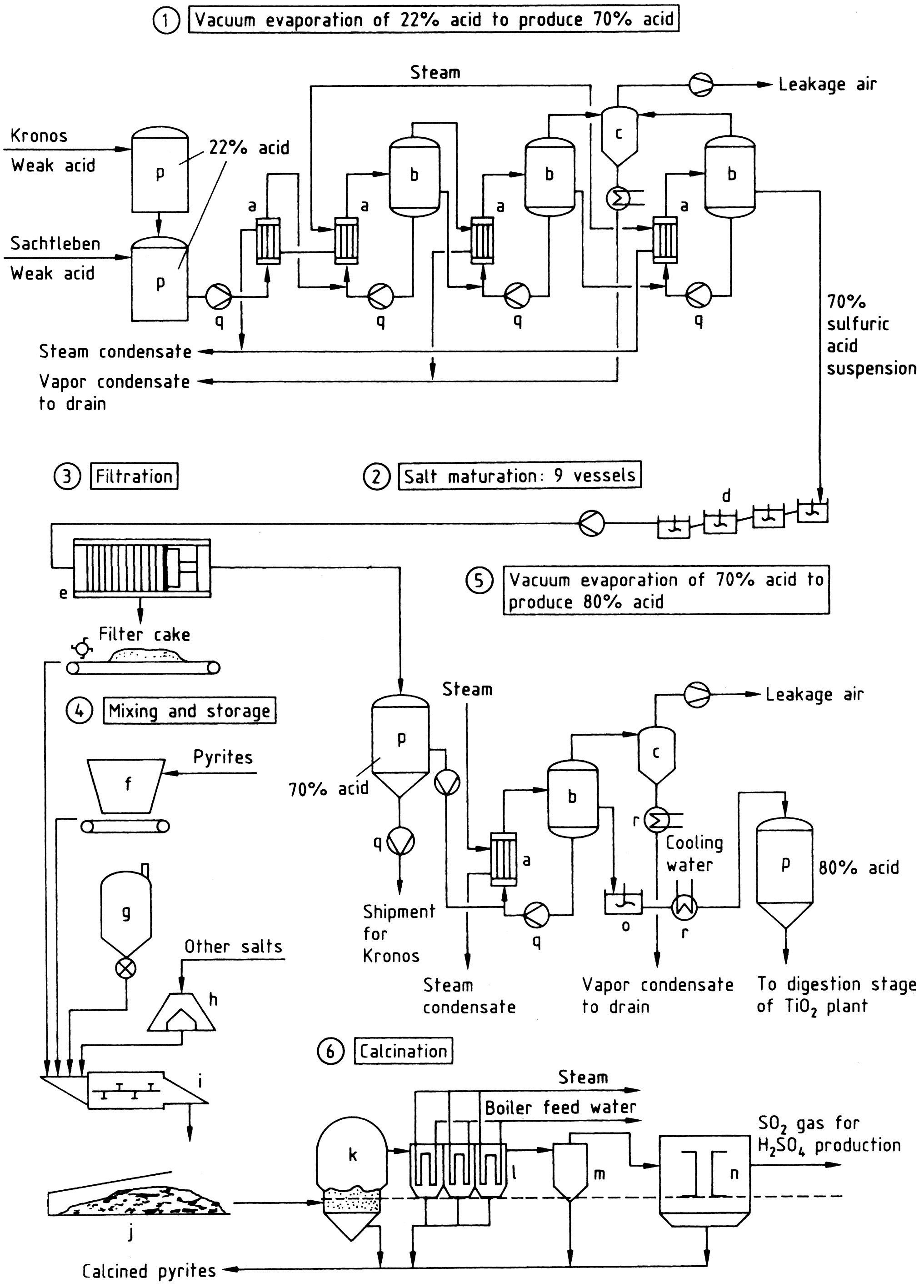

Fig. 2.4 Weak acid recovery plant used by Sachtleben Chemie (based on know-how of Bayer AG).a) Heat exchanger; b) Evaporator; c) Injection condenser; d) Stirred salt maturing vessels; e) Filter press; f) Bunker for pyrites; g) Coal silo; h) Bunker; i) Mixing screw unit; j) Covered store for mixed filter cake; k) Calcination furnace; l) Waste-heat boiler; m) Cyclone; n) Electrostatic precipitator; o) Stirred tank; p) Storage tank; q) Pump; r) Cooler

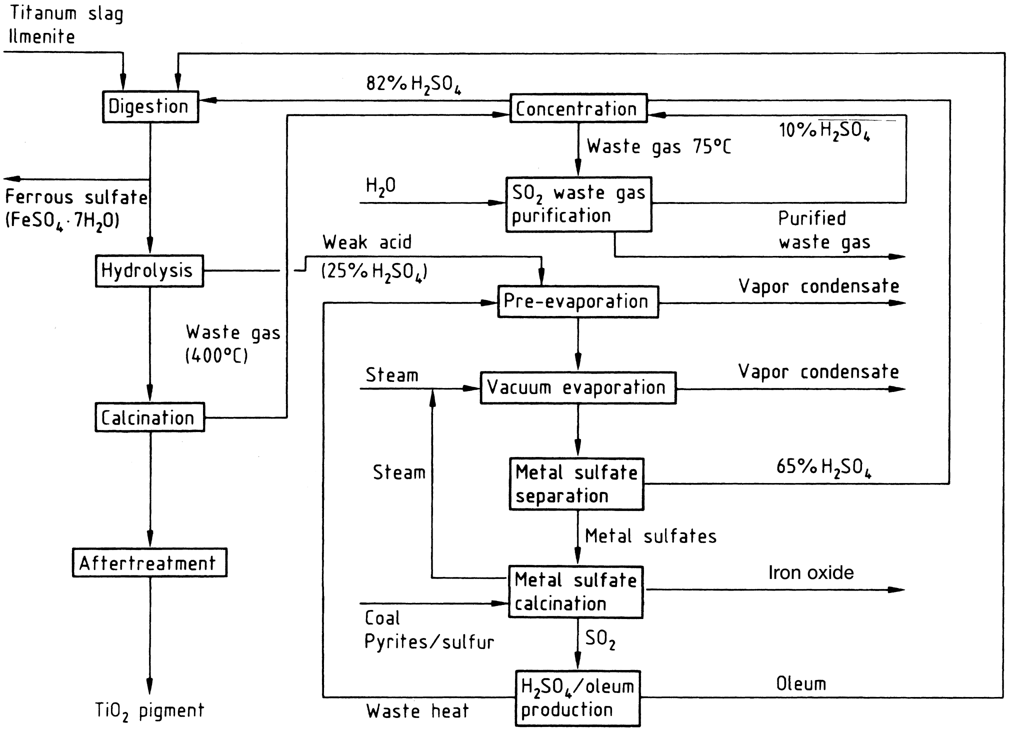

Fig. 2.5 Waste heat recovery and sulfuric acid recycling during weak acid treatment (Kerr-McGee).

As a result of energy requirements only acid containing >20% H_2SO_4 can be economically recovered by evaporation. The weak acid is concentrated from ca. 20–25% to ca. 28% with minimum heat (i.e., energy) consumption, e.g., by using waste heat from sulfuric acid produced by the contact process [2.53], or from the waste gases from the calcination kilns used in TiO_2 production (Figure 2.5) [2.54].

Following preliminary evaporation, further concentration is carried out in multi-effect vacuum evaporators. Since the water vapor pressure decreases strongly as the H_2SO_4 concentration increases, in general only two-stage evaporation can effectively exploit the water vapor as a heating medium. Evaporation produces a suspension of metal sulfates in 60–70% sulfuric acid (stage 1 in Figure 2.4). The suspension is cooled to 40–60 °C in a series of stirred tanks (stage 2, d) [2.55], giving a product with good filtering properties and an acid of suitable quality for recycling to the digestion process. Filtration (stage 3, e) is usually carried out with pressure filters [2.56] because they give a filter cake with an extremely low residual liquid content.

The concentration of the acid recycled to the digestion process depends on the quality of the titanium-containing raw material. For raw materials with a high titanium content, the 65–70% sulfuric acid separated from the metal sulfates must be further concentrated to give 80–87% acid (stage 5).

Concentration can be carried out in steam-heated vacuum evaporators, or by using the heat from the TiO_2 calcination kilns [2.57]. Cooling the acid obtained after this concentration process yields a suspension of metal sulfates that can be directly used for digestion of the raw material. The metal sulfates recovered from the sulfuric acid in stage 3 contain sulfuric acid. They can be converted to a disposable material by reaction with calcium compounds [2.58]. Recently these metal sulfates (containing mainly ferrous sulfate) have found application as reducing agent for chromate in cement. Thermal decomposition of the metal sulfates to form the metal oxides, sulfur dioxide, water, and oxygen is energy intensive, but is advantageous from the ecological point of view. The energy requirement is ca. 4×10^9 J per tonne of filter cake. Thermal decomposition is carried out at 850–1100 °C in a fluidized-bed furnace (stage 6). The energy is supplied by coal, pyrites, or sulfur. The sulfur dioxide produced by the thermal decomposition is purified by the usual methods, dried, and converted into sulfuric acid or oleum. This pure acid or oleum is mixed with the recovered sulfuric acid and used in the digestion process.

The metal oxides produced by thermal decomposition contain all the elements initially present in the raw material apart from the titanium, which has been converted into pigment. The mixture of metal oxides, mainly iron oxide, can be used as an additive in the construction materials or cement industry.

The continually increasing demand for environmentally friendly industrial processes has also led to the development of techniques for recycling the 5–30% sulfate remaining in the acidic wash water. [2.59]. In modern processes, up to 99% of the sulfuric acid can be recovered and reused in production.

The solid residue from the digestion reaction is most often disposed of after neutralization. A recently developed application for this material is its use as Ti source in blast furnaces for stabilizing the inner lining and increasing the life of the blast furnace [2.60].

In the *chloride process*, wastewater problems can arise, especially if the raw material contains $<90\%$ TiO_2. The metal chloride by-products are sometimes disposed of in solution by the "deep-well injection" method (e.g., at Du Pont). The metal chloride solutions are pumped via deep boreholes into porous geological strata. Special geological formations are necessary to avoid contamination of the groundwater by impurities.

Increasing restrictions also apply to the chloride process, so that efforts are continually being made to use the iron chloride byproduct, e.g., in water treatment and as a flocculation agent. [2.61]. A process for treating metal chlorides with cement and alkaline compounds to produce rocklike aggregates for road building is described in [2.62]. Another option is to turn the iron chloride into iron oxide by means of the Ruthner process with recovery of hydrochloric acid [2.63]. At present many facilities using the chloride process have to neutralize their waste metal chlorides with subsequent disposal of the iron hydroxide obtained.

The recent development in the EU legislation concerning the necessity for reducing chromate in cement [2.32] might also have impact on the waste management from the chloride process. By turning the waste metal chlorides into $FeSO_4$ with sulfuric acid (especially using spent acid) an $FeSO_4$ reducing agent for cement can be obtained [2.64].

Waste Gas Problems

The gases produced in the calcination kiln are cooled in a heat exchanger, and entrained pigment is removed, washed, and recycled to the process. The SO_2 and SO_3 formed during calcination are then scrubbed from the gases to form dilute sulfuric acid which is recycled.

2.1.4
Economic Aspects

The burning of $TiCl_4$ with oxygen usually results in rutile pigments, whereas the calcination of TiO_2 hydrolyzates produces either anatase or rutile pigments, depending on the doping and lattice stabilization. Most of the pigments sold are coated with oxides or hydroxides of various elements. Different treatments necessarily depend on the field of application, and all major pigment producers have a large number of pigment grades. Product groups are listed in Table 2.7. Pigments of all grades are available with or without organic treatment. More than 100 different TiO_2 pigment grades are produced and marketed by the major TiO_2 suppliers. Including the grades from small suppliers, there are several hundred TiO_2 grades in the market. Table 2.8 lists the capacities and processes of the most important pigment producers.

Tab. 2.7: Classification of TiO_2 pigments according to composition (DIN 55912-2, issue 1999, ISO 591-1 : 2000).

Pigment	Class	TiO_2 (min.), wt%	Water-soluble salts, wt%	Volatiles (max.), wt%
Anatase	A1	98	0.6	0.5
(Type A)	A2	92	0.5	0.8
Rutile	R1	97	0.6	0.5
(Type R)	R2	90	0.5	to be agreed
	R3	80	0.7	to be agreed

A considerable increase of capacity has been achieved by debottlenecking and building new plants. Pigment plant capacity will continue to grow, especially due to new capacities in China.

Powdered TiO_2 pigments are usually supplied in 25 kg sacks (50 lbs, USA) or in big bags containing 0.5–1 t pigment. Aqueous suspensions with solids contents of 68–75% are also available and can have advantage concerning the distribution and metering of the pigment in aqueous systems. The dust formation that occurs with dry pigment is also avoided. With the development of products with improved flow properties and modern pneumatic delivery technology, supply in silo trucks is rapidly increasing.

Tab. 2.8: TiO_2 pigment producers (2003).

Country	Company	Location	Capacity, 1000 t a^{-1}		
			Chloride	Sulfate	Total
United States	DuPont	New Johnsonville	450	–	450
		De Lisle	300	–	300
		Edge Moore	135	–	135
	Millenium Inorganic Chemicals	Baltimore	52	–	52
		Ashtabula	198	–	198
	Kerr-McGee	Savannah	110	–	110
		Hamilton	225	–	225
	Huntsman Tioxide/Kronos (50:50 JV)	Lake Charles	128	–	128
Canada	Kronos	Varennes	65	16	81
Brazil	Millenium Inorganic Chemicals	Salvador	–	70	70
Mexico	DuPont	Altamira	120	–	120
Total America					1869
Germany	Kronos	Leverkusen	124	22	146
		Nordenham		60	60
	Kerr-McGee	Krefeld-Uerdingen	–	107	107
	Sachtleben Chemie	Duisburg-Homberg	–	100	100
United Kingdom	Huntsman Tioxide	Grimsby	–	80	80
		Greatham	100	–	100
	Millenium Inorganic Chemicals	Stallingborough	150	–	150
France	Millenium Inorganic Chemicals	Le Havre	–	95	95
		Thann	–	30	30
	Huntsman Tioxide	Calais	–	100	100
Finland	Kemira	Pori	–	130	130
Italy	Huntsman Tioxide	Scarlino	–	82	82
Belgium	Kronos	Langerbrugge	69	–	69
Spain	Huntsman Tioxide	Huelva	–	90	90
Netherlands	Kerr-McGee	Botlek	72	–	72
Norway	Kronos	Fredrikstad	–	30	30
Total Western Europe					*1441*

2.1.5
Pigment Properties

The most important pigment properties of TiO_2 pigments are: scattering power, hiding power (tinting strength), brightness, mass-tone (or color), gloss formation, gloss haze, dispersibility, lightfastness, and weather resistance. These properties are a function of chemical purity, lattice stabilization, particle size and size distribution,

Tab. 2.8: Continued.

Country	Company	Location	Capacity, $1000\ t\ a^{-1}$		
			Chloride	Sulfate	Total
Russia	AO Pigment	Chelyabinsk	–	10	10
	Ural Titan	Ekaterinburg	–	50	50
	others	various sites	–	15	15
Ukraine	Krymsky Titan	Armyansk	–	80	80
	Sumsky Titan	Sumy	–	40	40
Poland	Zachem	Police	–	36	36
Slovenia	Cinkarna	Celje	–	38	38
Czech Rep.	Precheza	Prerov	–	35	35
Total Eastern Europe					*304*
Rep. of South Africa	Huntsman Tioxide	Umbogintwini	–	40	40
Total Africa					*40*
Australia	Millenium Inorganic Chemicals	Kemerton	95	–	95
	Kerr-McGee	Kwinana	97	–	97
Total Australia					*192*
Japan	Ishihara Sangyo	Yokkaichi	55	100	155
	Tayca	Saidaiji	–	60	60
	Sakai Chemical	Onahama	–	60	60
	Furukawa Mining	Osaka	–	10	10
	Fuji Titanium	Kobe	–	16	16
Total Japan					*301*
India	Kerala Minerals & Metals	Kerala	60	–	60
	Travancore Titanium	Trivandrum	–	25	25
	others	various	–	9	9
South Korea	Hankook Titanium	Incheon	–	25	25
		Onsan	–	40	40
Taiwan	China Metal & Chemicals	Chin Shin	–	15	15
	DuPont	Kuan Yin	110	–	110
Malaysia	Huntsman Tioxide	Teluk Kalung	–	65	65
S. Arabia	Cristal	Yanbu	92	–	92
Singapore	Ishihara Sangyo	Jurong	45	–	45
GreaterChina	> 20 different	various	–	480	480
Total Far East (excl. Japan)					*966*
Total world capacity			*2852*	*2261*	*5113*

and the coating. These properties also depend on the matrix and often cannot be accurately described in simple terms. Some of these properties of TiO_2 pigments are described below.

2.1.5.1
Scattering Power

The refractive indices of rutile and anatase are outstanding (n = 2.80 and 2.55, respectively). This is even higher than the refractive index of diamond (n = 2.42). Even after incorporation in a wide range of binders, the relative refraction coefficient (refraction index of pigment / refraction index of matrix) is typically between 1.5 and 2. The scattering power depends on the particle size, and for TiO_2 it is at a maximum at a particle size of 0.2 μm (Mie's theory) [1.33]. The scattering power also depends on the wavelength; smaller TiO_2 pigment particles scatter light of shorter wavelengths more strongly and therefore show a slight blue tone, while larger particles exhibit a more yellow tone.

2.1.5.2
Mass-Tone (or Color)

The whiteness (brightness and mass-tone/color) of TiO_2 pigments depends primarily on the crystalline modification, the purity, and the particle size of the TiO_2 (see above). As the absorption band (385 nm) of anatase pigments is shifted into the UV region compared with rutile pigments they have less yellow undertone. Any transition elements present in the crystal structure have an adverse effect on the whiteness, therefore sophisticated manufacturing conditions are of high importance. Thus, pigments produced by the chloride process (which includes distillative purification of $TiCl_4$ prior to the oxidation step) have higher color purity and very high brightness values.

2.1.5.3
Dispersion

Good disintegration and dispersion of the TiO_2 pigments in the medium are necessary to obtain high gloss and low gloss haze. These requirements are satisfied by intensive grinding and by coating the pigment surface with organic compounds. The compounds used for this surface treatment depend on the field of application (see Section 2.1.3.4.).

2.1.5.4
Lightfastness and Weather Resistance

Weathering of paints and coatings containing TiO_2 leads to pigment chalking [2.65]. If weathering occurs in the absence of oxygen, or in binders with low permeability to oxygen (e.g., in melamine–formaldehyde resins), no chalking is observed, but graying takes place, which decreases on exposure to air. Graying is greatly reduced in the absence of water. Both effects are more severe with anatase pigments. Empirical stabilization processes have been developed by pigment producers, e.g., doping with zinc or aluminum prior to calcination or during oxidation.

According to recent understanding, impairment of the lightfastness and weather resistance of TiO_2 pigments proceeds according to the following cycle [2.66]:

1. Molecules of water are bound to the TiO_2 surface, forming hydroxyl groups on the surface.
2. Absorption of light of short wavelength (anatase <385 nm, rutile <415 nm) occurs, producing an electron and an electron defect or "hole" (exciton) in the crystal lattice, which migrate to the surface of the pigment.
3. At the surface of the pigment, an OH^- ion is oxidized to an $OH^\cdot$ radical by an electron "hole". The OH^- ion is then desorbed and can oxidatively break down the binder. A Ti^{3+} ion is simultaneously produced by reduction of Ti^{4+} with the remaining electron of the exciton.
4. The Ti^{3+} ion can be oxidized by adsorbed oxygen with formation of an O_2^- ion. The latter reacts with H^+ and is converted into an $HO_2\cdot$ radical.
5. The cycle ends with the binding of water to the regenerated TiO_2 surface.

The chalking process can be regarded as the reaction of water and oxygen to form $OH^\cdot$ and $HO_2^\cdot$ radicals under the influence of shortwave radiation and the catalytic activity of the TiO_2 surface:

$$H_2O + O_2 + h\nu \rightarrow OH^\cdot + HO_2^\cdot$$

The enthalpy requirement for this reaction (312 kJ mol^{-1}) is provided by radiation of wavelength 385 nm. The cycle (1)–(5) is broken by excluding air or water. If oxygen is excluded or a binder is chosen in which the diffusion of oxygen is rate determining, a concentration of Ti^{3+} ions builds up. Graying then takes place, but this decreases with gradual exposure to oxygen. If water is excluded, rehydration and formation of surface hydroxyl groups do not take place; breakdown of the binder therefore ceases. Despite this photochemical breakdown of the binder, treated rutile pigments are used to stabilize many binders. This is because nonpigmented coatings are degraded by exposure to light and weathering; the added TiO_2 pigments prevent light from penetrating the deeper layers of the coating film and thus inhibit breakdown of the binder. High-quality TiO_2 pigments must satisfy high requirements with respect to weather resistance. These pigments must withstand the severe climatic conditions of the Florida test, resisting a two-year exposure without appreciable chalking or deterioration of gloss.

2.1.6
Analysis

The crystal structure of the pigments is determined by X-ray analysis which is sensitive enough to determine 0.3–0.5% anatase in the presence of 99.7–99.5% rutile. For standards, see Table 1.1 (Titanium dioxide pigments; "Methods of analysis" and "Specification").

A qualitative test for TiO_2 is a blue–violet coloration of beads of microcosmic salt ($NaNH_4HPO_4 \cdot 4\,H_2O$), or a yellow–orange coloration produced when hydrogen peroxide is added to a test solution in hot, concentrated sulfuric acid containing ammonium sulfate. For quantitative determination, the pigment is dissolved or digested in sulfuric acid and the solution is reduced to Ti^{3+} with cadmium, zinc, or aluminum. The Ti^{3+} ions are then usually titrated with a standard solution of iron(III) ammonium sulfate solution, with potassium rhodanide as an indicator, or using potentiometric end point determination.

Trace impurities can be determined by wet analysis, X-ray fluorescence, or spectrographic analysis (e.g., atomic absorption or ICP spectroscopy).

Typical analytical data for an untreated rutile pigment are TiO_2 99.4%, K_2O 0.24%, P_2O_5 0.21%, Fe_2O_3 40 ppm, Sb_2O_3 24 ppm, Al_2O_3 20 ppm, Mg 5 ppm, Zn 3 ppm, Cr 2 ppm, Mn, Cu, Hg, Cd, Co, Ni, Se, Sn, Ag <1 ppm.

2.1.7
Uses of Pigmentary TiO_2

Titanium dioxide is used universally, having almost completely replaced other white pigments. Consumption figures for 2003 are given in Table 2.9 [2.4]. Figures from different sources may differ significantly. The greatest annual increase in use will be for coloring of plastics (3.0%), followed by the coloring of paper. Geographically, the increase in consumption of TiO_2 has been and will be the greatest in Asia.

Tab. 2.9: Worldwide consumption of TiO_2 pigments in 2003 and predicted annual growth rates per market segment.

Segment	**Consumption %**	**Growth rate % p. a.**
Coatings	57	2.6
Paper	12	0.9
Plastics	22	3.4
Other	9	1.8
Total	100	2.5

2.1.7.1
Paints and Coatings

These account for the largest volume of TiO_2 production. The presence of the pigment enables the protective potential of the coating material to be fully exploited. As a result of continuing developments in TiO_2 pigments, coatings only a few micrometers thick fully cover the substrate. Commercially available pigments permit paint manufacture with simple dispersion equipment, such as disk dissolvers. Organic treatment (see Section 2.1.3.4.) prior to steam jet micronization yields pigments with improved gloss properties and reduced gloss haze for use in stoving enamels. Sedimentation does not occur when these products are stored, and they possess good lightfastness and weather resistance.

2.1.7.2
Printing Inks

Modern printing processes operate at coating thicknesses of <10 μm, and therefore require the finest possible TiO_2 pigments. These very low film thicknesses are only possible with TiO_2 pigments that have a lightening (reducing) power seven times that of lithopone. Because of its neutral mass-tone, TiO_2 is especially suitable for lightening (reducing) colored pigments.

2.1.7.3
Plastics

Titanium dioxide is widely used to color durable and nondurable goods such as toys, appliances, automobiles, furniture, and plastic packaging films. Furthermore, TiO_2 pigments absorb UV radiation with a wavelength <415 nm and thus protect the pigmented goods from these harmful rays.

2.1.7.4
Fibers

Titanium dioxide pigments give a solid appearance to synthetic fibers, eliminating the greasy appearance caused by their translucent properties. Anatase pigments are used for this because their abrasive effect on the spinning operation is about one quarter that of the rutile pigments. The poor lightfastness of anatase pigments in polyamide fibers can be improved by appropriate coating.

2.1.7.5
Paper

In Europe, fillers such as kaolin, chalk, or talc are preferred as brightening agents and opacifiers in paper manufacture. Titanium dioxide pigments are suitable for very white paper that has to be opaque even when very thin (air mail or thin printing paper). The TiO_2 can be incorporated into the body of the paper or applied as a coating to give a superior quality ("art" paper).

Laminated papers are usually colored with extremely lightfast rutile pigments before being impregnated with melamine–urea resin for use as decorative layers or films.

2.1.7.6
Other Areas of Application

These include the enamel and ceramic industries, the manufacture of white cement, and the coloring of rubber and linoleum.

Titanium dioxide pigments are also used as UV absorbers in sunscreen products, soaps, cosmetic powders, creams, toothpaste, cigar wrappers, and in the food and cosmetics industry. Their most important properties are their lack of toxicity, compatibility with skin and mucous membranes, and good dispersibility in organic and inorganic solutions and binders.

Electrically conducting TiO_2 pigments have been produced by specific aftertreatment to give a coating of mixed oxides of indium and tin, or antimony and tin [2.67].

These pigments are applied to fibers used in photosensitive papers for electrophotography, and for the production of antistatic plastics.

2.1.8
Uses of Nonpigmentary TiO_2

A lot of industrial products require TiO_2 starting materials with well-defined properties for specific applications. Some of the most important of these grades of titanium dioxide are those with a high specific surface area, a small particle size, and very high reactivity. Specific requirements often exist regarding purity and property consistency. The most important applications for nonpigmentary TiO_2 are vitreous enamels, glass and glass ceramics, electroceramics, catalysts and catalyst supports, welding fluxes, colored pigments, electrical conductors, chemical intermediates (e.g., potassium fluorotitanate), structural ceramics, UV absorbers, and refractory coatings [2.68].

2.1.8.1
Electroceramics

Titanates, for example, barium, strontium, calcium, and lead titanate, prepared from finely divided, high-purity TiO_2 substrates, are used in capacitors, PTC-resistors, and piezoelectric materials. The specifications of the TiO_2 starting materials with respect to purity, reactivity, and sintering properties are increasingly challenging. The global market is several thousand tons of TiO_2 per year. Strong annual growth is anticipated.

2.1.8.2
Catalysts

Titania is an active catalyst for various reactions, inorganic and organic, thermal and photochemical. It may be self-supported, or it may be supported on other material. For catalysis it is usually doped with other elements in order to enhance the desired effect

The most important catalytic application for TiO_2 is the removal of nitrogen oxides from waste gases from power stations, industrial incinerators and automotives with diesel engines. The nitrogen oxides in the waste gas are brought into reaction with ammonia in the presence of oxygen over the catalyst to produce nitrogen and water (SCR, Selective Catalytic Reduction) [2.69]. The world market for SCR catalysts is ca. 10×10^3 t per year as TiO_2. In addition to TiO_2 the catalysts usually contain ca. 10 wt.% tungsten oxide and 1 wt.% V_2O_5 and are extruded into a honeycomb shape or supported in thin layers on metal sheets. There are high requirements with respect to purity, particle size, and porosity to ensure that the desired catalytic activity is obtained.

An increasing demand is expected for the removal of nitrogen oxides from waste gases from stationary and mobile diesel engines.

2.1.8.3
Mixed Metal Oxide Pigments

The starting material is an anatase pigment or a TiO_2 hydrolyzate, which is calcined with oxides of transition metals to form chromium rutile or nickel rutile pigments (see Section 3.1.3.).

2.1.8.4
UV Absorption

Nanostructured TiO_2 particles (particle size 5–50 nm) are used as sunscreens in the cosmetic industry. Nanosized TiO_2 is an effective absorber of UV-B (280–320 nm) and UV-A radiation (320–400 nm). Because of its small particle size, it appears transparent [2.70]. Intensive research work is in progress worldwide aimed at utilizing the photoactivity of TiO_2. Titanium dioxide catalyzes the decomposition of organic compounds in wastewater [2.71].

2.1.9
Toxicology

Titanium dioxide is highly stable and is regarded as completely nontoxic. Investigations on animals, which have been fed TiO_2 over a long period give no indication of titanium uptake [2.68]. Absorption of finely divided TiO_2 pigments in the lungs does not have any TiO_2-related specific carcinogenic effect [2.72].

Generally, inhalation of smaller particles into the lung is more detrimental compared to larger particles. But there are no known specific chemical reactions of TiO_2 resulting in inflammation [2.68].

A more detailed outline of the toxicological effects of TiO_2 with a helpful list of labeling, registration and permission requirements can be found in Ref. [2.68].

2.2
Zinc Sulfide Pigments [2.73–2.75]

White pigments based on zinc sulfide were first developed and patented in 1850 in France. Although they are still of economic importance, they have continually lost market volume since the early 1950s when titanium dioxide was introduced. Only one modern production installation for zinc sulfide pigments still exists in the western hemisphere (Sachtleben Chemie, Germany). All other production plants are located in China.

The zinc-sulfide-containing white pigment with the largest sales volume is *lithopone* [*1345-05-7*], which is produced by coprecipitation and subsequent calcination of a mixture of zinc sulfide [*1314-98-3*], ZnS, M_r 97.43, and barium sulfate [*7727-43-7*], $BaSO_4$, M_r 233.40. For standards, see Table 1.1 (Lithopone pigments; “Specification”). Pure zinc sulfide is marketed as *Sachtolith*.

White zinc sulfide pigments maintain their market position in areas of use where not only their good light scattering ability but also other properties such as low abrasion, low oil number, and low Mohs hardness are required.

They are sometimes produced from many types of industrial effluents. This recycling relieves pressure on the environment, as these materials would otherwise have to be disposed of.

2.2.1
Properties

Some physical and chemical properties of ZnS and $BaSO_4$ are given in Table 2.10.

Tab. 2.10: Properties of the components of zinc sulfide pigments.

Property	Zinc sulfide	Barium sulfate*
Physical properties		
Refractive index *n*	2.37	1.64
Density, g cm^{-3}	4.08	4.48
Mohs hardness	3	3.5
Solubility in water (18 °C), wt.%	6.5×10^{-5}	2.5×10^{-4}
Chemical properties		
Resistance to acids/bases	soluble in strong acids	insoluble
Resistance to organic solvents	insoluble	insoluble

*Component of lithopone.

A white pigment must not absorb light in the visible region (wavelength 400–800 nm), but should disperse incident radiation in this region as completely as possible. The spectral reflectance curves of zinc sulfide and barium sulfate (Figure 2.6) fulfill these conditions to a large extent. The absorption maximum for ZnS at ca. 700 nm is a result of lattice stabilization with cobalt ions, whose function is explained in Section 2.2.2.2. The absorption edge in the UV-A region is responsible for the bluish-white tinge of zinc sulfide. Depending on the production process, zinc sulfide has a sphalerite or wurtzite lattice type.

The refractive index n of ZnS, which determines its scattering properties, is 2.37 and is much greater than that of plastics and binders (n = 1.5–1.6). Spheroidal ZnS particles have their maximum scattering power at a diameter of 294 nm. Barium sulfate does not directly contribute to the light scattering due to its relatively low refractive index (n = 1.64), but acts as an extender, and increases the scattering efficiency of the ZnS.

The barium sulfate in lithopone can be identified thermoanalytically by a reversible endothermic transformation at 1150 °C. Both Sachtolith and lithopone are thermally stable up to ca. 550 °C in the presence of air. Due to their low Mohs hardness, they are less abrasive than other white pigments. Barium sulfate is practically inert toward acids, bases, and organic solvents. Zinc sulfide is stable in aqueous media

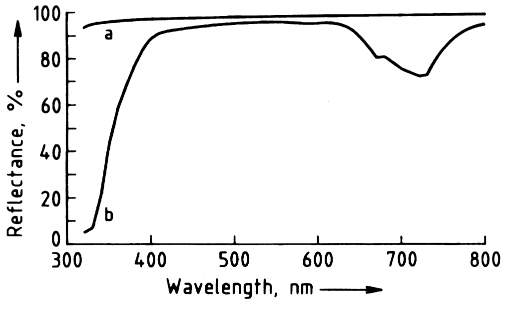

Fig. 2.6 Spectral reflectance curves of barium sulfate and zinc sulfide. a) Barium sulfate, b) Zinc sulfide (Co-doped)

between pH 4 and 10, and is largely inert toward organic media. In the presence of water and oxygen, it can be oxidatively decomposed by the action of UV radiation.

2.2.2
Production

2.2.2.1
Raw Materials

The source of zinc can be zinc oxide from a smelter, zinc dross or sweepings, ammonium chloride slag from hot dip galvanizing, or liquid waste such as pickle liquors from galvanizing plants. Variations in the price of zinc have a large effect on the economics of zinc sulfide pigments.

The starting material for water-soluble barium compounds is fused barium sulfide produced by coke reduction of naturally occurring barite with a low silica and strontium content. Suitable barite is readily available from many deposits worldwide.

2.2.2.2
Lithopone

The reaction of equimolar quantities of $ZnSO_4$ and BaS produces a white, water-insoluble coprecipitate with the theoretical composition 29.4 wt.% ZnS and 70.6 wt.% $BaSO_4$:

$$ZnSO_4 + BaS \rightarrow ZnS + BaSO_4$$

By using a different molar ratio, this composition can be changed; for example, precipitation according to the following equation gives a product containing 62.5 wt.% ZnS and 37.5 wt.% $BaSO_4$:

$$ZnSO_4 + 3\ ZnCl_2 + 4\ BaS \rightarrow 4\ ZnS + BaSO_4 + 3\ BaCl_2$$

Figure 2.7 is a flow diagram of lithopone production. The *solutions of zinc salts* contain impurities (e.g., salts of iron, nickel, chromium, manganese, silver, cadmium) that depend on their origins. The main sources of zinc sulfate solutions are zinc electrolyses and the reprocessing of zinc scrap and zinc oxide. The first stage of purification consists of chlorination. Iron and manganese are precipitated as oxide-hydroxides, and cobalt, nickel, and cadmium as hydroxides. The solutions are then mixed with zinc dust at 80 °C. All the elements more noble than zinc (cadmium, indium, thallium, nickel, cobalt, lead, iron, copper, and silver) are almost completely precipitated, while zinc goes into solution. The metal slime is filtered off and recycled. A small quantity of a water-soluble cobalt salt is added to the purified zinc salt solution. The cobalt (0.02–0.5%) becomes incorporated into the ZnS lattice during subsequent calcination to stabilize the final product against light. Zinc sulfide, that is not treated in this way becomes gray in sunlight.

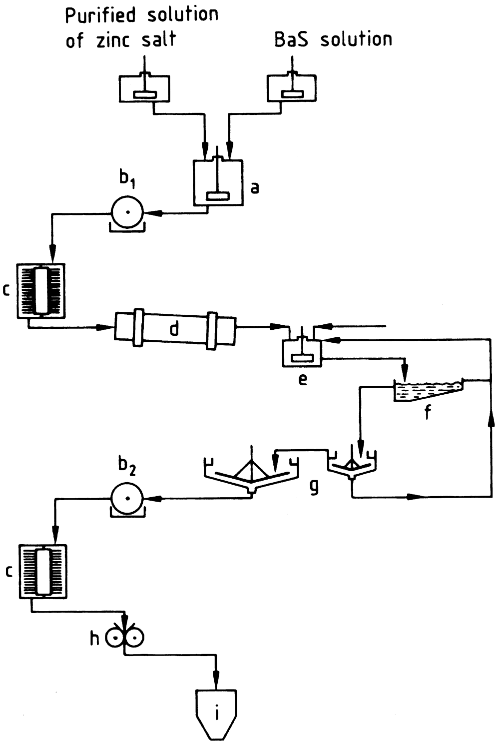

Fig. 2.7 Flow diagram for lithopone production. a) Precipitation vessel; b) Rotary filter, c) Turbo dryer; d) Rotary kiln; e) Chilling vessel; f) Rake classifier; g) Thickener; h) Grinder; i) Silo.

The *barium sulfide solution* is produced by dissolving fused barium sulfide in water. The barium sulfide is obtained by reducing an intimate mixture of crushed barite (ca. 1 cm lumps) with petroleum coke according to the following equation in a directly heated rotary kiln at 1200–1300 °C:

$$BaSO_4 + 2C \rightarrow BaS + 2CO_2$$

The warm solution (60 °C) containing ca. 200 g L^{-1} barium sulfide is filtered and immediately pumped to the precipitation stage. Further purification is not necessary. Unreacted gangue and heavy metals are collected as insoluble sulfides in the filter cake. The almost clear solution can be stored only for a short period. Longer storage leads to undesirable polysulfide formation.

The zinc salt and BaS solutions are mixed thoroughly under controlled conditions (vessel geometry, temperature, pH, salt concentration, and stirring speed, see (a) in Figure 2.7). The precipitated "raw lithopone" does not possess pigment properties. It is filtered off (b_1) and dried (c); ca. 2 cm lumps of the material are calcined in a rotary kiln (d), then directly heated with natural gas at 650–700 °C. Crystal growth is controlled by traces of sodium, potassium and magnesium salts. The temperature profile and residence time in the kiln are controlled to obtain ZnS with an optimum particle size of ca. 300 nm.

The hot product from the kiln is quenched in water (e), passed via classifiers and hydroseparators (f) into thickeners (g), filtered on rotary filters (b_2), and washed until salt-free. The dried product is ground in high-intensity mills (g) and may undergo organic treatment depending on the application.

Figure 2.8 shows a scanning electron micrograph of lithopone. The ZnS and $BaSO_4$ particles can be distinguished by means of their size. The average particle diameter of $BaSO_4$ is 1 µm.

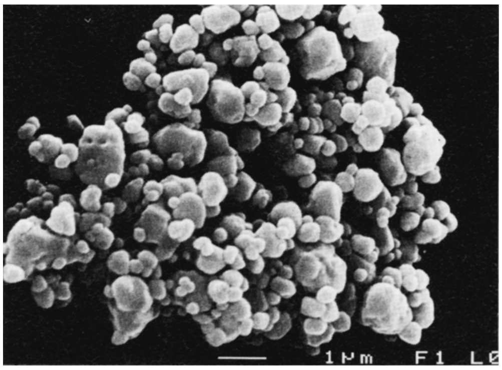

Fig. 2.8 Scanning electron micrograph of lithopone. The larger particles are barium sulfate (mean size 1.0 µm) and the smaller particles are zinc sulfide (mean particle size 0.3 µm).

2.2.2.3
Sachtolith

Production is similar to that of lithopone.

A Na_2S solution is mixed with a zinc salt solution under precisely controlled conditions. The resulting zinc sulfide precipitate is calcined and processed to give the finished product.

$$Na_2S + ZnSO_4 \rightarrow ZnS + Na_2SO_4$$

2.2.2.4
Hydrothermal Process

Crystal growth of ZnS can be achieved by using a hydrothermal process instead of by calcination. The raw lithopone is precipitated with a slight excess of sulfide at pH 8.5. The pH is then adjusted to 12–13 with sodium hydroxide solution, and 0.5% sodium carbonate is added. The suspension is then autoclaved for ca. 15–20 min at 250–300 °C. In contrast to the wurtzite structure of the calcined product, the hydrothermal product has a sphalerite structure with a ca. 10% greater scattering power. Although the product is of better quality, the hydrothermal process is less economic due to the high cost of the materials required for lining the autoclave (e.g., tantalum or a zirconium alloy).

2.2.2.5
Environmental Protection

During the reduction of barite and the calcination of Sachtolith and lithopone, sulfur dioxide is liberated. This is removed from the waste gas in a purification stage, which is based on the reversible, temperature-dependent solubility of sulfur dioxide in polyglycol. The absorbed sulfur dioxide can be recovered as a liquid product or as a raw material for sulfuric acid. Traces of soluble barium in the residue from the dissolution of the fused BaS are removed by treatment with Na_2SO_4.

2.2.3
Commercial Products

Commercial lithopone grades contain 30% ZnS (red seal) and 60% ZnS (silver seal). The ZnS content of Sachtolith is >97%. Various chemical surface modification swith hydrophilic or hydrophobic organic or inorganic substances are made to obtain products for special applications. The technical data for commercial red seal lithopone and Sachtolith are given in Table 2.11.

Tab. 2.11: Technical data for red seal lithopone and Sachtolith.

Parameter	Standard	Sachtolith	Red seal lithopone
ZnS, wt.%	DIN 55910	>97	ca. 29
ZnO, wt.%	DIN 55910	0.2	0.1
$BaSO_4$, wt.%	DIN 55910	<3	ca. 70
Brightness*		98	98–99
Lightening power	DIN 53192	400	120
Water-soluble salts, wt.%	DIN 53197	<0.2	<0.2
Sieve residue**, wt.%		0.02	<0.1
Oil number	DIN 53192	12	8
pH	DIN 53200	6–8	7
Specific surface area, $m^2\ g^{-1}$		8	3

*$BaSO_4$ white standard = 100.

**Test sieve 45 µm, DIN 4188, ISO DIS 3310/1.

2.2.4
Uses

2.2.4.1
Lithopone

This is mainly used in *coating materials* with relatively high pigment concentrations (Table 2.12). Examples are primers, plastic masses, putties and fillers, artists' colors, and emulsion paints. An important property of lithopone is its low binder requirement, giving paint products with good flow and application properties. It is suitable for almost all binder media, and has good wetting and dispersing properties. With optimum feed composition, good dispersion can be achieved simply by the action of a dissolver. It can be economically advantageous to use lithopone in combination with TiO_2 pigments; the good hiding power of the TiO_2 pigments is combined with the economic and technical advantages of lithopone. Due to the strong shift of the absorption band towards the blue, lithopone is especially useful as a white pigment for UV-cured paint systems. Zinc compounds have fungicidal and algicidal effects, and inclusion of lithopone or Sachtolith in paint formulations for exterior use therefore helps prevent the growth of algae or fungi.

Tab. 2.12: Uses of Sachtolith and lithopone (as percentage of total consumption).

Use	Sachtolith	Lithopone
Paints	22	90
Plastics	70	10
Lubricants	8	–

The material advantages of lithopone are used in *plastics* (e.g., good lightfastness and clear bluish-white shade). The product also imparts very good extruding properties to the plastic resulting in high throughput rates and economic extruder operation. In fire-resistant systems, ca. 50% of the flame retardant antimony trioxide can be replaced by nontoxic lithopone without any adverse effect.

2.2.4.2
Sachtolith

This is mainly used in plastics (Table 2.12). Functional properties such as lightening and hiding power are criteria for the use of Sachtolith. It has proved to be very useful for coloring many thermoplasts. During the dispersion process it does not cause abrasion of metallic production machinery or adversely effect the polymer, even at high operating temperatures or during multistage processing. Even ultrahigh molecular mass thermoplasts can be colored without problems. In glass-fiber-reinforced plastics, the soft texture of Sachtolith prevents mechanical fiber damage during extrusion. Sachtolith is also used as a dry lubricant during the fabrication of these materials.

The low abrasiveness of Sachtolith prolongs the operating life of stamping tools used in the manufacture of industrial rubber articles. The lightfastness and ageing resistance of many elastomers are improved by using Sachtolith. It is also used as a dry lubricant for roller and plain bearings, and as a white pigment for greases and oils.

2.2.5
Economic Aspects

Total world production of zinc sulfide pigments in 2003 was 260 $\times 10^3$ t. This was subdivided as follows (10^3 t):

Germany	20
People's Republic of China	200
Others	40

Only estimated figures are available for the People's Republic of China.

A decrease in output is to be expected because replacement by TiO_2 is not yet at an end, especially in coating materials. In the long term, only the high-quality grades can maintain their place in the market, i.e. those in which technical properties are required in addition to light scattering.

2.2.6
Toxicology

The use of zinc sulfide and barium sulfate in contact with foods is permitted by the FDA (United States) and in most European countries. Some restrictions apply in France, Italy, the United Kingdom, and Czechoslovakia.

Soluble zinc is toxic in large amounts, but the human body requires small quantities (10–15 mg d^{-1}) for metabolism. Zinc sulfide is harmless in the human due to its low solubility. The acid concentration in the stomach and the rate of dissolution following ingestion are not sufficient to produce physiologically significant quantities of soluble zinc. LD_{50} values in the rat exceed 15 g kg^{-1}. No cases of poisoning or chronic damage to health have been observed in the manufacture of zinc sulfide pigments.

2.3
Zinc Oxide (Zinc White) [2.76–2.80]

2.3.1
Introduction

Zinc oxide [*1314-13-2*], ZnO, M_r 81.38, was formerly used only as a white pigment, and was named zinc white (C.I. Pigment White 4), Chinese white, or flowers of zinc.

The term zinc white now denotes zinc oxide produced by the combustion of zinc metal according to the indirect or French process.

Historical Aspects: Zinc oxide has long been known as a byproduct of copper smelting. The Romans called it "cadmia" and used it as such in the production of brass. They also purified it for use in ointments by reduction followed by oxidation. In the Middle Ages, the alchemists thought that cadmia could be converted into gold.

In the mid-18th century, the German chemist Cramer discovered that cadmia could be obtained by the combustion of metallic zinc. Courtois began to produce zinc white in 1781 in France, but it was not until 1840 that industrial production was started by Leclaire (indirect or French process). The use of this white pigment spread rapidly. Zinc oxide replaced white lead because it had the advantages of being nontoxic, of not darkening in the presence of sulfurous gases, and of having better hiding power.

Around 1850, S. Wetherill of the New Jersey Zinc Company perfected a roasting furnace in which a grate was charged with coal and then covered with a mixture of zinc ore and coal. The zinc was reduced by the partial combustion of the coal and reoxidized at the furnace exit (direct or American process). These furnaces were subsequently improved but are now no longer used in Europe and America but are still in operation in China. During the second half of the nineteenth century, the use of ZnO in rubber was introduced to reduce the time needed for vulcanization. The discovery of the first organic accelerators for vulcanization in 1906 added to the importance of ZnO, which acts as an activator in these materials.

A third industrial production process exists but this wet process is less widely used.

2.3.2
Properties

2.3.2.1
Physical Properties

Zinc oxide is a fine white powder that turns yellow when heated above 300 °C. It absorbs UV light at wavelengths below 366 nm. Traces of monovalent or trivalent elements introduced into the crystal lattice impart semiconducting properties. The elementary particles of ZnO obtained by the thermal method may be granular or nodular (0.1–5 μm) or acicular (needle-shaped, 0.5–10 μm). Particles produced by the wet process have an amorphous character (sponge form, particles up to 50 μm). Some physical properties are given below:

Density	5.65–5.68 g cm^{-3}
Refractive index	1.95–2.1
Melting point	1975 °C
Heat capacity 25 °C	40.26 J mol^{-1} K^{-1}
Heat capacity 100 °C	44.37 J mol^{-1} K^{-1}
Heat capacity 1000 °C	54.95 J mol^{-1} K^{-1}
Thermal conductivity	25.2 W m^{-1} K^{-1}
Crystal structure	hexagonal, wurtzite
Mohs hardness	4–4.5

2.3.2.2
Chemical Properties

Zinc oxide is amphoteric; it reacts with organic and inorganic acids, and also dissolves in alkalis and ammonia solution to form zincates. It combines readily with acidic gases (e.g., CO_2, SO_2, and H_2S). It reacts at high temperatures with other oxides to form compounds such as zinc ferrites.

2.3.3
Production

The total production capacity in Europe is approximately 265,000 tons p. a., about 5–7% thereof is produced by the wet process, 10–20% by the direct process, and the main quantities (>81%) are manufactured by the indirect process.

2.3.3.1
Raw Materials

In the early days, the raw materials were mainly zinc ores or concentrates for the direct process, or metal from zinc producers for the indirect process. Nowadays, zinc oxide manufacturers mainly use residues and secondary zinc. This fact, combined with the demand for chemical purity imposed by the users, means that processes have had to be modified and a number of purification techniques are used.

2.3.3.2
Direct or American Process

The direct process is noted for its simplicity, low cost, and excellent thermal efficiency. It consists of an initial high-temperature reduction (1000–1200 °C) of a zinc-containing material (as oxide), the reducing agent being coal. Reduction takes place according to Boudouard's equations:

$$ZnO + C \rightarrow Zn + CO$$

$$ZnO + CO \rightarrow Zn + CO_2$$

$$C + O_2 \rightarrow CO_2$$

$$CO_2 + C \rightarrow 2CO$$

The zinc vapor and the CO gas are then oxidized to zinc oxide and carbon dioxide above the reaction bed or at the furnace exit. Various zinc-containing materials are used, e.g. zinc concentrates (mainly in China), metallization residues, skimmings from casting furnaces, oxidic residues from the indirect process and above all zinc ashes from hot dip galvanization. The ash from galvanization must first be treated to remove chloride and lead by heating at ca. 1000 °C in rotary kilns.

Only rotary kilns are now used in the EU for the direct process; the use of static furnaces has been discontinued. The zinc content of raw materials is between 60 and 75%. There are two types of rotary kiln:

1. A long (ca. 30 m), fairly narrow (2.5 m diameter) kiln, heated by gas or oil. The raw material (a mixture of zinc-containing material and coal) is charged continuously either countercurrent or cocurrent to the combustion gases. The residues, which still contain some zinc and unburnt coal, leave the furnace continuously at the end opposite to the feed end. The excess coal is sieved out and recycled. The combustion gases, containing zinc vapor, ZnO, and CO, pass into a chamber where oxidation is completed and large particles of impurities settle out. The gases are then cooled in a heat exchanger or by dilution with air. The zinc oxide is collected in bag filters.
2. A rotary kiln that is shorter (5 m) and has a larger diameter (ca. 3 m).Charging is continuous, but the dezincified residues are removed batchwise.

In both cases, operating conditions are controlled to obtain a high yield and to give the required particle shape and size. Provided no contamination is introduced, chemical purity is determined solely by the composition of the raw materials used.

2.3.3.3
Indirect or French Process

The zinc is boiled, and the resulting vapor is oxidized by combustion in air under defined conditions. The crystallographic and physical properties of the ZnO can be controlled by adjustment of the combustion conditions (e.g., flame turbulence and air excess). The chemical composition of the ZnO is solely a function of the composition of the zinc vapor.

Many types of furnace are available to produce vapor of the required purity from various raw materials and obtain a high yield of zinc. Pure zinc (super high grade, SHG; high grade, HG) or, to an increasing extent, metal residues (e.g., scrap zinc, die casting dross, or galvanizer's top or bottom dross) are used as raw materials. Various liquid- or vapor-phase separation techniques are used for separating Cd, Pb, Fe, and Al from zinc metal before it is oxidized:

1. *Muffle Furnaces or Retorts of Graphite or Silicon Carbide.* The metal is fed into the furnace either batchwise as a solid or continuously as a liquid. The heat of vaporization is supplied by heating the outside of the retort with a burner. In a muffle furnace the vaporizing section is separated by a silicon carbide arch from the heating chamber. The heat from burning gas or oil in the heating chamber is transferred to the zinc bath from the arch by radiation.

   The nonvolatile residues (iron, lead and aluminum in the case of dross from smelting and casting) accumulate in the retort or in the muffle furnace and must be removed at intervals. This is facilitated by tipping the retorts.
2. *Fractional Distillation.* The vapor, containing Cd, Pb, Fe, Al, and Cu, can be purified by fractional distillation in columns (New Jersey Zinc Co.) with silicon carbide plates. Oxidation takes place at the exit of the column.
3. *Furnaces with Two Separate Chambers.* The metallic raw material, which can be in large pieces, is fed into the first chamber where it melts. This is connected to the second, electrically heated chamber where distillation takes place in the

absence of air. The first version of this type of furnace was constructed by Lundevall [2.81].

The nonmetallic residues are removed at the surface of the melting chamber. Impurities, such as Fe, Al, and some of the Pb, accumulate in the distillation chamber and are periodically removed in the liquid state. The last traces of lead are then removed by fractional distillation.

4. *Smelting Process in a Rotary Kiln.* Indirect zinc oxide is also made by smelting in a rotary kiln, starting from the same raw materials. Melting, distillation, and part of the oxidation all take place in the same zone, allowing utilization of a large part of the heat of combustion of the zinc. By controlling the temperature and partial pressures of carbon dioxide and oxygen, the impurity content (e.g. Pb) can be controlled and the shape and size of the ZnO particles can be adjusted.

2.3.3.4
Wet Process

Zinc oxide is also produced industrially from purified solutions of zinc sulfate or chloride by precipitating the basic carbonate, which is then washed, filtered, and finally calcined. This method produces a grade of zinc oxide with a high specific surface area.

Products of this type are also obtained from waste hydroxides which are purified by a chemical route and then calcined.

2.3.3.5
Aftertreatment

Thermal treatment at temperatures up to 1000 °C improves the pigment properties of the ZnO and is mainly applied to oxide produced by the direct method. Controlled atmospheric calcination also improves the photoconducting properties of the high-purity oxide used in photocopying.

The ZnO surface is made more organophilic by coating it with oil and propionic acid. The ZnO is often deaerated and increasingly pelletized or granulated to improve handling properties.

2.3.4
Quality Specifications

Many standard specifications have been laid down for the more important uses of ZnO (rubber, paints, and the pharmaceutical industry). For standards, see Table 1.1 (“Zinc oxide pigments; Methods of analysis” and “Specification”). Various methods of classification are used, often based on the production process and the chemical composition. The most well known are pharmacopeias (USP, BP; DAB, Ph. Eur.); ISO 9298, T31 006 NF, ASTM D79 – 86 and ASTM D 4295 – 89. Table 2.13 shows a classification with typical data for commercially available zinc oxide grades (more detailed standard specifications see standards mentioned above).

Tab. 2.13: Classification of commercially available grades of zinc oxide (typical data).

Parameter				
	Indirect Process Pharmaceutical grade	Indirect Process Chemical pure grade	Direct Process Chemical pure grade	Wet process Chemical pure grade
ZnO (wt.%)	99.5	99.0	98.5	93
Pb (wt.%)	0.005	0.2	0.2	0.001
Cd (wt.%)	0.001	0.01	0.005	0.001
Cu (wt.%)	0.0005	0.001	0.005	0.001
Mn (wt.%)	0.0002	0.0005	0.005	0.001
Loss on ignition (wt.%)	0.2	0.25	0.25	1–5
Specific surface area (m^2 g^{-1})	3–10	3–10	1–4	3–80
Sieve residue (%, 320 mesh)	0.02	0.04	0.02	0.1

Normally manufactures have their own standards. The terms gold seal, silver seal, red seal, green seal and white seal are still common in Europe.

2.3.5
Uses

Zinc oxide has many uses. By far the most important is in the *rubber industry*. Almost half the world's ZnO is used as an activator for vulcanization accelerators in natural and synthetic rubber. The reactivity of the ZnO is a function of its specific surface area, but is also influenced by the presence of impurities such as lead and sulfates. The ZnO also ensures good durability of the vulcanized rubber, and increases its thermal conductivity. The ZnO content is usually 2–5%.

In *paints and coatings*, zinc oxide is no longer the principal white pigment, although its superb white color is used by artists. It is used as an additive in exterior paints for wood preservation. It is also utilized in antifouling and anticorrosion paints [2.82]. It improves film formation, durability, and resistance to mildew (having a synergistic effect with other fungicides) because it reacts with acidic products of oxidation and can absorb UV radiation.

The *pharmaceutical and cosmetic industries* use ZnO in powders and ointments because of its bactericidal properties. It is also used to form dental cements by its reaction with eugenol.

In the field of *glass, ceramics, and enamels*, ZnO is used for its ability to reduce thermal expansion, to lower the melting point, and to increase chemical resistance. It can also be used to modify gloss or to improve opacity.

Zinc oxide is used as a *raw material* for many products: stearates, phosphates, chromates, bromates, organic dithiophosphates, and ferrites (ZnO, MnO, Fe_2O_3). It is used as a source of zinc in animal feeds and in electrogalvanization . It is also used for desulfurizing gases.

Zinc oxide is used as a *catalyst* in organic syntheses (e.g., of methanol), often in conjunction with other oxides. It is present in some adhesive compositions.

The highest purity material is calcined with additives such as Bi_2O_3 and used in the manufacture of varistors [2.83]. The photoconducting properties of ZnO are used in photoreproduction processes. Doping with alumina causes a reduction in electrical resistance; hence, it can be used in the coatings on the master papers for offset reproduction [2.84].

2.3.6
Economic Aspects

A yearly market demand of 260,000 t of zinc oxide can be assumed for the EU. The annual world consumption is in the region of 750,000 t, representing ca. 8% of the world zinc metal production.

The rubber industry consumes ca. 45% of the total and the remainder is divided among a large number of industries.

2.3.7
Toxicology and Occupational Health

Zinc is not considered to be toxic or dangerous. It is an essential element for humans, animals and plants [2.85]. The human body contains ca. 2 g of zinc and a daily intake of 15 mg for humans is recommended. The oral LD_{50} value for rats is >15,000 mg ZnO kg^{-1} (OECD 401).

Exposure to zinc oxide will mainly take place in the workplace by means of the inhalation and dermal exposure route. Exposure due to handling of solid zinc oxide is in the form of dust.

The individual national occupational exposure limits for dust should be supervised while handling zinc oxide. The so-called zinc fever is caused by ultrafine zinc oxide particles, existing in zinc fumes generated by e.g. welding galvanized steel. Commercial grades of zinc oxide do not cause this fever. Zinc Oxide has no skin irritating properties, no sensitization potential, is not an eye irritant and there is no evidence of carcenogenicity, genotoxicty and reproduction toxicity in man.

2.3.8
Ecological Aspects

The EC50 value for ZnO (Selenastrum capricornicum 72 h) was determined to be 170 $\mu g\ L^{-1}$.

In consequence zinc oxide is classified as dangerous for the environment (EU Classification 67/548/EEC, 29ATP 2004) with the Risk Phrases R50/53 (Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

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3
Colored Pigments

Colored pigments differ from black and white pigments in that their absorption and scattering coefficients are wavelength dependent with widely varying absolute values. The dependence of these coefficients on wavelength, particle size, particle shape, and their distributions determine the color, and hiding power of the pigments (see Section 1.3.1).

3.1
Oxides and Hydroxides

Transition metals are responsible for color in many inorganic pigments. Metal oxides and oxide hydroxides are particularly important as colored pigments because of their optical properties, low price, and ready availability. Colored pigments based on oxides and oxide hydroxides are either composed of a single component or mixed phases.

3.1.1
Iron Oxide Pigments

The continually increasing importance of iron oxide pigments is based on their non-toxicity, chemical stability, wide variety of colors ranging from yellow, orange, red, brown, to black, and good performance/price ratio. Natural and synthetic iron oxide pigments consist of well-defined compounds with known crystal structures (Table 3.1) [3.1, 3.2].

Nevertheless the inconsistency of the CAS-Numbers cannot be explained, but must be taken into consideration. Regulatory orders are using these figures concurrently! Mixed metal oxide pigments containing iron oxide are also used (see Section 3.1.3.). Magnetic iron oxide pigments are discussed in Section 5.1. Transparent iron oxide pigments are described in detail in Section 5.4.1. Methods of analysis and specifications of iron oxide pigments are listed in the standards given in Table 1.1.

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Tab. 3.1: Iron oxides used as pigments.

Formula	Synonym	CAS-No.	Structure	Properties
α-FeOOH	goethite C.I. Pigment Yellow 42	1310-14-1 20344-49-1 20344-49-4 51274-00-1	diaspore	color changes with increasing particle size from green–yellow to brown–yellow
γ-FeOOH	lepidocrocite	12022-37-6	boehmite	color changes with increasing particle size from yellow to orange
α-Fe_2O_3	hematite C.I. Pigment Red 101	1317-60-8 1317-63-1 1309-37-1	corundum	color changes with increasing particle size from light red to dark violet
γ-Fe_2O_3	maghemite	12134-66-6	ordered spinel	ferrimagnetic color: brown
Fe_3O_4	magnetite C.I. Pigment Black 11	1317-61-9 1309-38-2 12227-89-3	spinel	ferrimagnetic color: black
“Iron Oxide”	unspecified	1332-37-2	unspecified	low value products

3.1.1.1
Natural Iron Oxide Pigments

Naturally occurring iron oxides and iron oxide hydroxides were used as pigments in prehistoric times (Altamira cave paintings) [3.3]. The Egyptians, Greeks, and ancient Romans also used them as coloring materials.

Hematite (α-Fe_2O_3) has attained economic importance as a red pigment, geothite (α-FeOOH) as yellow, and the umbers and siennas as brown pigments. Deposits with high iron oxide contents are exploited preferentially. Naturally occurring magnetite (Fe_3O_4) has poor tinting strength as a black pigment, and has found little application in the pigment industry. The natural iron oxides and hydroxides are described in detail by Cornell and Schwertmann [3.2].

Hematite is found worldwide but in large quantities in the vicinity of Malaga in Spain (Spanish red) and near the Persian Gulf (Persian red). The Spanish reds have a brown undertone. Their water-soluble salt content is very low and their Fe_2O_3 content often exceeds 90%. The Persian reds have a pure hue, but their water-soluble salt content is disadvantageous for some applications. Other natural hematite deposits are of only local importance. A special variety occurs in the form of platelets and is extracted in large quantities in Kärnten (Austria). This micaceous iron oxide (MIO) is mainly used in corrosion protection coatings.

Goethite is the colored component of yellow ocher, a weathering product mainly of siderite, sulfidic ores, and feldspar. It occurs in workable amounts mainly in the Republic of South Africa and France. The Fe_2O_3 content gives an indication of the iron oxide hydroxide content of the ocher, and is ca. 20% in the French deposits and ca. 55% in the South African ones.

Umbers are mainly found in Cyprus. In addition to Fe_2O_3 (45–70%), they contain considerable amounts of manganese dioxide (5–20%). In the raw state, they are deep brown to greenish brown and when calcined are dark brown with a red undertone (burnt umbers).

Siennas, mainly found in Tuscany, have an average Fe_2O_3 content of ca. 50%, and contain <1% manganese dioxide. They are yellow-brown in the natural state and red-brown when calcined [3.4].

The processing of natural iron oxide pigments depends on their composition. They are washed, slurried, dried, ground, or dried immediately and then ground in ball mills, or more often in disintegrators or impact mills [3.5].

Siennas and umbers are calcined in a directly fired furnace, and water is driven off. The hue of the products is determined by the calcination period, temperature, and raw material composition [3.6].

Natural iron oxide pigments are mostly used as inexpensive marine coatings or in coatings with a glue, oil, or lime base. They are also employed to color cement, artificial stone, and wallpaper. Ocher and sienna pigments are used in the production of crayons, drawing pastels, and chalks [3.7].

For standards see Table 1.1 (Iron, manganese oxide pigments: “Methods of analysis”; “Natural, specification”; “Sienna, specification”; and "Umber, specification"). The economic importance of the natural iron oxide pigments has decreased in recent years in comparison with the synthetic materials.

3.1.1.2

Synthetic Iron Oxide Pigments

Synthetic iron oxide pigments have become increasingly important due to their pure hue, consistent properties, and tinting strength. Single-component forms are mainly produced with red, yellow, orange, and black colors. Their composition corresponds to that of the minerals hematite, geothite, lepidocrocite, and magnetite. Brown pigments usually consist of mixtures of red and/or yellow and/or black; homogeneous brown phases are also produced, e.g., $(Fe,Mn)_2O_3$ and γ-Fe_2O_3, but quantities are small in comparison to the mixed materials. Ferrimagnetic γ-Fe_2O_3 is of importance for magnetic recording materials (see Section 5.1.).

Several processes are available (Table 3.2) for producing high-quality iron oxide pigments with controlled mean particle size, particle size distribution, particle shape, etc.

1. Solid-state reactions (red, black, brown)
2. Precipitation and hydrolysis of solutions of iron salts (yellow, red, orange, black)
3. Laux process involving reduction of nitrobenzene (black, yellow, red)

The raw materials are mainly byproducts from other industries: steel scrap obtained from deep drawing, grindings from cast iron, $FeSO_4 \cdot 7\ H_2O$ from TiO_2 production or from steel pickling, and $FeCl_2$ also from steel pickling.

Tab. 3.2: Reaction equations for the production of iron oxide pigments.

Color	Reaction				Process
Red	$6\ FeSO_4 \cdot x\ H_2O + 1\frac{1}{2}\ O_2$	$\rightarrow$	$Fe_2O_3 + 2\ Fe_2(SO_4)_3 + 6\ H_2O$	(3.1a)	copperas process
	$2\ Fe_2(SO_4)_3$	$\rightarrow$	$2\ Fe_2O_3 + 6\ SO_3$	(3.1b)	
	$2\ Fe_3O_4 + \frac{1}{2}\ O_2$	$\rightarrow$	$3\ Fe_2O_3$	(3.2)	calcination
	$2\ FeOOH$	$\rightarrow$	$Fe_2O_3 + H_2O$	(3.3)	calcination
	$2\ FeCl_2 + 2\ H_2O + \frac{1}{2}\ O_2$	$\rightarrow$	$Fe_2O_3 + 4\ HCl$	(3.4)	Ruthner process
	$2\ FeSO_4 + \frac{1}{2}\ O_2 + 4\ NaOH$	$\rightarrow$	$Fe_2O_3 + 2\ Na_2SO_4 + 2\ H_2O$	(3.5)	precipitation
Yellow	$2\ FeSO_4 + 4\ NaOH + \frac{1}{2}\ O_2$	$\rightarrow$	$2\ \alpha\text{-}FeOOH + 2\ Na_2SO_4 + H_2O$	(3.6)	precipitation
	$2\ Fe + 2\ H_2SO_4$	$\rightarrow$	$2\ FeSO_4 + 2\ H_2$	(3.7a)	Penniman process
	$2\ FeSO_4 + \frac{1}{2}\ O_2 + 3\ H_2O$	$\rightarrow$	$2\ \alpha\text{-}FeOOH + 2\ H_2SO_4$	(3.7b)	
	$2\ Fe + \frac{1}{2}\ O_2 + 3\ H_2O$	$\rightarrow$	$2\ \alpha\text{-}FeOOH + 2\ H_2$	(3.7c)	
	$2\ Fe + C_6H_5NO_2 + 2\ H_2O$	$\rightarrow$	$2\ \alpha\text{-}FeOOH + C_6H_5NH_2$	(3.8)	Laux process
Orange	$2\ FeSO_4 + 4\ NaOH + \frac{1}{2}\ O_2$	$\rightarrow$	$2\ \gamma\text{-}FeOOH + 2\ Na_2SO_4 + H_2O$	(3.9)	precipitation
Black	$3\ FeSO_4 + 6\ NaOH + \frac{1}{2}\ O_2$	$\rightarrow$	$Fe_3O_4 + 3\ Na_2SO_4 + 3\ H_2O$	(3.10)	1-step precipitation
	$2\ FeOOH + FeSO_4 + 2\ NaOH$	$\rightarrow$	$Fe_3O_4 + Na_2SO_4 + 2\ H_2O$	(3.11)	2-step precipitation
	$9\ Fe + 4\ C_6H_5NO_2 + 4\ H_2O$	$\rightarrow$	$3\ Fe_3O_4 + 4\ C_6H_5NH_2$	(3.12)	Laux process
	$3\ Fe_2O_3 + H_2$	$\rightarrow$	$2\ Fe_3O_4 + H_2O$	(3.13)	reduction
Brown	$2\ Fe_3O_4 + \frac{1}{2}\ O_2$	$\rightarrow$	$3\ \gamma\text{-}Fe_2O_3$	(3.14)	calcination
	$3\ Fe_3O_4 + Fe_2O_3 + MnO_2 + \frac{1}{2}\ O_2$	$\rightarrow$	$(Fe_{11},Mn)O_{18}$	(3.15)	calcination

Iron oxides obtained after flame spraying of spent hydrochloric acid pickle liquor, red mud from bauxite processing, and the product of pyrites combustion are of minor importance. They yield pigments with inferior color properties that contain considerable amounts of water-soluble salts. They can therefore only be used in low-grade applications.

Solid-State Reactions of Iron Compounds

Black iron oxides obtained from the Laux process (see below) or other processes may be calcined in rotary kilns with an oxidizing atmosphere under countercurrent flow to produce a wide range of different red colors, depending on the starting material (Eq. (3.2)). The pigments are ground to the desired particle size in pendular mills, pin mills, or jet mills, depending on their hardness and intended use.

The calcination of yellow iron oxide produces pure red iron oxide pigments with a high tinting strength (Eq. (3.3)). Further processing is similar to that of calcined black pigments. High-quality pigments called copperas reds are obtained by the thermal decomposition of $FeSO_4 \cdot 7\ H_2O$ in a multistage process (Eq. (3.1 a) and (3.1 b)), (Figure 3.1). If an alkaline-earth oxide or carbonate is included during calcination, the sulfate can be reduced with coal or carbon-containing compounds to produce sulfur

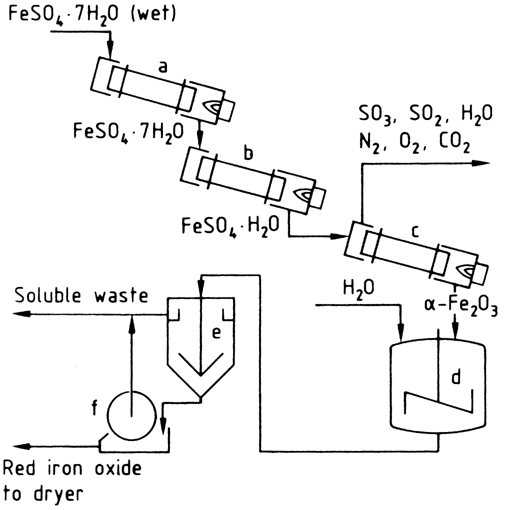

Fig. 3.1 Production of copperas red. a) dryer, b) rotary kiln (dewatering), c) rotary kiln, d) tank, e) thickener, f) filter.

dioxide, which is oxidized with air to give sulfuric acid [3.8–3.11]. The waste gases and the dissolved impurities that are leached out in the final stage present ecological problems, however.

Lower quality products can be obtained by single-stage calcination of iron(II) sulfate heptahydrate in an oxidizing atmosphere. The pigments have a relatively poor tinting strength and a blue tinge. Decomposition of iron(II) chloride monohydrate in air at high temperatures (Eq. (3.4)) also yields a low-quality red iron oxide pigment [3.12]. In a new process, micaceous iron oxide is obtained in high yield by reacting iron(III) chloride and iron at 500–1000 °C in an oxidizing atmosphere in a tubular reactor [3.13].

Black Fe_3O_4 pigments with a high tinting strength can be prepared by calcining iron salts under reducing conditions [3.14]. This process is not used industrially because of the furnace gases produced.

Controlled oxidation of Fe_3O_4 at ca. 500 °C (Eq. (3.14)) produces a single-phase brown γ-Fe_2O_3 with a neutral hue [3.15].

Calcination of α-FeOOH with small quantities of manganese compounds gives homogeneous brown pigments (Eq. (3.15)) with the composition $(Fe,Mn)_2O_3$ [3.16]. Calcination of iron and chromium compounds that decompose at elevated temperatures yields the corresponding pigments with the composition $(Fe,Cr)_2O_3$ [3.17].

Precipitation Processes

In principle, all iron oxide hydroxide phases can be prepared from aqueous solutions of iron salts (Table 3.2). However, precipitation with alkali produces neutral salts (e.g., Na_2SO_4, NaCl) as byproducts, which enter the wastewater.

Precipitation is especially suitable for producing soft pigments with a pure, bright hue. The manufacture of α-FeOOH yellow is described as an example (Eq. (3.6)). The raw materials are iron(II) sulfate ($FeSO_4 \cdot 7\ H_2O$) or liquors from the pickling of iron and steel ($FeSO_4$ or $FeCl_2$ [3.18]), and alkali (e.g. NaOH, $Ca(OH)_2$, ammonia, or magnesite [3.19]). The pickle liquors usually contain appreciable quantities of free acid, and are therefore first optionally neutralized by reaction with scrap iron. Other metallic ions should not be present in large amounts, because they have an adverse effect on the hue of the iron oxide pigments.

The solutions of the iron salts are first mixed with alkali in open reaction vessels (Figure 3.2, left-hand side) and oxidized, usually with air. The quantity of alkali used is such that the pH remains acidic. The reaction time (ca. 10–100 h) depends on the temperature (10–90 °C) and on the desired particle size of the pigment. This method yields yellow pigments (α-FeOOH) [3.20, 3.21]. If yellow nuclei are produced in a separate reaction (Figure 3.2, tank a), highly consistent yellow iron oxide pigments with a pure color can be obtained [3.22].

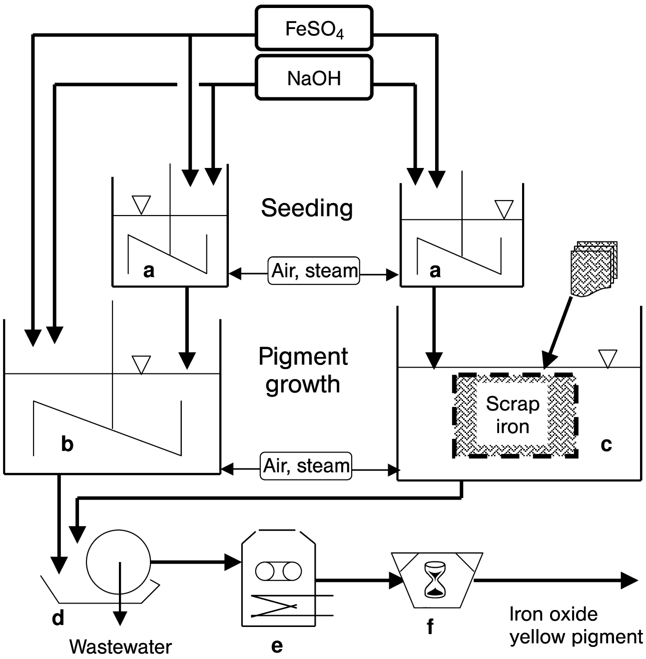

Fig. 3.2 Production of yellow iron oxide by the precipitation (left) and Penniman (right) process. a) seeding tank, b) precipitation pigment reactor, c) Penniman pigment reactor with scrap basket, d) filter, e) dryer, f) mill.

If precipitation is carried out at ca. 90 °C while air is passed into the mixture at ca. pH ≥7, black iron oxide pigments with a magnetite structure and a good tinting strength are obtained when the reaction is stopped at a FeO : Fe_2O_3 ratio of ca. 1 : 1 (Eq. (3.10)). The process can be accelerated by operating at 150 °C under pressure; this technique also improves pigment quality [3.23]. Rapid heating of a suspension of iron oxide hydroxide with the necessary quantity of $Fe(OH)_2$ to ca. 90 °C also produces black iron oxide (Eq. (3.11)) of pigment quality [3.24, 3.25].

Orange iron oxide with the lepidocrocite structure (γ-FeOOH) is obtained if dilute solutions of the iron(II) salt are precipitated with sodium hydroxide solution or other alkalis until almost neutral. The suspension is then heated for a short period, rapidly cooled, and oxidized (Eq. (3.5)) [3.26, 3.27].

Very soft iron oxide pigments with a pure red color may be obtained by the *direct red*-method: first preparing α-Fe_2O_3 nuclei, and then continuously adding solutions of iron(II) salt with atmospheric oxidation at 80 °C. The hydrogen ions liberated by oxidation and hydrolysis are neutralized by adding alkali and keeping the pH constant [3.28]. Pigment-quality α-Fe_2O_3 is also obtained when solutions of an iron(II) salt, preferably in the presence of small amounts of other cations, are reacted at 60–95 °C with excess sodium hydroxide and oxidized with air [3.29].

The *Penniman process* is probably the most widely used production method for yellow iron oxide pigments [3.30, 3.31]. This method considerably reduces the quantity of neutral salts formed as byproducts. The raw materials are iron(II) sulfate, sodium hydroxide solution, and scrap iron. If the sulfate contains appreciable quantities of salt impurities, these must be removed by partial precipitation. The iron must be free of alloying components. The process usually consists of two stages (Figure 3.2, right-hand side).

In the first stage, nuclei are prepared by precipitating iron(II) sulfate with alkali (e.g., sodium hydroxide solution) at 20–50 °C with aeration (tank a). Depending on the conditions, yellow, orange, or red nuclei may be obtained. The suspension of nuclei is pumped into vessels charged with scrap iron (reactor c) and diluted with water. Here, the process is completed by growing the iron oxide hydroxide or oxide onto the nuclei. The residual iron(II) sulfate in the nuclei suspension is oxidized to iron(III) sulfate by blasting with air at 75–90 °C. The iron(III) sulfate is then hydrolyzed to form FeOOH or α-Fe_2O_3. The liberated sulfuric acid reacts with the scrap iron to form iron(II) sulfate, which is also oxidized with air (Eq. (3.7 a–c)). The reaction time can vary from days to several weeks, depending on the conditions chosen and the desired pigment. At the end of the reaction, metallic impurities and coarse particles are removed from the solid with sieves or hydrocyclones; water-soluble salts are removed by washing. Drying is carried out with band or spray dryers (e) and disintegrators or jet mills are used for grinding (f). The main advantage of this process over the precipitation process lies in the small quantity of alkali and iron(II) sulfate required. The bases are only used to form the nuclei and the relatively small amount of iron(II) sulfate required initially is continually renewed by dissolving the iron by reaction with the sulfuric acid liberated by hydrolysis. The process is thus considered environmentally friendly. The iron oxide pigments produced by the Penniman process are soft, have good wetting properties, and a very low flocculation tendency [3.30–3.38].

Under suitable conditions the Penniman process can also be used to produce reds directly. The residual scrap iron and coarse particles are removed from the pigment, which is then dried [3.39] and ground using disintegrators or jet mills. These pigments have unsurpassed softness. Depending on the raw materials, they usually have purer color than the harder red pigments produced by calcination, but the moisture content is higher and the change in hue with intensive milling should not be neglected.

The Laux Process

The Béchamp reaction (i.e., the reduction of aromatic nitro compounds with antimony or iron), which has been known since 1854, normally yields a black–gray iron oxide mud that cannot be transformed into an inorganic pigment. By adding iron(II) chloride or aluminum chloride solutions, sulfuric acid, and phosphoric acid, Laux modified the process to yield high-quality iron oxide pigments (Eq. (3.8) and (3.12)) [3.40]. Many types of pigments can be obtained by varying the reaction conditions. The range extends from yellow to brown (mixtures of α-FeOOH and/or α-Fe_2O_3 and/or Fe_3O_4) and from red to black. If, for example, iron(II) chloride is added, a black pigment with very high tinting strength is produced [3.40]. However, if the nitro compounds are reduced in the presence of aluminum chloride, high-quality yellow pigments are obtained [3.41]. Addition of phosphoric acid leads to the formation of light to dark brown pigments with good tinting strength [3.42]. Calcination of these products (e.g., in rotary kilns) gives light red to dark violet pigments (Eq. (3.2)). The processes are illustrated in Figure 3.3.

The type and quality of the pigment are determined not only by the nature and concentration of the additives, but also by the reaction rate. The rate depends on the grades of iron used, their particle size, the rates of addition of the iron and nitrobenzene (or other nitro compound), and the pH value. No bases are required to precipitate the iron compounds. Only ca. 3% of the theoretical amount of acid is required to dissolve all of the iron. The aromatic nitro compound oxidizes the Fe^{2+} to Fe^{3+} ions, acid is liberated during hydrolysis and pigment formation, and more metallic iron is dissolved by the liberated acid to form iron(II) salts; consequently, no additional acid is necessary.

The iron raw materials used are grindings from iron casting or forging that must be virtually free of oil and grease. The required fineness is obtained by size reduction in edge runner mills and classification with vibratory sieves. The iron and the nitro compound are added gradually via a metering device to a stirred tank (a) containing the other reactants (e.g., iron(II) chloride, aluminum chloride, sulfuric acid, and phosphoric acid). The system rapidly heats up to ca. 100 °C and remains at this temperature for the reaction period. The nitro compound is reduced to form an amine (e.g., aniline from nitrobenzene), which is removed by steam distillation. Unreacted iron is also removed (e.g., in shaking tables, c). The pigment slurry is diluted with water in settling tanks (d) and the pigment is washed to remove salts, and filtered on rotary filters (e). It may then be dried on a band, pneumatic conveyor, or spray dryers to form yellow or black pigments, or calcined in rotary kilns (h) in an oxidizing atmosphere to give red or brown pigments. Calcination in a nonoxidizing atmosphere at 500–700 °C improves the tinting strength [3.43]. The pigments are then ground to the desired fineness in pendular mills, pin mills, or jet mills, depending on their hardness and application.

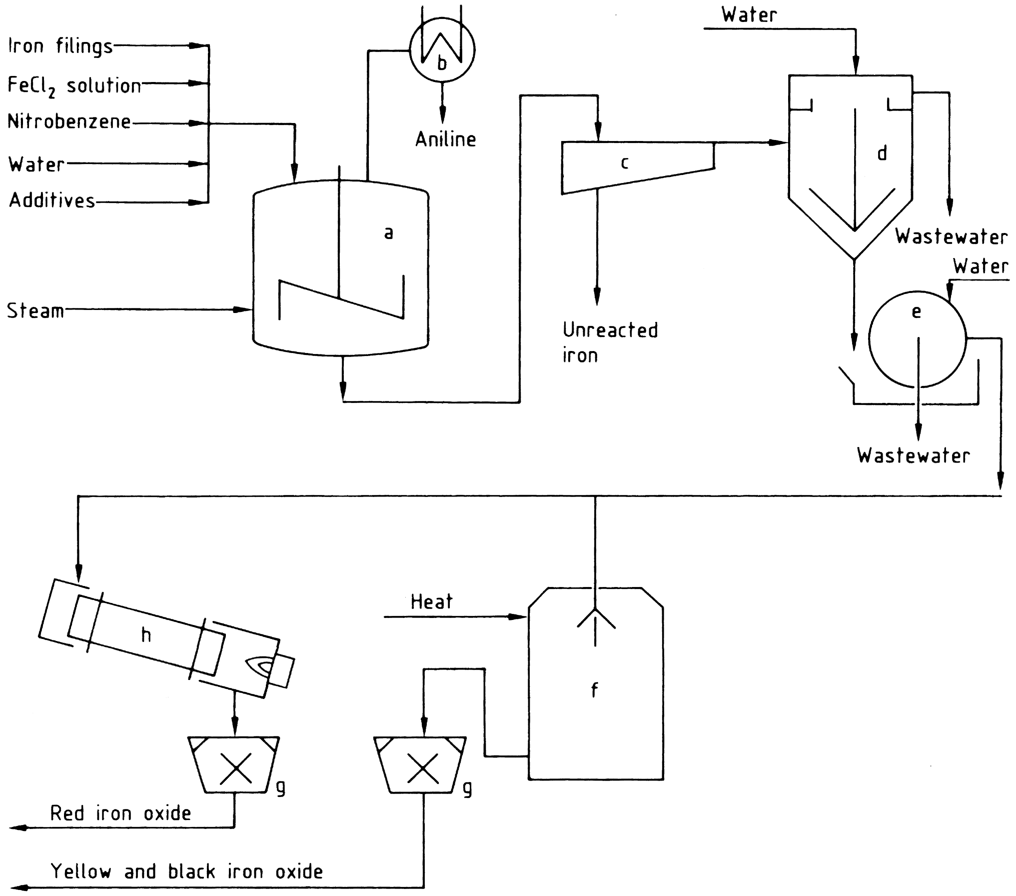

Fig. 3.3 Production of iron oxide pigments by the Laux process.a) reactor, b) condenser, c) classifier, d) thickener, e) filter, f) dryer, g) mill, h) rotary kiln.

The Laux process is a very important method for producing iron oxide because of the coproduction of aniline; it does not generate byproducts that harm the environment.

Other Production Processes

The three processes already described are the only ones that are used on a large scale. The following processes are used on a small scale for special applications:

1. Thermal decomposition of $Fe(CO)_5$ to form transparent iron oxides (see Section 5.4.1) [3.44]
2. Hydrothermal crystallization for the production of α-Fe_2O_3 in platelet form [3.45].

3.1.1.3
Toxicology and Environmental Aspects

The Berufsgenossenschaft der Chemischen Industrie (Germany's workers health authority for the chemical industry) has recommended that all iron oxide pigments should be classified as inert fine dusts with an MAK value of 3 mg m^{-3} [3.46].

Iron oxide pigments produced from pure starting materials may be used as colorants for food and pharmaceutical products [3.47]. Synthetic iron oxides do not contain crystalline silica and therefore are not considered to be toxic, even under strict Californian regulations.

3.1.1.4
Quality

The red and black iron oxide pigments produced by the methods described have a Fe_2O_3 content of 92–96 wt.%. For special applications (e.g., ferrites) analytically pure pigments with Fe_2O_3 contents of 99.5–99.8 wt.% are produced. The Fe_2O_3 content of yellow and orange pigments lies between 85 and 87 wt.% corresponding to FeOOH contents of 96–97 wt.%. For standards, see Table 1.1 (Iron oxide pigments: "Black, specification"; "Red, specification"; "Yellow, specification"; and "FeO content"). Variations of 1–2% in the iron oxide content are of no importance with respect to the quality of the pigments. Pigment quality is mainly determined by the quantity

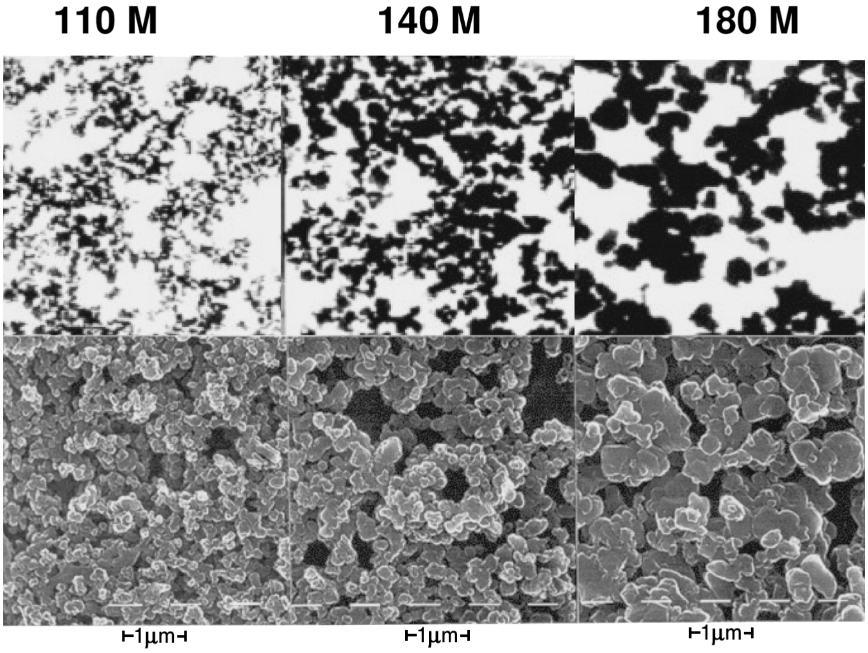

Fig. 3.4 Transmission electron microscopic pictures (upper parts) and scanning electron microscopic pictures (lower parts) of iron oxide red of different particle size (bar = 0.5 µm). Bayferrox® 110M shows a yellow tinge, while Bayferrox® 180M shows a bordeaux tinge.

and nature of the water-soluble salts, the particle size distribution (hue and tinting strength are affected) and the average particle size of the ground product. The hue of red iron oxide is determined by the particle diameter, which is ca. 0.1 µm for red oxides with a yellow tinge and ca. 1.0 µm for violet hues (Figure 3.4).

The optical properties of the yellow, usually needle-shaped, iron oxide pigments depend not only on the particle size, but also on the length to width ratio (e.g., length = 0.3–0.8 µm, diameter = 0.05–0.2 µm, length : diameter ratio = ca. 1.5–8). In applications for which needle-shaped particles are unsuitable, spheroidal pigments are available (Figure 3.5) [3.48]. Black iron oxide pigments (Fe_3O_4) have particle diameters of ca. 0.1–0.6 µm. An electron microscopic picture is given in Figure 5.7 in Section 5.1.6.

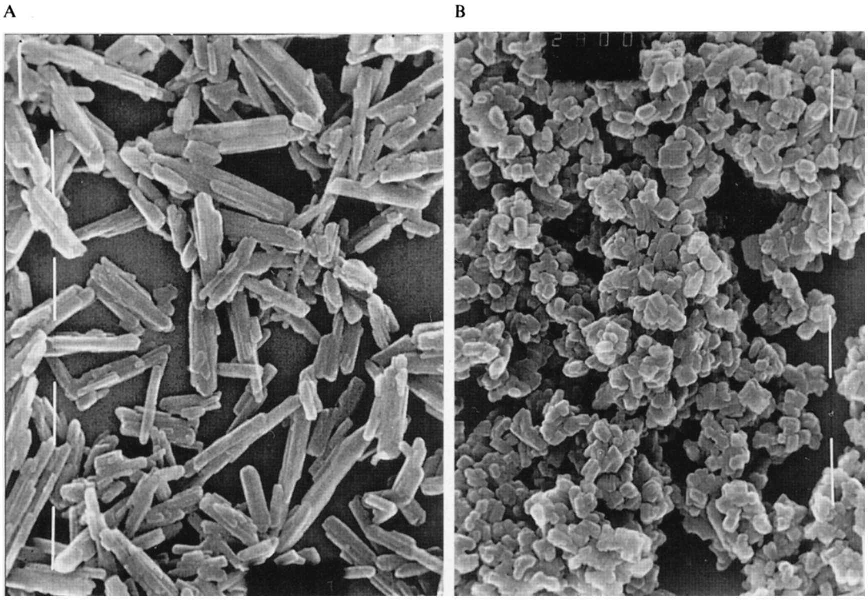

Fig. 3.5 SEM pictures of α-FeOOH pigments. A) needle-like pigment (Bayferrox® 420) with standard silking, B) spheroidal pigment (Bayferrox® 915) with low silking effect.

Some iron oxide pigments have a limited stability on heating. Red iron oxide is stable up to 1200 °C in air. In the presence of oxygen, black iron oxide changes into brown γ-Fe_2O_3 at ca. 180 °C and then into red α-Fe_2O_3 above 350 °C. Yellow iron oxide decomposes above ca. 180 °C to form red α-Fe_2O_3 with liberation of water. This temperature limit can be increased to ca. 260 °C by stabilization with basic aluminum compounds. The thermal behavior of brown iron oxides produced by mixing depends on their composition.

3.1.1.5
Uses

All synthetic iron oxides possess good tinting strength and excellent hiding power. They are also lightfast and resistant to alkalis. These properties are responsible for their versatility. The principle areas of use are shown in Table 3.3 [3.49, 3.50]. The main usage is in the construction industry followed by coatings but this differs by geographical region.

Tab. 3.3: Main areas of use for natural and synthetic iron oxide pigments.

Use	Amount, %		
	Europe	United States	World
Coloring construction materials	64	50	50
Paints and coatings	30	31	28
Plastics and rubber	4	18	6
Miscellaneous	2	1	16

Iron oxide pigments have long been used for coloring construction materials. Concrete roof tiles, paving bricks, fibrous cement, bitumen, mortar, rendering, etc. can be colored with small amounts of pigment that do not affect the setting time, compression strength, or tensile strength of the construction materials. Synthetic pigments are superior to the natural pigments due to their better tinting power and purer hue.

Natural rubber can only be colored with iron oxides that contain very low levels of copper and manganese ($Cu < 0.005\%$, $Mn < 0.02\%$). Synthetic rubber is less sensitive. In the paint and coating industries, iron oxide pigments can be incorporated in many types of binders. Some reasons for their wide applicability in this sector are pure hue, good hiding power, good abrasion resistance, and low settling tendency. Their high temperature resistance allows them to be used in enamels and ceramics.

The low tendency of migration and bleeding is of great advantage in plastics. Pure grades of iron oxide pigments are allowed for coloring of plastic articles for food and commodities [3.51].

The use of iron oxide as a polishing medium for plate glass manufacture has decreased sharply with the arrival of the float glass technology.

3.1.1.6
Economic Aspects

Accurate production figures for natural and synthetic iron oxide pigments are difficult to obtain, because statistics often also include nonpigmentary oxides (e.g., red mud from bauxite treatment, intermediate products used in ferrite production). World production of synthetic iron oxides in 2002 was estimated to be 700,000 t with a value of about 970 millions US$; production of natural oxides was estimated between 100,000 and 200,000 t. This uncertainty is due to the definition of the usage as pigment. The most important producing countries for synthetic pigments are Germany, the United States, Peoples Republic of China, Italy, Brazil, and Japan. The natural oxides are mainly produced in France, Spain, Cyprus, India, Iran, Italy, and Austria.

Important manufacturers are Lanxess (formerly Bayer) (Germany), Elementis (USA), Rockwood (USA), Deqing Huayuan Pigments (China) and Toda (Japan) [3.52].

3.1.2
Chromium Oxide Pigments

Chromium oxide pigments, also called chromium oxide green pigments, consist of chromium(III) oxide [*1308-38-9*], Cr_2O_3, M_r 151.99. Chromium oxide green is one of the few single-component pigments with green coloration. Chrome green is a blend of chrome yellow and iron blue pigments; phthalochrome green is a blend of chrome yellow and blue phthalocyanine pigments.

Natural, profitable deposits of chromium oxide are not known. In addition to pigment grade, chromium oxide producers usually also offer a technical grade for applications based on properties other than coloration. These include:

1. Metallurgy: aluminothermic production of chromium metal by reaction of aluminum powder and Cr_2O_3
2. Refractory industry: production of thermally and chemically resistant bricks and lining materials
3. Ceramic industry: coloring of porcelain enamels, ceramic frits, and glazes
4. Pigment industry: raw material for the production of chromium-containing stains and pigments based on mixed metal oxide phases
5. Grinding and polishing agent: chromium(III) oxide is used in brake linings and polishing agents due to its high hardness

Chromium oxide hydroxide and hydrated chromium oxide pigments (Grignets Green) have a very attractive blue–green color. They are of low opacity, but provide excellent lightfastness and good chemical resistance. Loss of water on heating limits the application temperature. These pigments are no longer of industrial importance [3.53].

3.1.2.1
Properties

Chromium(III) oxide crystallizes in the rhombohedral structure of the corundum type; space group $D_{3d}{}^6 - R\bar{3}c$, $\rho = 5.2\ \mathrm{g\ cm^{-3}}$. Because of its high hardness (ca. 9 on the Mohs scale) the abrasive properties of the pigment must be taken into account in certain applications [3.54]. It melts at 2435 °C but starts to evaporate at 2000 °C. Depending on the manufacturing conditions, the particle sizes of chromium oxide pigments are in the range 0.1–3 μm with mean values of 0.3–0.6 μm. Most of the particles are isometric. Coarser chromium oxides are produced for special applications, e.g., for applications in the refractory area.

Chromium oxide has a refractive index of ca. 2.5. Chromium oxide green pigments have an olive green tint. Lighter greens with yellowish hues are obtained with finely divided pigments, and darker, bluish tints with larger particle diameters; the darker pigments are weaker colorants. The maximum of the reflectance curve lies in the green region of the spectrum at ca. 535 nm (Figure 3.6, curve a). A weaker maximum in the violet region (ca. 410 nm) is caused by Cr–Cr interactions in the crystal lattice. Chromium oxide green pigments are used in IR-reflecting camouflage coatings because of their relatively high reflectance in the near infrared (Figure 3.6, curve b).

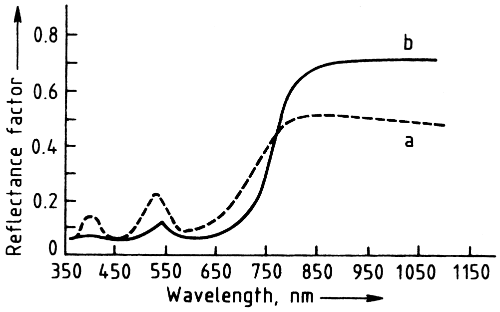

Fig. 3.6 Dependence of the reflectance of chromium oxide on the wavelength. a) Regular pigment, b) special product with larger particle size and high IR reflectance.

Since chromium(III) oxide is virtually inert, chromium oxide green pigments are remarkably stable. They are insoluble in water, acid, and alkali and are thus extremely stable to sulfur dioxide and in concrete. They are light-, weather-, and temperature-resistant. A change of the tint only occurs above 1000 °C due to particle growth.

3.1.2.2
Production

Alkali dichromates are used as starting materials for the production of chromium(III) oxide pigments. They are available as bulk industrial products in the required purity. High impurity levels have an unfavorable effect on the hue.

Reduction of Alkali Dichromates

In industrial processes, solid alkali dichromates are reacted with reducing agents such as sulfur or carbon compounds. The reaction is strongly exothermic, and with sulfur proceeds as follows:

$$Na_2Cr_2O_7 + S \rightarrow Cr_2O_3 + Na_2SO_4$$

Washing can then easily separate sodium sulfate because it is water-soluble. The use of sulfur was first described in 1820 [3.55]. Roth described the use of $K_2Cr_2O_7$ in 1927 [3.56]. If charcoal is used in place of sulfur, Na_2CO_3 is formed as byproduct [3.57].

Finely divided sodium dichromate dihydrate is mixed homogeneously with sulfur. This mixture is then reacted in a furnace lined with refractory bricks at 750–900 °C. An excess of sulfur is used to ensure completion of the reaction. The reaction mass is leached with water to remove water-soluble components such as sodium sulfate and non-reacted chromate. The solid residue is then separated, dried, and ground.

If potassium dichromate is used instead of sodium dichromate, a green pigment with a more bluish hue is obtained.

If it is to be used as a pigment in paints and lacquers, chromium oxide green can be subjected to jet milling (micronization) to obtain the required properties (e.g., gloss).

Reduction of Ammonium Dichromate

Chromium(III) oxide can be obtained by thermal decomposition of ammonium dichromate. Above ca. 200 °C, a highly voluminous product is formed with elimination of nitrogen [3.58]. The pigment is obtained after addition of alkali salts (e.g., sodium sulfate) and subsequent calcination [3.59].

In the industrial process, a mixture of ammonium sulfate or chloride and sodium dichromate is calcined [3.60]:

$$Na_2Cr_2O_7 \cdot 2\,H_2O + (NH_4)_2SO_4 \rightarrow Cr_2O_3 + Na_2SO_4 + 6\,H_2O + N_2$$

The workup is then carried out as described above. A chromium oxide pigment obtained by this process typically contains (wt.%):

Cr_2O_3	99.0–99.5
SiO_2	0.05 (max.)
Al_2O_3	0.1 (max.)
Fe_2O_3	0.05 (max.)
S	ca. 0.02
Water	ca. 0.3

Chromium oxides with minimal sulfur content are preferred for metallurgical applications. These are obtained by reacting sodium dichromate with ammonium chloride or sulfate in a deficiency of 10 mol% [3.61]. Chromium(III) oxides with a low sulfur content can also be obtained by thermal aftertreatment [3.62]. Thermal decomposition of chromic acid anhydride (CrO_3) yields high-purity chromium(III) oxide [3.63].

The pigment properties of chromium oxides can be modified by precipitation of hydroxides (e.g., of titanium or aluminum), and subsequent calcining. This treatment changes the color to yellow–green, and decreases the flocculation tendency [3.64]. Aftertreatment with organic compounds (e.g., alkoxylated alkylsulfonamides) is also used [3.65].

Other Processes

Other production processes are suggested in the patent literature, but have not so far gained industrial importance. For instance, sodium dichromate can be mixed with heating oil and reacted at 300 °C. The soda formed must be washed out prior to calcining at 800 °C to avoid reoxidation in the alkaline melt [3.66].

In alkaline solution, sodium chromate can be reduced with sulfur at atmospheric pressure with formation of sodium thiosulfate. After neutralization, more sodium chromate is added to exhaust the reducing capacity of the thiosulfate. The mixture is calcined at 900–1070 °C [3.67].

Another process involves the shock heating of sodium dichromate in a flame at 900–1600 °C in the presence of excess hydrogen and chlorine to bind the alkali as sodium chloride [3.68]. This method is suitable for the preparation of pigment-grade chromium oxide of high purity, with especially low sulfur content.

Environmental Protection

Since alkali dichromates or chromic acid anhydride are used as starting materials for the production of chromium(III) oxides, occupational health requirements for the handling of hexavalent chromium compounds must be observed [3.69]. The sulfur dioxide formed on reduction with excess sulfur must be removed from the flue gases according to national regulations, e.g., by oxidation and absorption to H_2SO_4.

Process wastewater may contain small amounts of unreacted chromates; recovery is uneconomical. Prior to release into drainage systems, the chromates in these wastewater streams must be reduced (e.g., with SO_2 or $NaHSO_3$) and precipitated as chromium hydroxide [3.70]. In Germany, for example, the minimum requirements for wastewater in the production of chromium oxide pigments are specified in Ref. [3.71].

3.1.2.3
Quality Specifications and Analysis

International, technical specifications for chromium oxide pigments are defined in ISO 4621 (1986), they must have a minimum Cr_2O_3 content of 96 wt.%.

Various grades are defined according to their particle fineness as measured by the residue on a 45 μm sieve: grade 1, 0.01% residue (max.); grade 2, 0.1% (max.); and grade 3, 0.5% (max.).

ISO 4621 (1986) also specifies analytical methods. Usually, analysis of chromium and the byproducts is preceded by melting with soda and sodium peroxide. The content of water-soluble or acid-soluble chromium is becoming important from the toxicological and ecological point of view. It is determined according to DIN 53780 with water, or according to ISO 385615 with 0.1 mol L^{-1} hydrochloric acid.

3.1.2.4
Storage and Transportation

Chromium(III) oxide pigments are thermally stable and insoluble in water. They are not classified as hazardous materials and are not subject to international transport regulations. As long as they are kept dry their utility as a pigment is practically unlimited.

3.1.2.5
Uses

The use of chromium(III) oxide as a pigment for toys, cosmetics, and in plastics and paints that come into contact with food is permitted in national and international regulations [3.72–3.79]. Maximum limits for heavy metals or their soluble fractions are usually a prerequisite. Because pure starting materials are used, these limits are satisfied by most types of chromium oxide.

Chromium oxide is equally important as a colorant and in its other industrial applications. As a pigment, it is used predominantly in the paint and coatings industry for high-quality green paints with special requirements, especially for steel constructions (coil coating), facade coatings (emulsion paints), and automotive coatings.

A series of RAL (Reichs-Ausschuss für Lieferbedingungen) tints (e.g., Nos. 6003, 6006, 6011, 6014, and 6015) can be formulated based on chromium oxide. As mentioned previously, chromium oxide is also an important pigment for the formulation of green camouflage coatings (e.g., RAL 6031-F 9, Natogreen 285, Stanag 2338, and Forestgreen MIL-C-46168 C).

Except for the expensive cobalt green, chromium oxide is the only green pigment that meets the high color stability requirements for building materials based on lime and cement [3.80]. In plastics, however, chromium oxide green is only of minor importance because of its dull tint, but is widely used in coloring beer crates.

The industrial significance of chromium oxide is due to its chemical and physical properties. Its high purity makes it suitable as a starting material for the aluminothermic production of very pure chromium metal.

Since the late 1970s chromium oxide has gained significance as a raw material in the refractory industry. The addition of chromium oxide to bricks and refractory concrete based on alumina significantly improves their stability against slag in the production and processing of pig iron. Chromium oxide bricks containing ca. 95 wt.% Cr_2O_3 have become important in the production of E-glass reinforcement fibers for lining melting tanks. These linings have substantially improved furnace stability (i.e., prolonged furnace life).

The high hardness of chromium oxide resulting from its crystal structure is exploited in polishing agents for metals and in brake linings. Addition of a small amount of chromium oxide to magnetic materials of audio and videotapes imparts a self-cleaning effect to the sound heads.

3.1.2.6
Economic Aspects

Important producers are Elementis (USA and UK), Lanxess (Germany), NovoChrom (Novotroisk, Russia), ACCP (Aktubinsk, Kazakhstan) and Nihon Denko (Japan). Statistical data on the consumption of chromium oxide have not been published recently. However, it can be assumed that the world capacity in 2002 was about 100,000 t a^{-1}; the consumption as pigments in 2002 was estimated at 50,000 t.

3.1.2.7
Toxicology and Occupational Health

Toxicological or carcinogenic effects have not been detected in rats receiving up to 5% chromium(III) oxide in their feed [3.81] nor in medical studies performed in chemical plants producing chromium(III) oxide and chromium(III) sulfate [3.82]. The oral LD_{50} for chromium(III) oxide in the rat is >10,000 mg $kg^{g^{-1}}$; it does not irritate the skin or mucous membranes.

Chromium(III) oxide is not included in the MAK list (Germany), the TLV list (USA), or in the list of hazardous occupational materials of the EC [3.83]. In practice, this means that chromium(III) oxide can be regarded as an inert fine dust with a MAK value of 3 mg m^{-3} [3.84].

3.1.3
Mixed Metal Oxide Pigments

Mixed metal oxide (MMO) pigments are inorganic high performance pigments with outstanding fastness properties, which are used in paints, plastics, building materials, glass coatings and ceramics. For ceramics, numerous other complex inorganic colored mixed oxides (“stains”) exist, which can be consulted in the literature. The following description concentrates on mixed metal oxides for paints, plastics and concrete. In general, such pigments are finer in particle size and not always optimized for color stability in ceramic type applications.

From an application standpoint, high opacity, heat stability, IR reflectance, light- and weatherfastness as well as chemical resistance are the main reasons for using these pigments. Recent developments focus primarily on more economic higher strength versions, but there is also mention of new chemistries like Zn/Sn rutiles [3.85], new IR reflective chemistries [3.86, 3.87] as well as mixed metal oxides for new application fields like laser marking [3.88].

Chemically, MMO pigments are solid solutions, which means that a variety of metal oxides is homogenously distributed in the crystal lattice of the new chemical compound as if it were a solution but in the solid state. These compounds have different types of crystal structures including rutile, spinel, inverse spinel, hematite as well as the somewhat less common priderite and pseudobrookite (Table 3.4). Mixed metal oxides have their own chemical identity, which is not to be confused with a physical blend of its components. In the majority of available pigment chemistries, mixed metal oxides are highly inert chemical compounds, containing no relevant bio-available or degradable substances. Therefore, most pigments, referring to manufacturers statements on compliance, purity and safe handling [3.89], are considered non-toxic and comply with food contact as well as toy safety regulations [3.90, 3.91].

Structures can be modified with different metal oxides in order to support the reaction or to alter color properties. Also substitutions, particularly of antimony with tungsten or niobium in rutile structures, are common [3.92], resulting in different chemistries like the nickel rutile yellows Pigment Yellow 161 (NiNbTi), Pigment Yellow 162 (NiWTi), chromium rutile yellows Pigment Yellow 189 (CrNbTi), Pigment Yellow 163 (CrWTi) and manganese rutile browns Pigment Brown 37 (MnNbTi),

Tab. 3.4: Overview of predominant chemistries, comprising doped rutiles, hematites and (inverse) spinels.

Color Index	Chemical constituents	Structure	CAS-No.	Colors
Pigment Yellow 53	Ni(II), Sb(V), Ti(IV)	rutile	8007-18-9	green shade yellow
Pigment Brown 24	Cr(III), Sb(V), Ti(IV)	rutile	68186-90-3	ocher shade
Pigment Yellow 162	Cr(III), Nb(V), Ti(IV)	rutile	68611-42-7	ocher shade
Pigment Yellow 164	Mn(II), Sb(V), Ti(IV)	rutile	68412-38-4	brown
Pigment Yellow 119	Zn(II), Fe(II,III)	spinel	68187-51-9	ocher-brown
Pigment Blue 28	Co(II), Al(III)	spinel	1345-16-0	red shade blue
Pigment Blue 36	Co(II), Cr(III), Al(III)	spinel	68187-11-1	green shade blue
Pigment Green 26	Co(II), Cr(III)	spinel	68187-49-5	dark green
Pigment Green 50	Co(II), Ti(IV)	inverse spinel	68186-85-6	green
Pigment Brown 29/	Fe(II), Cr(III)	hematite	12737-27-8	brown
Pigment Green 17	Cr_2O_3, see Section 3.1.2		1308-38-9	
Pigment Brown 35	Fe(II,III), Cr(III)	spinel	68187-09-7	dark brown
Pigment Black 30	Ni(II), Fe(II,III), Cr(III)	spinel	71631-15-7	black
Pigment Black 26	Mn(II), Fe(II,III)	spinel	68186-94-7	black
Pigment Black 22 /	Cu(II), Cr(III)	spinel	55353-02-1	black
Pigment Black 28	Mn(II), Cu(II), Cr(III)	spinel	68186-91-4	
Pigment Black 27	Co(II), Cr(III), Fe(II)	spinel	68186-97-0	bluish black

Pigment Brown 45 (MnWTi). As it has become apparent that antimony is not bioavailable from doped rutiles, the trend for such substitutions with respect to food contact applications has strongly diminished. A more scientific survey on colored titanium MMO pigments is given by Maloney [3.93].

3.1.3.1
Manufacturing

Mixed metal oxide pigments are manufactured by a solid state chemical reaction at very high temperatures of approximately 800 to 1300 °C. Raw materials include metal oxides and salts, that can be converted into oxide upon heating. During the high temperature calcination process, the mixture of metal oxides is converted into a new chemical compound, which already possesses some color properties. Color and other physical properties are optimized for the end-use by finishing the crude pigment. This finishing involves micronizing and – in most cases – washing and drying the pigment. A manufacturing scheme is illustrated in Figure 3.7.

Detailed know-how and process control of each of the manufacturing steps is critical in achieving optimized pigment performance. Since, manufacturing involves solid-state chemistry and a high temperature process, much effort must be given to optimizing the process in order to obtain easily dispersible pigments with favorable color properties.

For rutile yellows, different colors can be obtained by variation of the calcination temperature. A higher calcination temperature gives darker grades with a higher chroma. However, the tinting strength drops in the same direction. With regard to opacity, optimum performance is found for medium shades, which can be explained by achieving a compromise between particle size (scattering) and lightness value (absorption) [3.94]. High strength versions have been introduced which both optimize particle size distribution and the amount of coloring ions that are included as dopants in the titanium oxide rutile structure.

For hematites and (inverse) spinels, color is also influenced by the calcination temperature. However, the main driving factor is the actual chemical composition, including the use of mineralizing agents. This opens numerous possibilities to obtain colored pigments with different shades.

3.1.3.2
Quality Aspects

The high temperature process explains the excellent heat stability of mixed metal oxides. One known exception is chrome antimony titanate. This compound is heat stable with regard to its composition, but it can still change color upon heat treatment in some engineering plastics or some specific enamels. It is assumed that this unwanted effect relates to the freezing of dopants (like chromium) in non-equilibrium positions, effecting changes in charge transfer bands. This effect can effectively be overcome using mineralizing agents, as mentioned in the patent literature [3.95, 3.96].

Another quality aspect relates to particle size and form. A narrow particle size distribution is normally required for favorable color properties. Due to the calcination process, larger agglomerates are easily formed. They may exist as oversized particles isolated from the main particle size distribution. Such oversized particles impact dispersibility by causing longer grinding times. This effect not only has an influence on the cost of dispersion, but also color stability problems should be anticipated. Mixed metal oxides, particularly the weaker colors like rutile yellows (Pigment Yellow 53, Pigment Brown 24), exhibit a strong color dependence on the grinding time, which is associated with the abrasion of these pigments. Abrasion is not only positively influenced by ensuring that oversized particles are eliminated from the main particle size

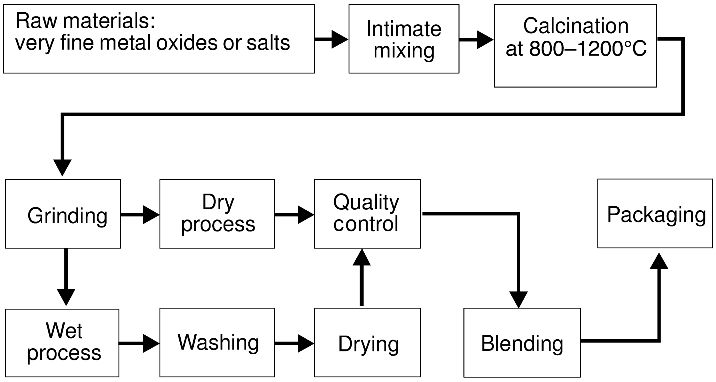

Fig. 3.7 Manufacturing scheme for mixed metal oxides.

distribution by extensive sieving or sifting processes, but also the particle form is of great impact. A spherical particle shape for rutile yellows is favorable, which tends to become more irregular with higher calcination temperatures. Recent developments have lead to darker, redder and more saturated chrome titanates, which still have a favorable spherical particle shape and thus lower abrasion.

Chemical conversion and the finishing process are typically controlled by ensuring that the produced batch fits coloristically the tight color specifications, which can be obtained for single pigment manufacturing. Properties like pH and water-soluble salts are also regularly monitored in order to ensure consistency in wetting and dispersion. Extractable metal analysis may complement quality control in order to ensure compliance with regulations.

3.1.3.3
Properties

Mixed metal oxides benefit from a low surface porosity (BET surfaces are typically in the range 3–6 $m^2\ g^{-1}$ for rutile yellows and 3–10 $m^2\ g^{-1}$ for cobalt greens and blues), resulting in low oil absorption numbers. As a consequence, high pigment loadings in color concentrates (pigment pastes, colorants and masterbatches) can be achieved. A high pigment concentration is often one of the few practical ways to overcome settling issues related to the high specific gravity (ca. 4–5 $g\ cm^{-3}$). Inorganic mixed metal oxide pigments are relatively easy to disperse, though shear stability issues may create difficulties in some particular resins and applications.

Most mixed metal oxide pigments show infrared reflectance, which is important for camouflage applications as well as applications with a defined minimum total solar reflectance [3.97]. Special pigments designed for infrared reflectance are the brownish to black pigments Pigment Brown 29, Pigment Green 17, Pigment Brown 35 and Pigment Black 30 (Table 3.4).

Rutile yellow pigments are often used in combination with high performance organic pigments in order to formulate brilliant colors that are non-toxic (as opposed to lead chromates, lead molybdates and supposedly cadmium pigments). Compared with titanium dioxide, nickel titanates give deeper colors when combined with organic pigments. Especially in combination with higher performance and more expensive organic pigments, the use of rutile yellow lowers the demand for organic pigment contents and thus overall pigmentation cost involved. Apart from enhancing color depth, chrome titanates also provide an increase in opacity. Rutile yellows are used in formulations of many standard industry colors (like RAL tone colors), which are less clean than the pure organic pigment. The main reason for formulating with rutile yellows is the improvement in weatherability due to the UV absorbing properties of nickel and chrome titanate yellows. Rutile yellows are also used as toners in pastel tone colors.

Zinc ferrites are excellent general-purpose pigments of yellowish brown color. As opposed to iron oxide yellows, zinc ferrites offer higher heat stability and can be used in plastics and coatings cured at temperatures above 120 °C. Zinc ferrites are coloristically not as clean as rutile yellows. Zinc ferrites can be slightly magnetic.

Manganese titanate brown pigments are mainly used because of their weathering properties. Particularly in rigid-PVC (vinyl siding), these iron-free browns have become important. Iron-containing pigments, particularly if highly soluble iron is involved, are known to catalyse the degradation of PVC by UV radiation [3.98].

Cobalt blue pigments exist in colors from a red shade to very greenish-turquoise-like. This bathochromic shift in the maximum absorption is obtained by substituting aluminum for chromium. Opacity is strongly increased and, as a consequence, the weatherability of pigmented coatings also tends to be better for Pigment Blue 36 than Pigment Blue 28. However, color and appearance (higher gloss) considerations often force the choice for Pigment Blue 28. Important progress has been reported by several manufacturers in providing high strength cobalt blues, with improved UV opacity and weathering properties. Furthermore, lowering of the pigmentation level to be used in engineering plastics minimizes any impact on mechanical strength properties. The use of cobalt blues and greens in plastics is driven by fastness properties as well as preventing warpage in polyolefins. Special areas are camouflage applications, which explicitly involve the cobalt chromite Pigment Green 26.

The role of brown and black pigments like Pigment Brown 29 (identical to Pigment Green 17), Pigment Brown 35 and Pigment Brown 30 is dominated by their ability to reflect in the near infrared as opposed to other inorganic brown pigments like iron oxides or other black pigments like copper chromite or carbon black [3.99]. The nickel–iron–chrome complex Pigment Brown 30 does not reflect as much in the near infrared as an iron chromite, but offers a more bluish tint. Brown colored iron chrome hematites are used in PVC pipe and window profiles as a non-toxic alternative to color formulations based on lead chromates, lead molybdates and some black (normally carbon black). Heat build-up on PVC profiles can be measured in accordance with ASTM D4803-96.

Copper chromite blacks are general-purpose pigments with outstanding durability and temperature resistance. Copper chromite blacks exhibit no infrared reflectance. The main application is in coatings for both dark grays and light colors. The more expensive cobalt chromites are only used in niche applications requiring higher heat stability. Manganese ferrites do not possess the weatherability and acid stability (Kesternich test) of copper chromite blacks, but can present a cost effective alternative if these properties are not required.

3.1.3.4
Economic Aspects

Statistical information is rarely available. The world demand in 1999 was estimated to be15,000–20,000 metric tons. The worldwide turnover with MMO was estimated to about US$ 300 millions for the same year. The main producers are BASF, CERDEC, Ciba, Heubach (Europe), Engelhard, Ferro (USA).

3.2
Cadmium Pigments

The term “cadmium pigments” is understood in the pigment industry to refer to the pure sulfides and sulfoselenides as well as zinc-containing sulfides of cadmium. Cadmium pigments containing mercury were still used up to the middle of the last century but, because of their toxic properties, are no longer industrially significant. Cadmium sulfide occurs naturally as cadmium blende or greenockite and has a hexagonal wurtzite crystal structure. However, the mineral itself does not have any pigment properties. The color of cadmium pigments can be controlled via the composition (Table 3.5) and the size of the primary particles. The relative size of cadmium pigment particles is indicated in Figure 3.8.

Tab. 3.5: Color, chemical composition and Color Index number of cadmium pigments.

	Formula		Color Index	CAS-No.
Cadmium yellow	(Cd,Zn)S	Pigment Yellow 35	77 205	8048-07-5
	CdS	Pigment Yellow 37	77 199	68859-25-6
Cadmium orange	Cd(S,Se) Se <10%	Pigment Orange 20	77 202	12656-57-4
Cadmium red	Cd(S,Se) Se >10%	Pigment Red 108	77 202	58339-34-7

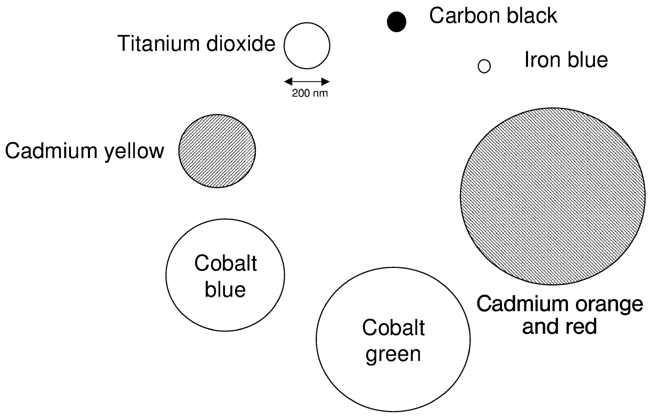

Fig. 3.8 Comparison of relative particle sizes of inorganic pigments.

Cadmium pigments are semiconductors. Their color is determined by the distance between the valence and conduction bands in the crystal lattice. The high color purity of the pigments is due to the steep reflectance spectra (Figure 3.9), compare also Figure 3.10 in Section 3.3. They cover a wide color range of the visible light spectrum.

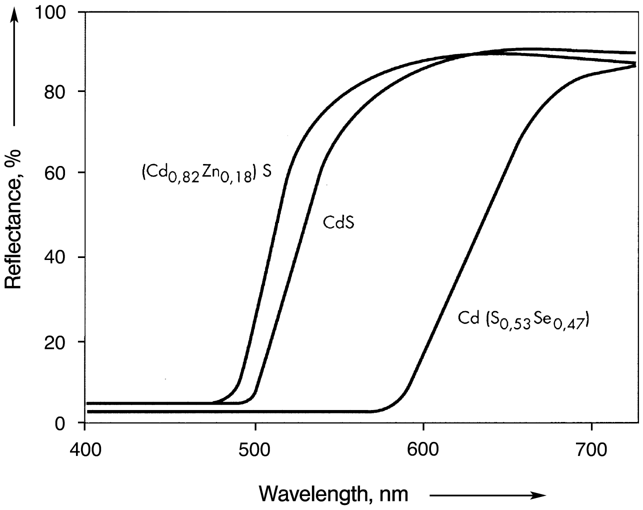

Fig. 3.9 Reflectance spectra of cadmium pigments [3.102].

3.2.1
Properties

Cadmium pigments are lightfast, stable at high temperatures, intensely colored and migration-resistant, but have only limited weather resistance. Their specific gravity is between 4.2 and 5.6 g cm^{-3} and their average particle size between 0.2 and 0.5 µm. They have very good hiding power and still find application in the coloring of engineering plastics and ceramics [3.100, 3.101]. They are practically insoluble in water and alkaline solutions, but are attacked and decomposed by acids. Care must be taken during application of these pigments, especially the red cadmium sulfoselenides, because of their sensitivity to friction. Excessive shear forces can cause a color change in the pigments.

The toxicological properties, identification requirements and application restrictions are described in detail in Ref. [3.102].

3.2.2
Manufacture

Two basic manufacturing processes are distinguished: the precipitation process and the powder process. Common to both of them is that the raw materials must be free of transition metal compounds, which form deeply colored sulfides (e.g. Cu, Fe, Ni, Co, Pb) [3.103].

In the precipitation process, a cadmium salt solution is reacted with sodium polysulfide solution. Zinc salts are then added to produce light yellow cadmium pigments; adding selenium allows hues ranging from orange and red to bordeaux. The precipitate is filtered off, dried, calcined in the absence of oxygen, wet-ground, dried and dry-ground.

In the powder process, finely divided cadmium carbonate or cadmium oxide is subjected to intensive mechanical mixing with sulfur and mineralizers and then calcined in the absence of oxygen. The addition of zinc or selenium produces the same effects as in the precipitation process. The product is worked up in the same way as in the precipitation process. The main producer of cadmium pigments is Millenium (USA).

3.3
Bismuth Pigments

Greenish yellow pigments based on bismuth orthovanadate [*14059-33-7*], $BiVO_4$, market introduction 1985, represent a class of pigments with interesting coloristic properties. They extend the familiar range of yellow inorganic pigments, e.g. iron yellow, chrome yellow, cadmium yellow, nickel titanium yellow, and chromium titanium yellow. In particular they substitute the greenish yellow lead chromate and cadmium sulfide pigments. In the Color Index they have been registered as C.I. Pigment Yellow 184.

The actual volume of bismuth vanadate pigments is estimated to be around 1200 $t\,a^{-1}$ and is steadily increasing.

Bismuth-containing special effect pigments based on platelet-shaped crystals of bismuth oxide chloride (bismuth oxychloride, BiOCl) have been known for a long time (see Section 5.3.1.3).

3.3.1
Historical and Economic Aspects

Bismuth vanadate occurs naturally as the brown mineral pucherite (orthorhombic), as clinobisvanite (monoclinic) and as dreyerite (tetragonal). However, these deposits are of no practical importance to the pigment industry. Its synthesis was first reported in 1924 in a patent for pharmaceutical uses [3.104]. The development of pigments based on $BiVO_4$ began in the mid-1970s. In 1976, DuPont described the preparation and properties of “brilliant primrose yellow” monoclinic bismuthvanadate [3.105]. Montedison developed numerous pigment combinations based on $BiVO_4$ [3.106]. Pigments containing other phases besides $BiVO_4$, e.g. Bi_2XO_6 ($X = Mo$ or W), have been reported by BASF [3.107] and became the first commercial product (trade name Sicopal® Yellow L 1110). Since then Bayer [3.108], Ciba-Geigy [3.109], BASF [3.110] and others [3.111] have published different methods for the manufacture of pigments based on $BiVO_4$. The following suppliers offer $BiVO_4$ pigments for the paint and plastic market: BASF AG, Ciba SC, Gebroeders Cappelle N.V. and Bruchsaler Farbenfabrik GmbH.

For 1999 the world consumption was estimated to about 500–750 t with a strong increase forecast.

BASF and Cappelle also offer reddish bismuth vanadate pigments within their product range [3.112, 3.113].

3.3.2
Properties

All commercial bismuth vanadate pigments are based on pure bismuth vanadate with monoclinic or tetragonal structure. The most important properties of all bismuth vanadate pigments are

- Excellent brightness of shade
- Very good hiding power
- High tinting strength
- Very good weather fastness
- High chemical resistance
- Easy dispersibility
- Environmentally friendly

In the following the physical and coloristic properties of a pure bismuth vanadate pigment are given (Sicopal® Yellow L 1100, BASF):

Density	$5.6\ \mathrm{g\ cm^{-3}}$
Refractive index n	2.45
Specific surface area (BET)	$10\ \mathrm{m^2\ g^{-1}}$
Oil absorption	27 g/100 g of pigment

Bismuth vanadate is a pigment with a greenish yellow shade. When compared with other yellow inorganic pigments, it most closely resembles cadmium yellow and chrome yellow in its coloristic properties (Figure 3.10).

Bismuth vanadate shows a sharp increase in reflection at 450 nm and considerably higher chroma than iron yellow or nickel titanium yellow. It has very good weather resistance both in full shade and in combination with TiO_2. General pigment properties are:

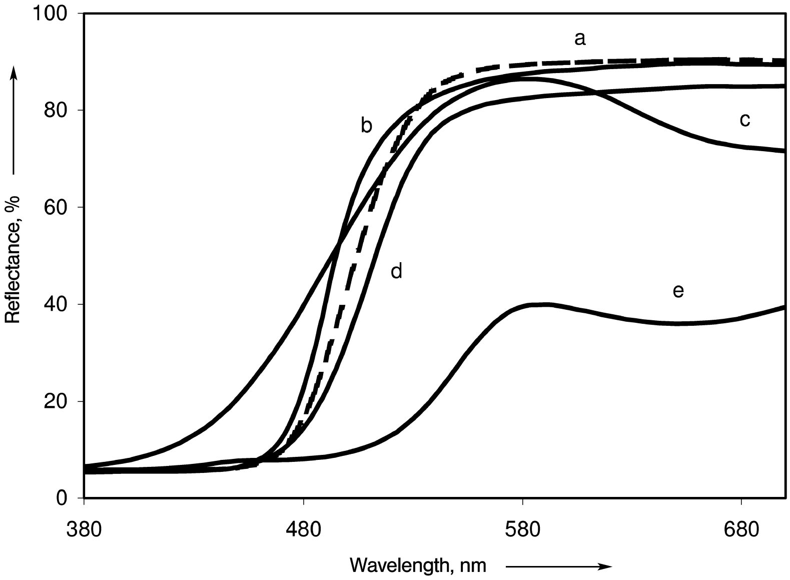

Fig. 3.10 Reflectance curves of inorganic yellow pigments. a) $BiVO_4$, b) CdS, c) $(Ti,Ni,Sb)O_2$, d) $PbCrO_4$–$PbSO_4$, e) FeOOH.

Mass-tone (alkyd/melamin system):	
Hue angle *H* ° (HGD, hue grade; CIELab)	93.8
Chroma C^* *ab* (CIELab)	95.4
Lightness L^* (CIELab)	87.1
Hiding power	at 42.5% by weight in dry film about 70 µm over black/white
Weather resistance (DIN 54002)	alkyd/melamine system
Full shade	4–5
Mixed with TiO_2, 1:11	4–5
Chemical resistance in cross-linked paint films	
acid	5 (2% HCl)
alkali	5 (2% NaOH)
Heat stability	180 °C

3.3.3
Production

Bismuth vanadate can be synthesized either 1. by solid state processing using the appropriate starting materials, e.g. Bi_2O_3 and V_2O_5, or 2. by co-precipitation from aqueous solutions.

1. Solid state reaction [3.105, 3.106, 3.108, 3.109]

$$Bi_2O_3 + V_2O_5 \; 2\,BiVO_4$$

2. Precipitation process [3.104–3.111]

$$Bi(NO_3)_3 + NaVO_3 + 2\ NaOH\ BiVO_4 + 3\ NaNO_3 + H_2O$$

Here bismuth vanadate is produced on combining an alkaline sodium or ammonium vanadate solution with an acidic bismuth nitrate solution. An amorphous product, of approximately bismuth-vanadium-oxide-hydroxide is formed in strongly acidic mediums (Figure 3.11). By heating the suspension to reflux and controlling pH, a transformation occurs producing a fine crystalline product (Figure 3.12). Selective formation of particular $BiVO_4$ modifications is possible by controlling the co-precipitation conditions. Only two of the four known polymorphs, i.e. the clinobisvanit (monoclinic) and the scheelit-like (tetragonal), are brilliant yellow in color. The tetragonal meta-stable modification is available for instance when doped with diverse elements, for example Ca and Mo [3.109]. The color tone and brilliance are strongly dependent upon the precipitation conditions; e.g. concentration, temperature and pH.

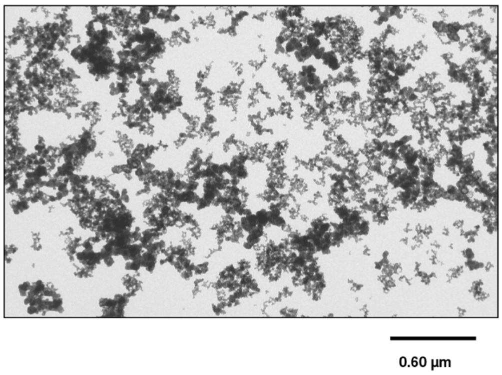

Fig. 3.11 Amorphous bismuth-vanadium-oxide-hydroxide before transformation.

Further incorporation of thermal processing into the manufacturing process leads to products with improved color properties. In the commercial paint sector, the use of inorganic stabilizers, for example calcium, aluminum or zinc phosphate or oxides like aluminum oxide, improves other pigment properties, e.g. photochromism, weathering and acid resistance.

For use in plastics the pigment is coated with a dense layer of silica (Figure 3.13) and other components to increase the stability in certain polymers, like polyamide, up to 300 °C [3.110].

To avoid any dust during handling, some suppliers offer the pigment in a fine granulated form (e.g. Sicopal® Yellow L 1100).

3.3.4
Uses

Bismuth vanadate pigments are used in the manufacture of lead-free, weather resistant, brilliant yellow colors for automotive OEM and re-finishes, industrial and

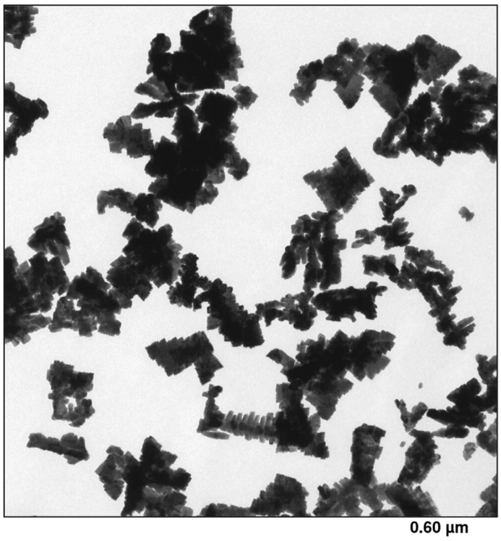

Fig. 3.12 Crystalline $BiVO_4$ after transformation.

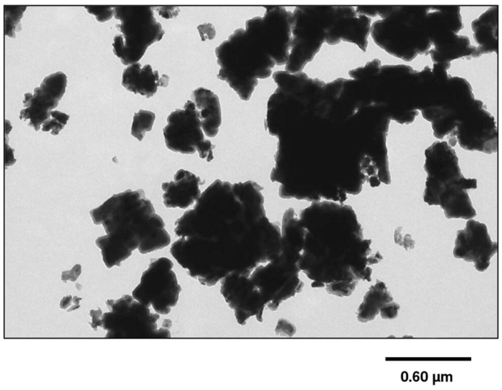

Fig. 3.13 $BiVO_4$ coated with SiO_2.

decorative paints, and partly for powder coatings and coil-coating systems. In combination with additional pigments, $BiVO_4$ can be used as a basis for important yellow, orange, red and green German standard colors RAL 1003, 1021, 1028, 2002, 3018, 6018, and 6029.

Thermostable bismuth vanadate pigments are available today with heat stability up to 300 °C. They exhibit very good fastness to light and weathering in plastics for outdoor use. The pigments have outstanding fastness to migration in plastics, and are easily dispersible. With their excellent heat stability, the thermostable types can be readily incorporated into polyolefins and ABS at 260–280 °C, and polyamide injection-molding materials at 280–300 °C.

3.3.5
Toxicology

Bismuth vanadate pigments are not acutely toxic either on inhalative or oral incorporation. Animal trials gave some indication of inhalational toxicity, which was probably due to the vanadium content. The "no effect level" for rats is 0.1 mg m^{-3} (exposure: 3 months, 6 h/day, 5 days/week) [3.114]. Toxic effects are observable only when the concentration in the lungs reaches levels that do not occur under the usual conditions of industrial hygiene. To diminish the associated risk, some manufactures supply bismuth vanadate pigments in a free flowing, low-dusting form, making them inaccessible to the lungs. Therefore the dust-free pigments can be handled under usual hygienic working conditions.

3.4
Chromate Pigments

The most important chromate pigments include the lead chromate (chrome yellow) and lead molybdate pigments (molybate orange and molybdate red) whose colors range from light lemon yellow to reds with a blue hue. Chrome yellow, molybdate orange, and molybdate red are used in the production of paints, coatings, and plastics, and are characterized by brilliant hues, good tinting strength, and good hiding power. Special treatment of the pigments has permitted continuous improvement of their resistance to light, weathering, chemicals, and temperature.

Chromate pigments may be combined with blue pigments (e.g., iron blue or phthalocyanine blue) to obtain high-quality chrome green and fast chrome green pigments. Molybdate orange and molybdate red pigments are often combined with red organic pigments, giving a considerable extension and fine-tuning of the color range.

Lead chromates, lead molybdates, chrome greens, and fast chrome greens are supplied as pigment powders, low-dust or dust-free preparations, or as pastes. The anticorrosive pigments zinc chromate, zinc tetraoxychromate, and strontium chromate are described in Section 5.2.4.2.

3.4.1
Chrome Yellow

The chrome yellow pigments [*1344-37-2*], C.I. Pigment Yellow 34:77600 and 77603, are pure lead chromate or mixed-phase pigments with the general formula $Pb(Cr,S)O_4$ [3.115] (refractive index 2.3–2.65, density ca. 6 g cm^{-3}).

Chrome yellow is insoluble in water. Solubility in acids and alkalis and discoloration by hydrogen sulfide and sulfur dioxide can be reduced to a minimum by precipitating inert metal oxides on the pigment particles.

Both lead chromate and lead sulfochromate (the latter is a mixed-phase pigment) can be orthorhombic or monoclinic; the monoclinic structure is the more stable [3.116]. The greenish-yellow orthorhombic modification of lead chromate is metastable at room temperature, and is readily transformed to the monoclinic modification under certain conditions (e.g., concentration, pH, temperature). The latter modification occurs naturally as crocoite.

Partial replacement of chromate by sulfate in the mixed-phase crystals causes a gradual reduction of tinting strength and hiding power, but allows production of the important chrome yellows with a greenish yellow hue.

3.4.1.1
Production

In large-scale production, lead or lead oxide is reacted with nitric acid to give lead nitrate solutions, which are then mixed with sodium dichromate solution. If the precipitation solutions contain sulfate, lead sulfochromate is formed as a mixed-phase pigment. After stabilization the pigment is filtered off, washed until free of electrolyte, dried, and ground.

The color of the pigment depends on the ratio of the precipitating components and other factors during and after precipitation (e.g., concentration, pH, temperature, and time). According to Wagner [3.117], the precipitated crystals are orthorhombic, but change very readily to the monoclinic form on standing; higher temperatures accelerate this conversion. Almost isometric particles that do not show any dichroism may be obtained by appropriate control of the process conditions. Needle-shaped monoclinic crystals should be avoided because they lead to disadvantages such as low bulk density, high oil absorption, and iridescence in the coating film.

Unstabilized chrome yellow pigments have poor lightfastness, and darken due to redox reactions. Recent developments have led to improvements in the fastness properties of chrome yellow pigments, especially towards sulfur dioxide and temperature. This has been achieved by coating the pigment particles with compounds of titanium, cerium, aluminum, antimony, and silicon [3.118–3.126].

Carefully controlled precipitation and stabilization provide chrome yellow pigments with exceptional fastness to light and weathering, and very high resistance to chemical attack and temperature, enabling them to be used in a wide field of applications. The following qualities are commercially available:

1. Unstabilized chrome yellows (limited importance)
2. Stabilized chrome yellows with higher color brilliance, stable to light and weathering
3. Highly stabilized chrome yellow pigments
    - very stable to light and weathering
    - very stable to light and weathering, and resistant to sulfur dioxide
    - very stable to high temperature, light, and weathering
    - very stable to high temperature, sulfur dioxide, light, and weathering
4. Low-dust products (pastes or powders)

Lightfast chrome yellow pigments that are coated with metal oxides (e.g., of aluminum, titanium, manganese) are produced by DuPont [3.119]. A chrome yellow that is coated with large amounts of silicate and alumina and which shows improved stability to temperature, light, and chemicals is also produced by DuPont [3.120].

Bayer described pigments containing lead chromate stabilized in aqueous slurry with silicate-containing solutions and antimony(III), tin(II), or zinc compounds [3.121].

ICI produces light- and weatherfast chrome yellow pigments stabilized with antimony compounds and silicates in the presence of polyhydric alcohols and hydroxyalkylamines [3.122].

Ten Horn describes a process for the production of lead sulfochromate containing at least 50% lead chromate [3.123]. This has a low acid-soluble lead content (<5% expressed as PbO, by BS 3900, Part B3, 1965).

BASF produces temperature-stable lead chromate pigments with a silicate coating obtained by hydrolysis of magnesium silicofluoride [3.124].

Heubach has developed a process for the alternative precipitation of metal oxides and silicates [3.125, 3.126]. A homogenizer is used to disperse the pigment particles during stabilization. Products obtained have a very good temperature resistance and very low lead solubility in acid (<1% Pb by DIN 55 770, 1986 or DIN/ISO 6713, 1985).

Continuous processes for the production of chromate pigments have been developed in the United States and Hungary [3.127, 3.128].

3.4.1.2
Uses

Chrome yellow pigments are mainly used for paints, coil coatings, and plastics. They have a low binder demand and good dispersibility, hiding power, tinting strength, gloss and gloss stability. Chrome yellows are used in a wide range of applications, not only for economic reasons but also on account of their valuable pigment properties. They are important base pigments for yellow colors in the production of automotive and industrial paints.

Chrome yellow pigments stabilized with a large amount of silicate play a major role in the production of colored plastics (e.g., PVC, polyethylene, or polyesters) with high temperature resistance. Incorporation into plastics also improves their chemical resistance to alkali, acid, sulfur dioxide, and hydrogen sulfide.

Chrome green and fast chrome green mixed pigments are produced by combining chrome yellow with iron blue or phthalocyanine blue.

World production of chrome yellow in 1999 was in the order of 30,000–35,000 metric tons.

3.4.2
Molybdate Red and Molybdate Orange

Molybdate red and molybdate orange [*12656-85-8*], C.I. Pigment Red 104:77605, are mixed-phase pigments with the general formula $Pb(Cr,Mo,S)O_4$ [3.115]. Most commercial products show a MoO_3 content of 4–6%, a refractive index of 2.3–2.65 and densities of about 5.4–6.3 g cm^{-3}). Their hue depends on the proportion of molybdate, crystal form, and particle size.

Pure tetragonal lead molybdate, which is colorless, forms orange to red tetragonal mixed-phase pigments with lead sulfochromate. The composition of molybdate red and molybdate orange pigments can be varied to give the required coloristic properties; commercial products usually contain ca. 10% lead molybdate. Lead molybdate pigments have a thermodynamically unstable tetragonal crystal modification that can be transformed into the undesirable stable yellow modification merely by dispersing [3.129]. This is especially true of the bluish varieties of molybdate red which have larger particles whose color can be changed to yellow by shear forces. The tetragonal modification of the lead molybdate pigments must therefore be stabilized after precipitation [3.130, 3.131].

The fastness properties of the molybdate orange and molybdate red pigments are comparable with those of the chrome yellows. As with the chrome yellows, the pigment particles can be coated with metal oxides, metal phosphates, silicates, etc., to give stabilized pigments with high color brilliance and good fastness properties, as well as highly stabilized grades with very good resistance to light, weathering, sulfur dioxide, and temperature, and with a very low content of acid-soluble lead (DIN 55770, 1986 or DIN/ISO 6713, 1985).

The colors of lead molybdate pigments vary from red with a yellow hue to red with a blue hue. Since chrome orange is no longer available (see Section 3.4.3), molybdate orange has become much more important.

3.4.2.1
Production

In the Sherwin–Williams process, a lead nitrate solution is reacted with a solution of sodium dichromate, ammonium molybdate, and sulfuric acid [3.132]. Instead of ammonium molybdate, the corresponding tungsten salt can be used, giving a pigment based on lead tungstate. The pigment is stabilized by adding sodium silicate (25% SiO_2) and aluminum sulfate ($Al_2(SO_4)_3 \cdot 18\ H_2O$) to the suspension, which is then neutralized with sodium hydroxide or sodium carbonate. The pigment is filtered off, washed until free of electrolyte, dried, and ground. Treatment with silicate increases the oil absorption; it also improves light fastness and working properties.

In the Bayer process, molybdate red is formed from lead nitrate, potassium chromate, sodium sulfate, and ammonium molybdate [3.121]. The pigment is then stabilized by adding water glass (28% SiO_2, 8.3% Na_2O) to the suspension with stirring, followed by solid antimony trifluoride, stirring for 10 min, and further addition of water glass. The pH is adjusted to 7 with dilute sulfuric acid and the pigment is filtered off, washed free of electrolyte, dried, and ground.

To give the lead molybdate pigments very good stability to light, weathering, chemical attack, and temperature, the same methods are used as those for the stabilization of chrome yellow pigments (see Section 3.4.1) [3.118–3.126].

3.4.2.2
Uses

Molybdate orange and molybate red are mainly used in paints, coil coatings, and for coloring plastics (e.g., polyethylene, polyesters, polystyrene). The temperature-stable grades are the most suitable for coil coatings and plastics.

Molybdate orange and molybdate red feature a low binder demand, good dispersibility, hiding power, and tinting strength, combined with very high lightfastness and weather resistance. Stabilization (see "Production") also yields high-grade pigments with good resistance to sulfur dioxide and high temperature.

Like chrome yellows, molybdate reds are used to produce mixed pigments. Combinations with organic red pigments provide a considerably extended color range. Such combinations have very good stability properties because the lightfastness and weather resistance of many organic red pigments are not adversely affected by molybdate pigments.

Total world production of molybdate orange and molybdate red in 1999 was in the order of 13000–15000 metric tons.

3.4.3
Chrome Orange

Chrome orange [*1344-38-3*], C.I. Pigment Orange 21:77601, is a basic lead chromate with the composition $PbCrO_4 \cdot PbO$ but is no longer of technical or economic importance. This product was obtained by precipitating lead salts with alkali chromates in the alkaline pH range. By controlling pH and temperature, the particle size and thus the hue could be varied between orange and red.

3.4.4
Chrome Green and Fast Chrome Green

Chrome greens, C.I. Pigment Green 15:77410 and 77600, are combined or mixed pigments of chrome yellow (see Section 3.4.1 and iron blue see Section 3.6) with the formula

$$Pb(S,Cr)O_4 + Fe_4^{III}[Fe^{II}(CN)_6]_3 \cdot x\, H_2O$$

Fast chrome greens, C.I. Pigment Green 48:77600, 74160 and 74260, are combinations of chrome yellow (see Section 3.4.1) and phthalocyanine blue or phthalocyanine green. For high-grade fast chrome greens, stabilized and highly stabilized chrome yellows are used in practice.

The density and refractive index of chrome greens and fast chrome greens depend on the ratio of the components of the mixture. Their hues vary from light green to dark blue-green, again depending on the ratio of their components.

3.4.4.1
Production

Chrome green and fast chrome green pigments can be prepared by dry or wet mixing.

Dry Mixing

The yellow and blue or green pigments are mixed and ground in edge runner mills, high performance mixers, or mills giving intimate contact of the pigment particles. Excessive increase of temperature must be avoided, because this can lead to spontaneous combustion [3.133]. Differences in the density and particle size of the components may result in segregation and floating of the pigment components in the coating systems. Wetting agents are therefore added to avoid these effects [3.134].

Wet Mixing

Pigments with brilliant colors, high color stability, very good hiding power, and good resistance to floating and flocculation are obtained by precipitating one component onto the other. Solutions of sodium silicate and aluminum sulfate or magnesium sulfate are then added for further stabilization [3.132].

Alternatively, the components are wet-milled or mixed in suspension and then filtered. The pigment slurry is dried, and the pigment is ground.

3.4.4.2

Uses

Chrome greens provide excellent dispersibility, resistance to flocculation, bleeding, and floating, and feature very good fastness properties. This is especially true of fast chrome greens that are based on high-grade phthalocyanine and highly stabilized chrome yellows. They are therefore used in the same applications as chrome yellow and molybdate red pigments (i.e., for the pigmentation of coating media and plastics).

Pigments or pigment preparations consisting of zinc potassium chromates combined with blue pigments are not relevant for industrial production anymore.

3.4.5

Toxicology and Occupational Health

3.4.5.1

Occupational Health

Precautions have to be taken and workplace concentration limits have to be observed when handling lead chromate and lead chromate pigments. MAK or Occupational Exposure Limits for lead chromate and lead chromate pigments themselves are not given.

General regulations exist for all lead-containing materials. Concentration limits are as follows:

MAK value (lead)	$<0.1\ \mathrm{mg\ m^{-3}}$
BAT values	
Lad (blood)	$<70\ \mathrm{\mu g\ dL^{-1}}$
Lead (blood – women	<45 years) $<30\ \mathrm{\mu g\ dL^{-1}}$
δ-aminolevulinic acid	
urine, Davies method	$<15\ \mathrm{mg\ L^{-1}}$
women <45 years	$<6\ \mathrm{mg\ L^{-1}}$
TLV-TWA value (lead)	$<0.15\ \mathrm{mg\ m^{-3}}$

It is accepted that the BAT limit has been complied with if the blood lead level does not exceed 50 $\mu g\ dL^{-1}$ (or for women of <45 years, 30 $\mu g\ dL^{-1}$).

Council Directive 82/605/EEC specifies maximum lead concentrations in the air of <150 $\mu g\ m^{-3}$ and permitted blood lead levels of 70–80 $\mu g\ dL^{-1}$, with δ-aminolevulinic acid values of 20 $mg\ g^{-1}$ creatinine [3.135, 3.136].

Additionally the TRK value/TLV-TWA value for chromium(VI) compounds of 0.05 $mg\ m^{-3}$ calculated as CrO_3 in total dust has to be complied with [3.137].

Lead chromate and lead chromate pigments are classified as toxic for reproduction (Unborn child: Rep. Cat. 1/category R_E 1, Fertility: Rep. Cat. 3/category R_F 3) and carcinogenic (Carc. Cat. 3/category C 3 [3.135, 3.138].

As far as carcinogenic effects are concerned, extensive epidemiological investigations have given no indication that the practically insoluble lead chromate pigments have any carcinogenic properties [3.139, 3.140]. Such properties have been reported for the more soluble zinc chromate and strontium chromate pigments.

Lead chromate pigments can be safely handled if the various rules and regulations regarding concentration limits, safe-working practices, hygiene and industrial medicine are adhered to.

3.4.5.2
Environmental Aspects

Air: Dust emissions from approved manufacturing plant must not exceed a total mass flow of 5 $g\ h^{-1}$ or a mass concentration of 1 $mg\ m^{-3}$ for the sum of lead and chromium (TA-Luft) [3.141].

Water: According to latest German wastewater legislation [3.142] for inorganic pigment manufacturing processes discharging directly into public streams of water, mass limits for lead and chromium related to approved tonnes of annual production capacity (t_{prod}) are:

Lead	0.04 kg/t_{prod}
Chromium (total)	0.03 kg/t_{prod}
Fish toxicity dilution index	2

Local or regional authorities, even for “non-direct” discharges into municipal sewer systems, might set lower limits.

In Germany lead chromate and lead chromate pigments are assigned to Water Hazard Class (WGK): 2 (hazardous to water) [3.143], resulting in handling and storage restrictions and requirements on leak tightness. The European Community considers lead chromate and lead chromate pigments as “Very toxic to aquatic organisms” [3.144].

Waste: Waste containing lead chromate pigments that cannot be recycled must be taken to a special waste disposal site under proper control.

3.4.5.3
Classification and Labeling

In the EC lead chromate and lead chromate pigments must be appropriately labeled. Such substances must carry the symbols and indications of danger T, Toxic (skull and crossbones) and N, Dangerous for the environment (dead fish/tree) [3.144]. Additionally, the following risk (R) and safety phrases (S) have to be applied:

R61	May cause harm to the unborn child.
R33	Danger of cumulative effects.
R40	Limited evidence of carcinogenic effect.
R50/53	Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.
R62	Possible risk of impaired fertility.
S53	Avoid exposure – obtain special instructions before use.
S45	In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible).
S60	This material and its container must be disposed of as hazardous waste.
S61	Avoid release to the environment. Refer to special instructions/safety data sheets.

According to Council Directive 1999/45/EC on Classification, Packaging and Labeling of Dangerous Preparations (Preparations Directive) [3.145] in conjunction with the 28th Adaption to Council Directive 67/548 on Classification, Packaging and Labeling of Dangerous Substances, Nota 1 [3.144], such preparations have to be labeled in accordance with the limits set for the single R-phrases if a lead content of 0.5% Pb in the preparation is exceeded.

With respect to improved protection of public health, special restrictions on cancerogenic and teratogenic substances and their corresponding preparations have been established by the Council Directive 94/60/EC (14th amendment of Council Directive 76/769/EEC) [3.146].

In accordance with the 14th amendment of Council Directive 76/769/EEC [3.146] and revised ChemVerbV [3.147], lead chromate based pigments and preparations are no longer permitted to be used by private consumers and have to be labeled with the phrase “Only for industrial purposes”.

Lead-containing coatings and paints with a total lead content exceeding 0.15% of the total weight of the preparation must carry the phrase: “Contains lead. Should not be used on surfaces liable to be chewed or sucked by children” in accordance with Council Directive 1999/45/EC [3.145] and German GefStoffV [3.147].

Lead chromate pigments are not permitted for use in packaging material intended to come in contact with food [3.148] or for coloring toys [3.149].

For road transport in accordance with GGVSE [3.150] and ADR 2003 [3.151], lead chromate pigments and lead chromate containing preparations are assigned to class 6.1 (T5), III (UN-No. 2291) and have to be labeled with hazard symbol 6.1 (Toxic), if the lead content soluble in hydrochloric acid [$c(\mathrm{HCl}) = 0.07\ \mathrm{mol\ L^{-1}}$] exceeds 5%. For maritime transport in accordance with IMDG code [3.152] such lead chromate pigments and lead chromate-containing preparations have to be labeled additionally as marine pollutant.

3.5
Ultramarine Pigments

The naturally occurring mineral lapis lazuli is found in very few places around the world with the best quality being obtained from Afghanistan and Chile. The name "Ultramarine" meaning from "across the sea" was given to the pigment derived from grinding the mineral. The deep blue color was used by many artists and can be seen in Giotto's chapel in Padua, on Duccio's Virgin and Child and on Renoir's La Parapluie amongst others. The cost of transport of the mineral and subsequent processing meant that the pigment was more expensive than gold. As a result, the French Government launched a competition in the 1820s, with the prize being given to the first synthetic and economic process to make ultramarine blue.

The result of the competition is shrouded in controversy, but the common view is that Guimet in France and Gmelin in Germany independently devised similar processes for synthetic preparation in 1828 [3.153]. The prize was awarded to Guimet and he is frequently referred to as the first person to produce ultramarine blue on a commercial scale.

Synthetic ultramarines are inorganic powder pigments, commercially available in three colors:

1. Reddish blue, C.I. Pigment Blue 29: 77007 [*57455-37-5*]
2. Violet, C.I. Pigment Violet 15: 77007 [*12769-96-9*]
3. Pink, C.I. Pigment Red 259: 77007 [*12769-96-9*]

The proportions of the chemical constituents can vary, but the typical lattice repeat unit of a blue ultramarine is $Na_{6.9}Al_{5.6}Si_{6.4}O_{24}S_{4.2}$. The violet and pink variants differ from the blue mainly in the oxidation state of the sulfur groups. This is reflected in somewhat lower sodium and sulfur contents.

3.5.1
Chemical Structure

Reviews of work on the structure of ultramarine are given in Refs. [3.154–3.156]. Ultramarine is essentially a three-dimensional aluminosilicate lattice with entrapped sodium ions and ionic sulfur groups. A simplified structure is shown in Figure 3.14. The lattice has the sodalite structure with a cubic unit cell dimension of 9.10 Å [3.157]. In synthetic ultramarine derived from china clay by calcination, the lattice distribution of silicon and aluminum ions is disordered. This contrasts with the ordered array in natural ultramarines.

In the simplest ultramarine structure, equal numbers of silicon and aluminum ions are present and the basic lattice unit is $Na_6Al_6Si_6O_{24}$ or $(Na^+)_6(Al^{3+})_6(Si^{4+})_6(O^{2-})_{24}$ with a net ionic charge of zero as required for structural stability.

The nature of the sulfur groups responsible for the color and their incorporation into the sodalite structure is reviewed in Refs. [3.158–3.162]. There are two types of

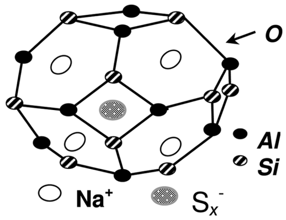

Fig. 3.14 Simplified structure of ultramarine blue.

sulfur groups in blue ultramarine, S_3^- and S_2^-, both being free radicals stabilized by lattice entrapment. In the predominant S_3^- species, the spacing between the three sulfurs is 0.2 nm and the angle between them is 10 °. S_3^- absorbs a broad energy band in the visible green-yellow-orange region centered at 600 nm, whilst S_2^- absorb in the violet-ultraviolet region at 380 nm (Figure 3.15).

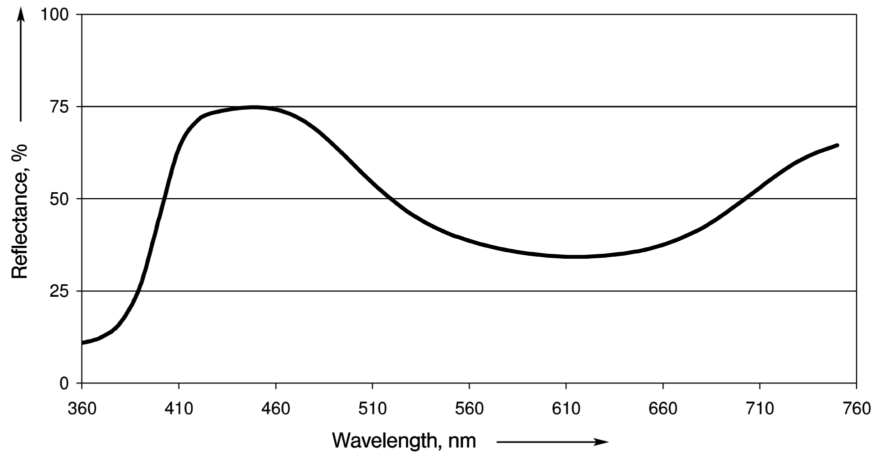

Fig. 3.15 Reflectance spectra for ultramarine blue.

The basic lattice $(Na^+)_6(Al^{3+})_6(Si^{4+})_6(O^{2-})_{24}$ is derived from $Si_{12}O_{24}$ by substituting six of the silicon ions by aluminum. Every Al^{3+} must be accompanied by a Na^+ so that the overall ionic charge for the structure is zero. Hence, six of the eight sodium sites are always filled by sodiums required for lattice stability and the remaining two sites are filled with sodiums associated with ionic sulfur groups. This means that only one S_3^{2-} polysulfide ion can be inserted into the lattice (as Na_2S_3) even though subsequent oxidation to S_3^- leads to loss of one of the accompanying sodium ions. This gives a basic ultramarine lattice formula of $Na_7Al_6Si_6O_{24}S_3$.

To increase the sulfur content and thereby improve color quality, the lattice aluminum content can be decreased by including high-silicon feldspar in the manufacturing recipe. This reduces the number of sodium ions needed for lattice stabilization and leaves more for sulfur group equivalence. A typical product would be $Na_{6.9}Al_{5.6}Si_{6.4}O_{24}S_{4.2}$ with a stronger, redder shade of blue than the simpler type. An alternative explanation for the improved color obtained by the inclusion of feldspar in the manufacturing recipe has been proposed [3.157].

In violet (Figure 3.16) and pink (Figure 3.17) ultramarines, the lattice structure is little changed, but the sulfur chromophores are further oxidized, possibly to S_3Cl^-, S_4, or S_4^-.

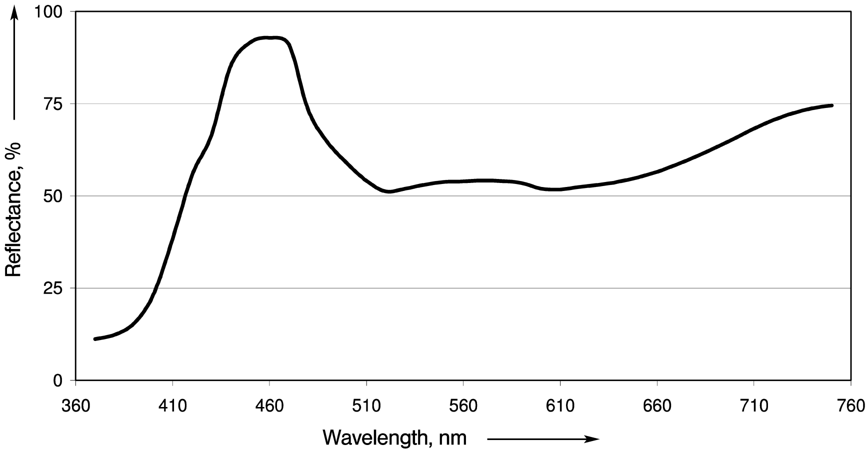

Fig. 3.16 Reflectance spectra for ultramarine violet.

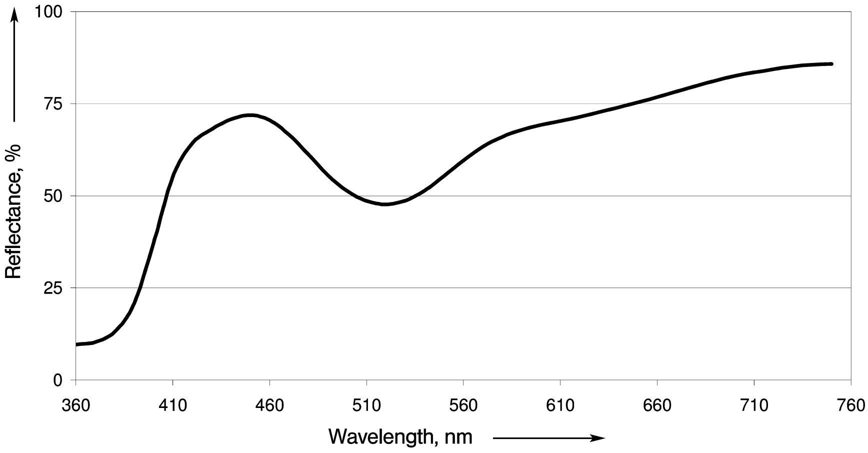

Fig. 3.17 Reflectance spectra for ultramarine pink.

Ultramarines are zeolites, though lattice paths are restricted by 0.4 nm diameter channels. The sodium ions can be exchanged for other metal ions (e.g., silver, potassium, lithium, copper). The exchange with potassium ions can result in a slightly redder shade of ultramarine blue [3.163].

3.5.2
Properties

The basic ultramarine color is a rich, bright reddish blue, the red–green tone varying with chemical composition. The violet and pink derivatives have weaker, less saturated colors (see Figures 3.15–3.17 for reflectance spectra).

The color quality of commercial pigments is developed by grinding to reduce particle size and thus enhance tinting strength. Mean particle size ranges typically from 0.7 to 5.0 µm. Figure 3.18 shows the particle size distribution of a coarse grade, which is typically, used for laundry applications, compared to the fine grade which is more commonly used in technical applications such as inks and plastics. Although the fine pigments are lighter in shade and rather greener than coarser grades, when reduced with white, their color is brighter and more saturated.

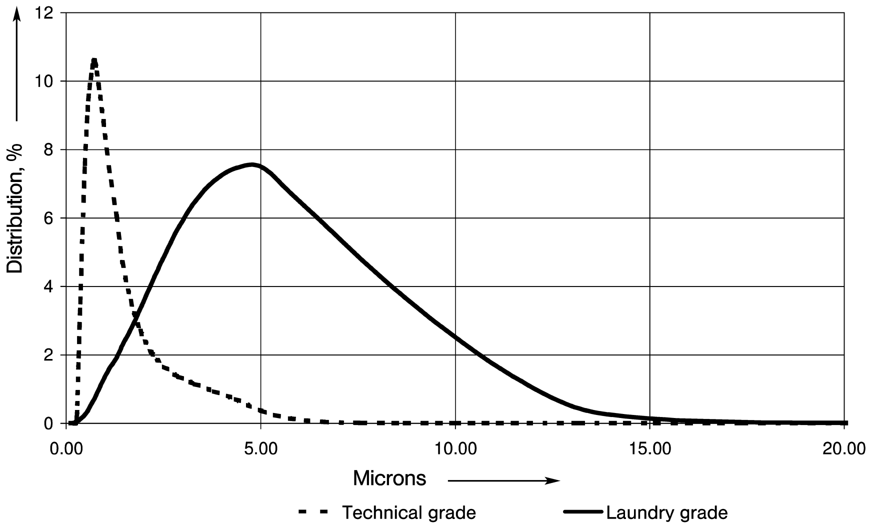

Fig. 3.18 Particle size distribution for ultramarine blue.

With a refractive index close to 1.5, similar to that of paint and plastics media, ultramarine gives a transparent blue in gloss paints and clear plastics. Opacity is obtained by adding a small quantity of a white pigment. Increasing quantities of white give paler shades and a trace of ultramarine added to a white enhances the whiteness and acceptability.

In many applications ultramarine blue is stable to around 400 °C, violet to 280 °C and pink to 220 °C. All have excellent light fastness with a 7–8 rating (full and reduced shades) on the International Blue Wool Scale. Color fade attributed to light exposure or moderate heat is almost always caused by acid attack. Ultramarines react with all acids, and if there is sufficient acid, the pigment is completely decomposed, losing all color, to form silica, sodium and aluminum salts, sulfur, and hydrogen sulfide. Evolution of hydrogen sulfide with acids is a useful test for ultramarine.

Grades resistant to transient acidity are available, in which the pigment particles are protected by a coating of impervious silica. Blue and violet grades are stable in mildly alkaline conditions, but pink tends to revert to a violet shade.

Ultramarines are insoluble in water and organic solvents, so the color does not bleed or migrate from paints or polymers. This has led to ultramarines being approved for a wide range of food contact applications.

Being macromolecular, the fine ultramarine particles have a high surface energy and are cohesive. The finer grades, with their greater surface area, are therefore less easy to disperse than the coarser types, and some are available with pigment surfaces treated to reduce energy and improve dispersibility.

Ultramarines absorb moisture on the external particle surfaces and at the internal surfaces of the zeolite structure. External surface moisture (1–2% according to particle size) is driven off at 100–105 °C, but the additional 1% of internal moisture needs 235 °C for complete removal.

Ultramarine particles are hard and have been known to cause abrasion in equipment handling either dry or slurried pigment.

Specific gravity is 2.35, but the bulk density of the pigment powder is much lower, varying with particle size between 0.5 and 0.9 g cm^{-3}.

Specific surface area varies with particle size and lies between 1 and 3 $m^2\ g^{-1}$. Oil absorption also varies with particle size (usually 30–40 g%). The pH lies between 6 and 9. Ultramarine pigments are largely odorless, non-flammable, and do not support combustion.

3.5.3
Production

Ultramarine is made from simple, relatively cheap materials, typically china clay, feldspar, anhydrous sodium carbonate, sulfur, and a reducing agent (oil, pitch, coal etc.).

3.5.3.1
Clay Activation

The transformation of kaolinite to metakaolinite is brought about by heating the clay to about 700 °C causing hydroxyl ions to be removed as water. The rate of dehydroxylation as a function of heating has been studied [3.164]. The reaction can either be a batch process with the clay in crucibles in a directly fired kiln, or a continuous process in a tunnel kiln, rotary kiln, or other furnace.

3.5.3.2
Blending and Heating Raw Materials

The activated clay is blended with the other raw materials and dry-ground, usually in batch or continuous ball mills, to a mean size approaching 15 μm. Typical recipes (in wt.%) are:

	Green Shade	Red Shade
Calcined clay	32.0	30.0
Feldspar		7.0
Sodium carbonate	29.0	27.0
Sulfur	34.5	33.0
Reducing agent	4.5	3.0

The ground mixture is heated to about 750 °C under reducing conditions, normally in a batch process. The traditional way to do this is to use directly fired kilns with the blend in lidded crucibles of controlled porosity, or muffle kilns. To improve throughput, the practice in the Holliday Pigments' production facilities is to densify the ground material to form bricks, which are then stacked in a pre-determined pattern and fired in chambers, which are indirectly heated using gas-fired burners. The sodium carbonate reacts with the sulfur and reducing agent at 300 °C to form sodium polysulfide [3.165]. At higher temperatures the clay lattice reforms into a three-dimensional framework, which at 700 °C is transformed to the sodalite structure, with entrapped sodium and polysulfide ions.

3.5.3.3
Oxidation

The furnace is allowed to cool to 500 °C when air is admitted in controlled amounts. The oxygen reacts with excess sulfur to form sulfur dioxide, which exothermically oxidizes the di- and triatomic polysulfide ions to S_2^- and S_3^- free radicals, leaving sodium sulfoxides and sulfur as by-products. When oxidation is complete, the furnace cools and is unloaded, a full kiln cycle takes between 3 and 4 weeks. The "raw" ultramarine product typically contains 75 wt.% blue ultramarine, 23 wt.% sodium sulfoxides, and 2 wt.% free (uncombined) sulfur with some iron sulfide.

3.5.3.4
Purification and Refinement

The purification and refinement operations can be batch or continuous. The raw blue is crushed and ground, slurried in warm water, then filtered and washed to remove the sulfoxides. Reslurrying and wet grinding release the sulfurous impurities and reduce the ultramarine particle size, often to 0.1–10.0 μm. The impurities are floated off by boiling or cold froth flotation, analogous to techniques used in the mining industry.

The liquor is then separated into discrete particle size fractions by gravity or centrifugal separation; flocculation and filtration reclaim residual fine particles. The separated fractions are dried and disintegrated to give pigment grades differentiated by particle size. These are blended to sales-grade standard, adjusting hue, brightness and strength to achieve specified color tolerance.

Violet ultramarine can be prepared by heating a mid-range blue grade with ammonium chloride at ca. 240 °C in the presence of air. Treating the violet with hydrogen chloride gas at 140 °C gives the pink derivative.

A good ultramarine pigment would meet the following specification:

Tinting strength/standard	±5% max
Reduced shade/standard	1 CIELAB unit max
Free sulfur	0.05% max
Water-soluble matter	1.0% max
Sieve residue (45 µm)	0.1% max
Moisture	1.0% max
Heavy metals	traces

3.5.4
Uses

The stability and safety of ultramarine pigments are the basis of their wide range of applications, which include the following:

- Plastics
- Paints and powder coatings
- Printing inks
- Paper and paper coatings
- Rubber and thermoplastic elastomers
- Latex products
- Detergents
- Cosmetics and soaps
- Artists' colors
- Toys and educational equipment
- Leather finishes
- Powder markets
- Roofing granules
- Synthetic fibers
- Theatrical paints and blue mattes
- Cattle salt licks
- White enhancement

3.5.4.1
Plastics

Blue ultramarine can be used in any polymer; violet ultramarine has a maximum processing temperature of 280 °C, and pink ultramarine has a maximum processing temperature of 220 °C. With PVC, acid-resistant grades are commonly used if color fades during processing. Surface-treated grades are available for enhanced dispersibility. Ultramarines do not cause shrinkage or warping of polyolefins. Ultramarine pigments are permitted worldwide for coloring food-contact plastics.

3.5.4.2
Paints

Ultramarine pigments are used in decorative paints, stoving finishes, transparent lacquers, industrial paints, and powder coatings. The transparent nature of the pigment leads to some impressive flamboyant coatings in combination with effect pigments such as mica [3.166].

3.5.4.3
Printing Inks

Ultramarine pigments can be used in inks for most printing processes including hot-foil stamping. Letterpress, flexography and gravure need high-strength grades; lithography needs water-repellent grades; any grade is suitable for screen inks, fabric printing and hot-foil stamping. Improved strength grades presented in a high solids aqueous dispersion are finding increasing use in flexographic printing applications [3.167].

3.5.4.4
Paper and Paper Coatings

Ultramarine pigments are used to enhance the hue of white paper or for colored paper. They can be added directly to the paper pulp, or used in applied coatings. They are particularly suitable for colored paper for children’s use.

3.5.4.5
Detergents

Ultramarine pigments are widely used to enhance the effects of optical brightening agents in improving the whiteness of laundered fabrics [3.168]. They do not stain or build up with repeated use.

3.5.4.6
Cosmetics and Soaps

Ultramarine pigments are widely used in cosmetics. Pink is not recommended for toilet soaps because of a color shift to violet. Advantages are complete safety, non-staining and conformance to all major regulations.

3.5.4.7
Artists’ Colors

This traditional use for ultramarine in all types of media is still an important application. Unique color properties, stability, and safety are highly prized.

3.5.4.8
Toys and other Articles/Materials for Children's Use

Ultramarine pigments are widely used in plastics and surface coatings for toys, children's paints and finger paints, modeling compositions, colored paper, crayons etc. They comply with major regulations and standards.

3.5.5
Toxicology and Environmental Aspects

Ultramarine pigments have a unique safety record. No other pigment has had such long term and widespread human and environmental exposure without any reported instances of ill effect. The principle uses for ultramarine in earlier times constituted a world wide test of human safety since it was sold and used around the world as an additive for sugar, to produce a whitening effect, and as a clothes whitening agent for use in the household wash. Whole populations ate sugar regularly. The use of ultramarine for whitening clothes was, and still is, widespread. This represents a test of safety in human ingestion and skin contact on a grand scale. Their only known hazard is the evolution of hydrogen sulfide on contact with acid.

Tests sponsored by Reckitt's Colors (now Holliday Pigments) confirm that acute oral toxicity in rats and mice (LD_{50}) is greater than 10,000 mg kg^{-1}. Fish toxicity (LC_{50} in rainbow trout) exceeds 32,000 mg L^{-1}. Ultramarine is non-mutagenic, non-irritant, and non-sensitizing to skin.

There is no listed threshold limit value or maximum exposure limit for the pigment. Normal practice is to consider it a nuisance dust with TLV 10 mg m^{-3}. The pigment is not listed as a dangerous substance in the EC nor in any similar national or international classification; neither is it classified as hazardous for disposal.

The production process evolves close to 1 t of gaseous sulfur dioxide and 0.3 t of water-soluble sodium sulfoxides for every metric ton of pigment produced. These must be disposed of in an environmentally acceptable manner. If the soluble salts are fully oxidized, they can be discharged safely into tidal waters. The legislation around the world requiring the reduction in discharges of sulfur dioxide has led to the demise of many ultramarine producers. The investment required is significant but can result in a dramatic reduction in the level of emissions. The solution implemented at the largest ultramarine factory in the world has reduced sulfur dioxide emissions by more than 99.5%. This is achieved by conversion of the SO_2 to SO_3 using a vanadium pentoxide catalyst and the subsequent condensation of the sulfur trioxide to produce very concentrated and pure sulfuric acid.

3.5.6
Economic Aspects

Ultramarines can be categorized as either laundry grades, which are low-strength and sometimes low-purity materials, or as industrial/technical grades, which are high-strength, high-purity pigments.

Factories in the People's Republic of China, and India produce on the whole laundry grade materials. There are only three major producers of high-grade ultramarine pigments – Holliday Pigments (United Kingdom, France), DKK (Japan), and Nubiola (Spain, Romania, India, Colombia). In 2000 total worldwide production of all ultramarine was ca. 25,000 $t\,a^{-1}$.

3.6
Iron Blue Pigments

The term iron blue pigment as defined in ISO 2495 has largely replaced a great number of older names (e.g. Paris blue, Prussian blue, Berlin blue, Milori blue, Turnbull's blue, toning blue, and nonbronze blue). These names usually stood for insoluble pigments based on microcrystalline Fe(II)Fe(III) cyano complexes; many were associated with specific hues. A standardized naming system has been demanded by users and welcomed by manufacturers, and has led to a reduction in the number of varieties [3.169].

Iron blue [*14038-43-8*], C.I. Pigment Blue 27:77510 (soluble blue is C.I. Pigment Blue 27:77520), was discovered in 1704 by Diesbach in Berlin by a precipitation reaction, and can be regarded as the oldest synthetic coordination compound. Milori was the first to produce it as a pigment on an industrial scale in the early nineteenth century [3.170].

3.6.1
Structure

X-ray and infrared spectroscopy show that iron blue pigments have the formula $M^{I}Fe^{II}Fe^{III}(CN)_6 \cdot x\,H_2O$ [3.171]. M^{I} represents sodium, potassium or ammonium, of which potassium and ammonium ions are preferred in industrial manufacture because they produce excellent hues; ammonium is the most common one.

The crystal structure of the $Fe^{II}Fe^{III}(CN)_6$ grouping is shown in Figure 3.19. A face-centered cubic lattice of Fe^{II} (ferrous ion) is interlocked with another face-centered cubic lattice of Fe^{III} (ferric ion), to give a cubic lattice with the corners occupied by ferrous ions. The CN ions are located at the edges of the cubes between each Fe^{II} ion and the neighboring Fe^{III}; the carbon atom of the cyanide is bonded to the Fe^{II} ion and the nitrogen atom is coordinatively bonded to the Fe^{III} ion. The alkali-metal ions and water molecules are inside the cubes formed by the iron ions.

The presence of coordinative water is essential for stabilization of the crystal structure. Removal of this water, however carefully carried out, destroys the pigment properties. Many investigations helped to elucidate the structure of iron blue [3.172–3.175].

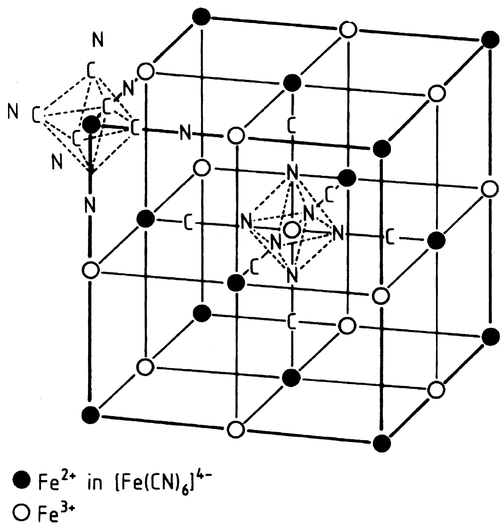

Fig. 3.19 Crystal structure of iron blue [3.172].

3.6.2
Production

Iron blue pigments are produced by the precipitation of complex iron(II) cyanides using iron(II) salts in aqueous solution. The product is a whitish precipitate of iron(II) hexacyanoferrate(II) $M^{II}{}_2Fe^{II}[Fe^{II}(CN)]$ or $M^{II}Fe^{II}[Fe^{II}(CN)_6]$, (Berlin white), which is aged and then oxidized to give the blue pigment [3.176].

Sodium or potassium hexacyanoferrate(II) or mixtures of these salts are used in most cases. When the pure sodium salt or a calcium hexacyanoferrate(II) solution is used, the pigment properties are obtained by adding a potassium or ammonium salt during the precipitation of the white paste product or prior to the oxidation stage. The iron(II) salt used is crystalline iron(II) sulfate or iron(II) chloride solution.

The oxidizing agent can be hydrogen peroxide, alkali chlorates, or alkali dichromates. Industrial precipitation is carried out batch-wise in large stirred tanks by simultaneous or sequential addition of aqueous solutions of alkali hexacyanoferrate(II) and the iron(II) compound to a diluted acid. The filtrate from the white paste product must contain a slight excess of iron. Temperature and concentration of the starting solutions have a decisive influence on the size and shape of the precipitated particles. The suspension of white paste is aged by heating. The ageing period varies in length and temperature depending on the required properties of the finished pigment. This is followed by oxidation to form the blue pigment by adding e.g. hydrochloric acid and sodium or potassium chlorate [3.177]. Finally, the suspension of the blue pigment is pumped into filter presses, either immediately or after washing with cold water and decanting. After filtering, it is washed until the absence of acids and salts. The washed filter cake (30–60% solids) is carefully dried in suitable driers to form a solid which is eventually ground, packed into bags, or stored in silos. Serve tunnel or belt driers as well as spray- or spin-flash driers are used. Another possibility is to form rods or pellets by extruding the washed filter cake with a granulator. After drying a dust-free iron blue pigment is obtained.

Dispersibility can be improved by adding organic compounds to the pigment suspension before filtering to prevent the particles from agglomerating during drying [3.178, 3.179]. In another method (the Flushing process), the water in the wet pigment paste is replaced by a hydrophobic binder [3.180]. Although these and other methods of pigment preparation produce fully dispersible products consisting mainly of iron blue and a binder, they have not become established on the market [3.181–3.183].

A "water-soluble" blue can be manufactured by adding peptizing agents (the latter improve the water solubility via an emulsifying action). This forms a transparent colloidal solution in water without the use of high shear forces [3.172].

3.6.3
Properties

Hue, relative tinting strength, dispersibility, and rheological behavior are the properties of iron blue pigments with the most practical significance. Other important properties are the volatiles content at 100 °C, the water-soluble fraction, and acidity (ISO 2495). Pure blue pigments are mostly used in their pure form (e.g. in printing inks) and do not need any additives to improve them. Finely divided iron blue pigments impart a pure black tone to printing ink.

Due to their small particle size iron blue pigments are very difficult to disperse (Table 3.6, Figures 3.20 and 3.21). A graph of cumulative particle size distribution is given in Figure 3.22 for a commercial quality iron blue and for a micronized grade with similar primary particle size. The micronized grade gives greater tinting strength in dry mixtures than the blues obtained from standard grinding. The average size of the aggregates in the micronized material is ca. 5 µm compared with ca. 35 µm for the normal quality product.

Iron blue pigments are thermally stable for short periods at temperatures up to 180 °C, and therefore can be used in stoving finishes. The powdered material presents an explosion hazard; the ignition point is 600–625 °C (ASTM D 93-52). The pigments are combustible in powder form, ignition in air being possible above 140 °C [3.172].

Iron blue pigments used alone have excellent light- and weatherfastness. When mixed with white pigments, these properties can disappear [3.184]. Recent investigations have shown that a topcoat (as commonly applied in automobile manufacture) overcomes this problem [3.185]. Figure 3.23 shows changes in residual gloss and color after a short weathering period. The pigments are resistant to diluted mineral acids and oxidizing agents, and do not bleed. They are decomposed by hot, concentrated acid and alkali. Other properties are listed in Table 3.6.

3.6.4
Uses

Total production of iron blue in 1975 was ca. 25,000 t a^{-1}, but in 1995 it was only ca. 15,000 t a^{-1}. A value of 9000 t a^{-1} was estimated for 2002. The main consumer

Tab. 3.6: Physical and chemical properties of iron blue pigments (Vossen Blau® and Manox® Blue Manox® Blue grades).

Type	**VOSSEN BLAU® 705**	**VOSSEN BLAU® 705 LS**[g]	**VOSSEN BLAU® 724**	**MANOX® Blue 460 D**	**MANOX® EASISPERSE® HSB 2**
Color Index Number	77510	77510	77510	77510	77510
Color Index Pigment	27	27	27	27	27
Tinting strength[a]	100 pure blue	100 pure blue	100 pure blue	115 pure blue	95[h] pure blue
Oil absorption[b], g/100 g	36–42	40–50	36–42	53–63	22–28
Weight loss on drying[c], %	2–6	2–6	2–6	2–6	2–6
Tamped density[d], g L^{-1}	500	200	500	500	550
Density[e], g cm^{-3}	1.9	1.9	1.9	1.8	1.8
Mean diameter of primary particles, nm	70	70	70	40	80
Specific surface area[f], m^2 g^{-1}	35	35	35	80	30
Thermal stability, °C	150	150	150	150	150
Resistance to acids	very good	very good	very good	very good	very good
Resistance to alkalines	poor	poor	poor	poor	poor
Resistance to solvents	very good	very good	very good	very good	very good
Resistance to bleeding	very good	very good	very good	very good	very good

a) DIN ISO 787/XVI and DIN ISO 787/XXIV. **b)** DIN ISO 787/V, ASTM D 281, or JIS K 5101/19 (JIS: Japanese Industrial Standard). **c)** DIN ISO 787/II, ASTM D 280, or JIS K 5101/21. **d)** DIN ISO 787/XI or JIS K 5101/18. **e)** DIN DIN ISO 787/X or JIS K 5101/17. **f)** DIN 66131. **g)** LS = Luftstrahlmühle (air jet mill). **h)** Surface-treated easily dispersible type.

in Europe and USA is the printing ink industry. The second largest use in Europe, especially of micronized iron blue pigments, is for coloring fungicides. Use in the paint industry is insignificant.

3.6.4.1
Printing Ink Industry

Iron blue pigments are important in printing, especially rotogravure, because of their deep hue, good hiding power and economic cost/performance-basis. Iron blue is often mixed with phthalocyanine pigments for multicolor printing. Another important use is in controlling the shade of black printing inks. Typical amounts used are 5–8% for full shade rotogravure inks and 2–8% for toning black gravure and offset inks.

Iron blue pigments are used in the manufacture of single- and multiple-use carbon papers and blue copying papers, both for toning the carbon black and as blue pigments in their own right [3.172].

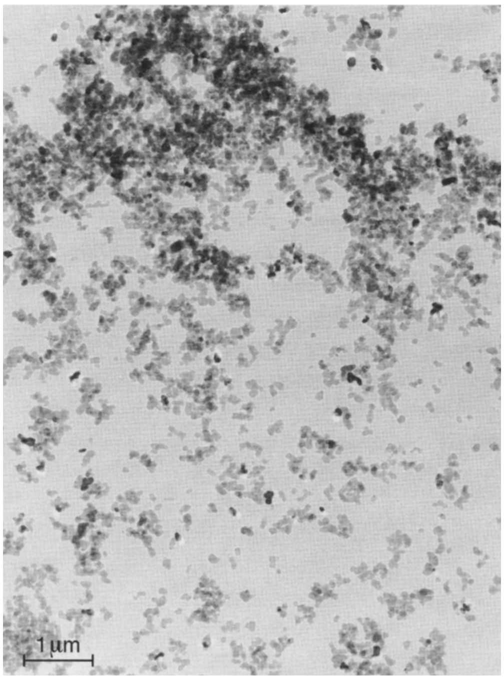

Fig. 3.20 Electron micrograph of an iron blue pigment of small particle size (Manox® Blue 460 D).

Toning of Black Gravure Inks

For the toning of black gravure inks, for example, 2 to 6% of Manox® Easisperse® HSB3 are used together with 6 to 12% of carbon black. Combinations with red pigments with a blue undertone are also common. When using organic pigments, resistance to solvents must be taken in account. Because of the poor dispersibility of iron blue compared with carbon black it is both economical and practical to disperse the blue pigment in a separate step.

While the visual judgment of black is influenced by the individual ability of the observer to distinguish small color differences in deep black, it is possible, with the help of photometric measurements, to graphically interpret objective evaluations by means of physical data [3.186].

Figure 3.24 illustrates the color changes of a low structure LCF-type carbon black by addition of Pigment Blue 27 (Vossen-Blau® 705) and Pigment Violet 27 or by toning with a 4:1 combination of Pigment Blue 27 and Pigment Red 57:1. A mixture of asphalt resin, calcium/zinc resinate and phenol resin was used as a binder. The pigment concentration for all was 13.2%. The toner was added in 2.2% steps up to 6.6% with a simultaneous reduction from 13.3% to 6.6%.

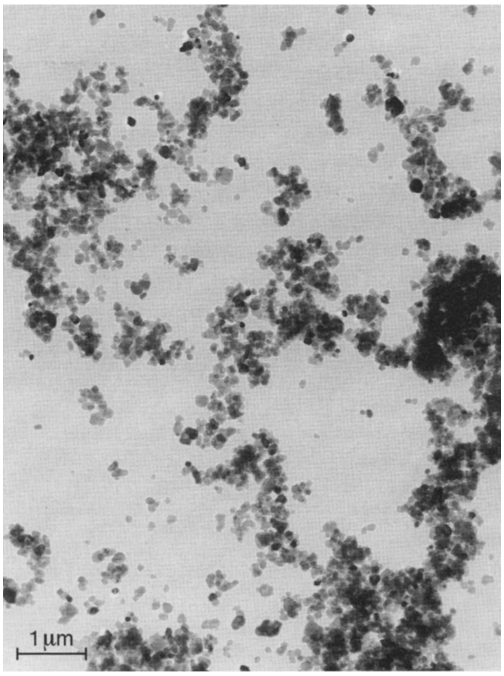

Fig. 3.21 Electron micrograph of an iron blue pigment of normal particle size (Vossen Blau® 705).

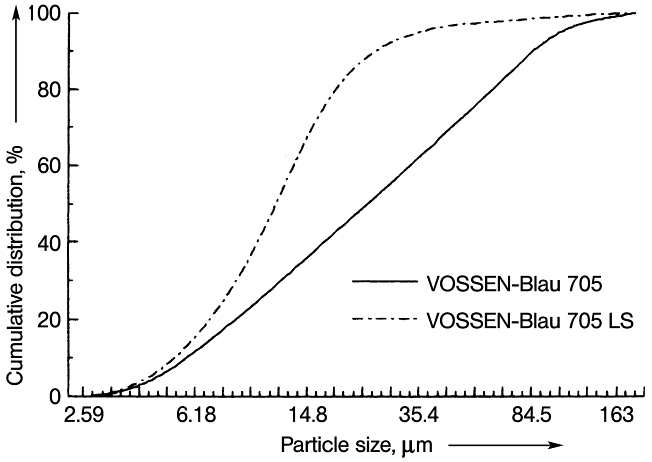

Fig. 3.22 Cumulative particle size distribution curve of a normal (VB 705) and a micronized (VB 705LS) iron blue pigment of equal primary particle size LS = Luftstrahlmühle (air jet mill).

Toning of Black Offset Printing Inks

The basic requirements for the successful use of iron blue as a toning agent in offset printing inks are resistance to damping or "fountain" solutions and good dis-

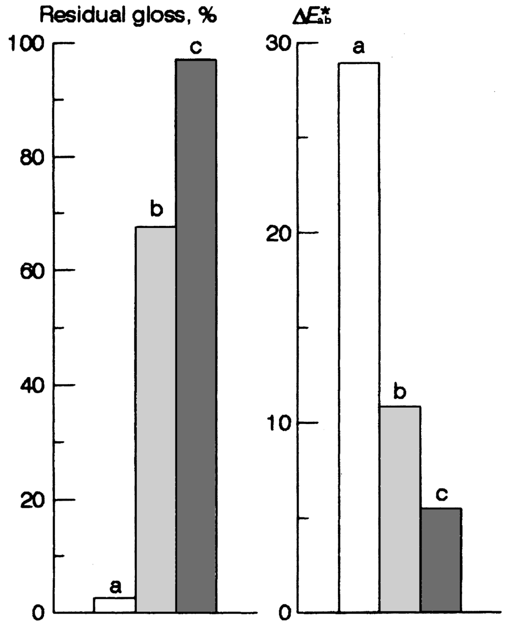

Fig. 3.23 Residual gloss and dE^*_{ab} values for isocyanate-cross-linked polyacrylate resins that contain 15 wt.% Vossen-Blau® 2000 (older pigment type which has been replaced by Manox® Blue 460 D) relative to the binder and 15 wt.% TiO_2 (rutile) relative to the iron blue pigment after 1000 h fast exposure to UV [3.185]. a) Without clearcoat, b) with clearcoat but without UV protection, c) with clearcoat and UV protection.

persibility. "Resistance" is understood here as the hydrophobic characteristics of the pigment.

This property prevents wetting of the pigment by water and therefore its peptization. Non-resistant iron blue can render the ink useless by adsorbing water to above the normal content. A negative side effect of peptization is the "dissolution" of the blue pigment from the printing ink and the resulting blue coloration of the fountain solution with the familiar problems of printing-plash contamination, which is known as scumming or toning.

The combined dispersion of pigments is only practical with colorants of similar dispersibility. Toning agents with a considerably higher resistance to dispersion than carbon black are therefore delivered by the manufacturer in the form of a predispersed paste or must be ground separately by the user.

Developments in the fields of iron blue technology have overcome these problems. A new generation of pigments has been generated which covers both the demand for a sufficient resistance against damping solutions and the request for a good dispersibility. Easily dispersible iron blue is preferred to be used for combined dispersion with carbon black in the so-called "co-grinding" process.

In the following section, the coloristic effects of these iron blue pigments are described, as obtained in toning experiments involving a LCF-type carbon black, in comparison with Pigment Blue 15:3 and Pigment Blue 61 (Figs. 3.24–3.26).

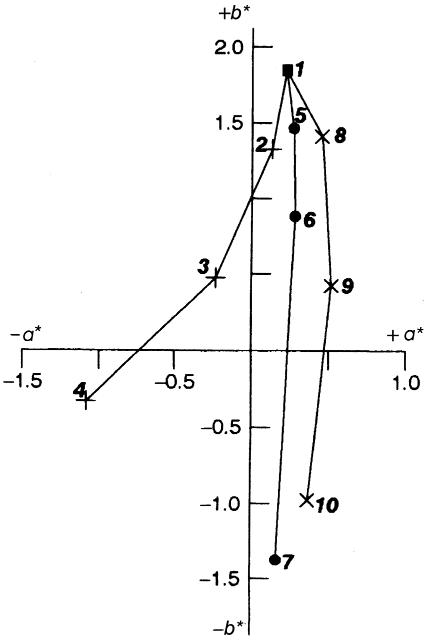

Fig. 3.24 Color coordinates of black gravure inks with different toning. 1: Pigment Black LCF = Printex® 35, + 2–4: Pigment Black LCF/Vossen-Blau© 705, •5–7: Pigment Black LCF/[VB 705 – Pigment Red 57:1 (4:1)], x 8–10: Pigment Black LCF/[VB 705 – Pigment Violet 27 (2:1)].

The pigment concentration of the inks is 24%, i.e. the amount of carbon black was reduced, corresponding with the addition of 3, 6, or 9% of blue pigment. Black inks containing 15 to 24% of carbon black are excluded from this experiment. They are presented to give an additional coloristic description of "pigment" black as regards the development of the hue when used as a self-color pigment in increasing concentrations.

In the visual and the colorimetric evaluation, the color location change of the carbon black when used as a self-color pigment is noticeable since there is a tendency to a black with a blue undertone at higher pigment concentration, even without the addition of toning agent. In Figure 3.25 these are the color locations 1, 2, 3 and 4 starting with 15% carbon black and in increasing additions in steps of 3 to a maximum concentration of 24%.

However, it is also clear that without the addition of a blue pigment the achromatic point cannot be achieved.

By adding various toning agents the desired color hue is achieved – although with varying red–green spread. Iron blue (Manox® Easisperse® 154) brings about a clear shift towards green with a relatively small shift in the blue direction (see color locations 5, 6 and 7). The required target is more successfully achieved by the use of a mixture of iron blue and Pigment Red 57:1 in the ratio 4:1. The color locations 8, 9 and 10 illustrate useful ways of approaching the achromatic point with the addition of 3, 6, and 9% of the mixture.

The addition of 3% of Pigment Blue 61 already results in a significant step towards blue/red and shows almost identical incremental changes with further additions (see color locations 11, 12 and 13). In addition, the bronze effect occurs, intensifying with increasing distance from the achromatic point. With Pigment Blue 15:3 in numerically equivalent increments, the hue of the black ink moves towards blue/green in the opposite direction from the achromatic point and with a negative shift (color locations 14–16).

3.6.4.2
Agriculture

Since ca. 1935, and especially in Mediterranean countries, blue inorganic fungicides based on copper and mostly used for treating vines, olives or citrus fruits have largely been replaced by colorless organic compounds. Micronized iron blue pigments are used to color these fungicides (normally at a concentration of 3–6 wt.%), so that even small amounts become visible due to the high color intensity, and precise control is possible. The fungicide is usually milled or mixed with a micronized iron blue pigment [3.187].

A welcome side effect of treating fungi (e.g. peronospora plasmopara viticola) with iron blue is the fertilizing of vines in soils that give rise to chlorosis. Leaf color is intensified, ageing of the leaves is retarded, and wood quality ("ripeness") is also

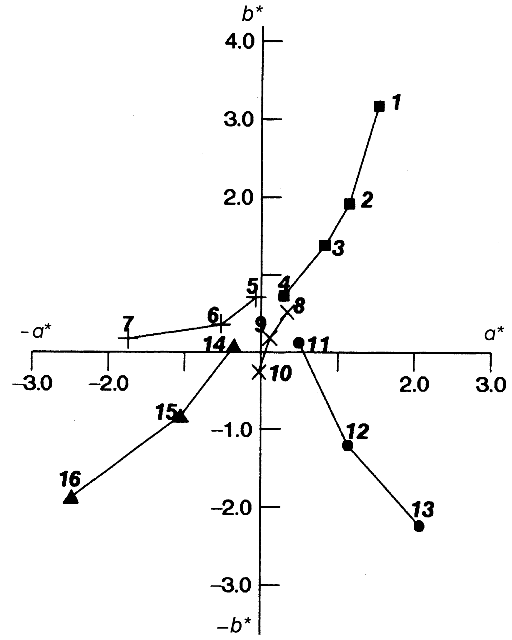

Fig. 3.25 Color locations of black offset printing inks with different toning. ■ 1–4: Pigment Black LCF (= Printex® 35), + 5–7: Pigment Black LCF/Manox® Easisperse®, x 8–10: Pigment Black LCF/[Manox® Easisperse®-Pigment Red 57:1 (4:1)], •11–13: Pigment Black LCF/Pigment Blue 61, ▲ 14–16: Pigment Black LCF/Pigment Blue 15:3.

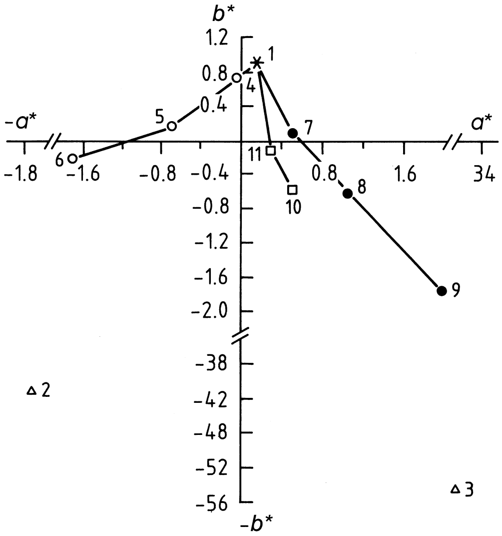

Fig. 3.26 Stepwise approach to the achromatic point of a Printex® 35 offset printing ink by using Manox® Easisperseⓡ and/or Pigment Blue 61 as toning pigment [3.191].1) Printex® 35, 2) Manoxⓡ Easisperseⓡ, 3) Pigment Blue 61, 4–6) Printex® 35/Manoxⓡ Easisperseⓡ, 7–9) Printex® 35/Pigment Blue 61, 10–11) Printexⓡ 35/Manoxⓡ Easisperse®/Pigment Blue 61. Points 4 and 7 contain 3% blue pigment; points 5 and 8, 6%; points 6 and 9, 9%. Point 10 results from mixing 2% Manox® Easisperseⓡ and 4% Pigment Blue 61; point 11 by mixing in the ratio 3:3.

improved [3.188–3.190]. Iron is necessary for chlorophyll synthesis, which improves grape quality and yield. Other iron salts do not have this effect [3.189].

3.6.4.3
Paints and Coatings

Iron blue pigments are used in the paint industry, e.g. for full, dark blue colors for automotive finishes. A full shade with good hiding power is produced by 4–8% iron blue pigments.

3.6.4.4
Paper

Adding “water-soluble” iron blue pigment directly to the aqueous phase can produce blue paper. Alternatively, a suitable iron blue pigment can be ground together with a water-soluble binder, applied to the paper, dried, and glazed (quantity applied: ca. 8% in the dispersion).

3.6.4.5
Pigment Industry

The importance of iron blue in the production of chrome green and zinc green pigments has greatly increased worldwide (see Section 3.4.4).

3.6.4.6

Medical Applications

Iron blue has become important as an agent for decontaminating persons or animals having ingested radioactive material. The isotope ^{137}Cs, which would otherwise be freely absorbed via the human or animal digestive tract, exchanges with the iron(II) of the iron blue [3.192], [3.193] and is then excreted into the feces [3.194]. Gelatin capsules containing 500 mg iron blue are marketed as "Radiogardase-Cs" (Heyl). Thallium ions have been found to behave similarly [3.195–3.197]. The gelatin capsules for this purpose are sold as "Antidotum Thalii" (Heyl) [3.198].

3.6.5

Toxicology and Environmental Aspects

Iron blue pigment compounds show no toxicity in animal studies, therefore they are not expected to cause any adverse effects on human health. No toxic effects were reported in humans when iron blue pigment compounds were used experimentally or therapeutically.

Toxico-kinetic studies showed, that the adsorption of iron blue pigments is very low. Following intravenous injection of a ^{59}Fe radio-labeled iron blue pigment, the $^{59}Fe(CN)_6$- ion was rapidly and virtually completely excreted with the urine. After oral administration of ferric hexacyanoferrate (^{59}Fe) approx. 2% of the labeled hexacyanoferrate ion was adsorbed by the gastro-intestinal tract [3.199]. Most of the substance is excreted with the feces [3.200] and there was no evidence of its decomposition.

The decomposition of iron blue to toxic cyanide in aqueous systems is very low. The HCN release of $KFe[Fe(CN)_6]$ in artificial gastric or intestinal juice was 141 or 26 $\mu g\ g^{-1}$ per 5 h respectively and in water 37 $\mu g\ g^{-1}$ per 5 h. The corresponding figures of $Fe_4[Fe(CN)_6]_3$ were 64, 15 and 22 $\mu g\ g^{-1}$ per 5 h [3.201].

In the breath of rats after intraperitoneal injection of ^{14}C-labeled $KFe[Fe(CN)_6]$, less than 0.01% (detection limit) was found, whereas in another study 0.04–0.08% of the orally administered dose was found in the exhaled air [3.202]. It can be concluded, that the hexacyanoferrate(II) complex disintegrates only to a small extent in the intestinal tract after oral administration. This is confirmed by the results of acute oral toxicity studies which show in high doses no clinical symptoms or lethality. The LD_{50} values are above 5000–15,000 mg kg^{-1} (limit tests) [3.203–3.205].

In primary irritation tests no or only slight effects were seen at the skin or in the eyes of the treated rabbits respectively [3.205, 3.206]. No skin sensitization occurred in a Guinea pig maximization test [3.203].

The subchronic (90–120 days) consumption of iron blue at concentrations of 1–2% in the food or drinking water influenced slightly the body weight gain, but no other clinical signs or histopathological changes were observed [3.207–3.210]. After the administration of daily doses of 200 or 400 mg kg^{-1} for ten days to dogs their body weight gained and the general condition remained unaffected [3.211].

In a bacterial test system (Ames test) no increase of mutagenicity was detected without or in the presence of a metabolic system [3.205].

In human volunteers who received 1.5 or 3.0 g ferric hexacyanoferrate(II) for up to 22 days apart from a slight obstipation no effects were reported [3.211, 3.212].

Prussian blue $Fe_4[Fe(CN)_6]_3$ can bind cesium; therefore it is used in clinical practice as an antidote for the treatment of humans contaminated with radioactive cesium (see also Section 3.6.4). Clinical use of ferric ferrocyanide in doses up to 20 g d^{-1} for decontaminations of persons exposed to radiocesium has not been associated with any reported toxicity [3.201].

Prussian blue is also used as an effective antidote for thallium intoxication. Ferric ferrocyanide interferes with the enterosystemic circulation of thallium ions and enhances their fecal excretion [3.213].

In a semistatic acute fish toxicity test (Leuciscus idus. melanotus, fresh water fish) a saturated solution with different iron blue compounds (with undissolved material on the bottom or filtered solution) no deaths occurred within 96 h. Based on the quantity weighed, the No Observed Effect Level (NOEL) is greater than 1000 mg L^{-1} (nominal concentrations) [3.214].

The bacterial toxicity was measured according DEV, DIN 38412, L3 [TTC(2,3,5-triphenyl-2H-tetrazoliumchloride) test]. The result gives an EC_{50} (effective concentration) varying between 2290 and 14,700 mg L^{-1}, and estimated NOEL values in the range of <10 to 100 mg L^{-1} [3.215].

There are no harmful effects on fish, but the toxic effects on bacteria constitute a slight hazard when iron blue is present in water.

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4
Black Pigments

Carbon black [*1333-86-4*] is virtually pure elemental carbon (diamond and graphite are other forms of nearly pure carbon) in the form of near-spherical colloidal particles that are produced by incomplete combustion or thermal decomposition of gaseous or liquid hydrocarbons. Its physical appearance is that of a black, finely divided pellet or powder, the latter sometimes small enough to be invisible to the naked eye. Its use in tires, rubber and plastic products, printing inks and coatings is related to the properties of specific surface area, particle size and structure, conductivity and color.

It is in the top 50 industrial chemicals manufactured worldwide, based on annual tonnage. Current worldwide production is about 15 billion pounds per year (6.81 million metric tons). Approximately 90% of carbon black is used in rubber applications, 9% as a pigment, and the remaining 1% as an essential ingredient in hundreds of diverse applications.

Modern carbon black products are direct descendants of early “lampblack”, first produced in China over 3500 years ago. These early lampblacks were not very pure and differed greatly in their chemical composition from current carbon blacks. Since the mid-1970s most carbon black has been produced by the oil furnace process, which is most often referred to as furnace black. Table 4.1 contains selected information on carbon black.

Unlike diamond and graphite, which are crystalline carbons, carbon black is an amorphous carbon composed of fused particles called aggregates. Properties, such as surface area, structure, aggregate diameter and mass differentiate the various carbon black grades.

Six types of carbon black are produced worldwide: acetylene black, channel black, furnace black, gas black, lamp black and thermal black. Specific physical and chemical properties of a carbon black grade are summarized on its material safety data sheet and the suppliers’ product technical bulletin.

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Tab. 4.1: Information on and properties of carbon black [4.1].

Chemical name	Carbon Black
Synonyms	Acetylene Black, Channel Black, Furnace Black, Gas Black, Lamp Black, Thermal Black
CAS name	Carbon Black
CAS registry number	1333-86-4
Chemical (Molecular) Formula	C
Physical state	Solid: powder or pellet
Flammable Limits (vapor)	LEL: not applicable UEL: not applicable
Lower Limit for Explosion	50 g m^{-3} (carbon black in air)
Minimum Ignition Temperature:	
VDI 2263 (German), BAM Furnace	>932 °F (>500 °C)
Godbert-Greenwald Furnace	>600 °F (>315 °C)
Minimum Ignition Energy	>10 J
Burn Velocity:	>45 s: not classifiable as
VDI 2263, ED Directive 84/449	“Highly Flammable” or “Easily Ignitable”
Flammability Classification (OSHA)	Combustible solid
Solubility	Water: insoluble Solvents: insoluble
Color	Black

4.1
Physical Properties

4.1.1
Morphology

Electron micrographs show that the primary particles of carbon black are almost spherical in shape. In general, a larger number of such primary particles build aggregates in the form of chains or clusters. In practice, the degree of aggregation is called the “structure” of carbon black. These aggregates tend to agglomerate.

The mean primary particle diameter, the width of the particle size distribution, and the degree of aggregation can be varied within relatively wide ranges by varying the production process and several process parameters (Figure 4.1).

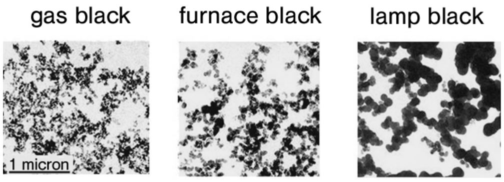

Fig. 4.1 Carbon black of different primary particle sizes.

The diameter of the primary particles ranges from 5 to 500 nm. Diffraction patterns produced by the so-called phase-contrast method in high-resolution electron microscopy show that the spherical primary particles are not amorphous (Figure 4.2). They consist of relatively disordered nuclei surrounded by concentrically deposited carbon layers [4.2]. The degree of order increases from the center to the periphery of each particle, a phenomenon that is important for understanding the chemical reactivity of carbon black.

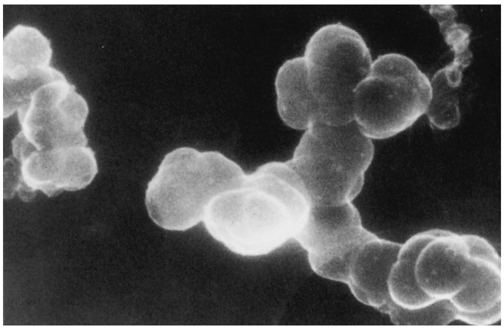

Fig. 4.2 Carbon black aggregate.

The carbon atoms within each layer are arranged in almost the same manner as in graphite. The layers are nearly parallel to each other. However, the relative position of these layers is random, so that there is no order as in the c direction of graphite ("turbostratic structure") [4.3]. X-ray diffraction permits the determination of "crystalline" regions within the carbon black primary particles. These regions are parts of more extended layers, not isolated crystallites. X-ray diffraction reflexes are observed wherever parts of at least three layers are parallel and equidistant. For most carbon blacks, these "crystalline" regions are 1.5–2 nm in length and 1.2–1.5 nm in height, corresponding to 4–5 carbon layers [4.4]. The "crystalline" or well-ordered carbon fraction in carbon blacks varies, according to oxidation kinetic studies, between 60 and 90%.

The morphology of carbon black primary particles indicates that during the formation of carbon black, the first nuclei of pyrolyzed hydrocarbons condense from the gas phase. Thereafter, further carbon layers or their precursors are adsorbed onto the surface of the growing particles. Due to this adsorption, the new layers are always orientated parallel to the existing surface. In the case of high-structure carbon blacks, several particles are joined by collision while they grow. Aggregates are formed by further carbon deposits on these initially loose agglomerates. Polyacetylene seems to play a role in the formation of precursors when aliphatic hydrocarbons are used as starting materials. With aromatic raw materials, however, it is more likely that remaining aromatic degradation products are the intermediates.

The carbon layers of carbon black rearrange to a graphitic order beginning at the particle surface at temperatures above 1200 °C. At 3000 °C, graphite crystallites are formed and the carbon black particles show a polyhedral shape.

4.1.2
Specific Surface Area

The specific surface area of industrial carbon black varies widely. While coarse thermal blacks have specific surface areas as small as 8 m^2 g^{-1}, the finest pigment grades can have specific surface areas as large as 1000 m^2 g^{-1}. The specific surface area of carbon blacks used as reinforcing fillers in tire treads lies between 80 and 150 m^2 g^{-1}. In general, carbon blacks with specific surface areas >150 m^2 g^{-1} are porous with pore diameters of less than 1.0 nm. The area within the pores of high-surface-area carbon blacks can exceed the outer (geometrical) surface area of the particles.

4.1.3
Adsorption Properties

Due to their large specific surface areas, carbon blacks have a remarkable adsorption capacity for water, solvents, binders, and polymers, depending on their surface chemistry. Adsorption capacity increases with increasing specific surface area and porosity. Chemical and physical adsorption not only determine wettability and dispersibility to a great extent, but are also most important factors in the use of carbon blacks as fillers in rubber as well as in their use as pigments. Carbon blacks with high specific surface areas can adsorb up to 20 wt.% of water when exposed to humid air. In some cases, the adsorption of stabilizers or accelerators can pose a problem in polymer systems.

4.1.4
Density

Density measurements using the helium displacement method yield values between 1.8 and 2.1 g cm^{-3} for different types of carbon black. A mean density value of 1.86 g cm^{-3} is commonly used for the calculation of electron microscopic surface areas. Graphitization raises the density to 2.18 g cm^{-3}. The lower density with respect to graphite (2.266 g cm^{-3}) is due to slightly greater layer distances.

4.1.5
Electrical Conductivity

The electrical conductivity of carbon blacks is inferior to that of graphite, and is dependent on the type of production process, as well as on the specific surface area and structure. Since the limiting factor in electrical conductivity is generally the transition resistance between neighbouring particles, compression or concentration of pure or dispersed carbon black plays an important role. Special grades of carbon black are used to equip polymers with antistatic or electrically conductive properties. Carbon blacks with a high conductivity and high adsorption capacity for electrolyte solutions are used in dry-cell batteries.

4.1.6
Light Absorption

The wide use of carbon blacks as black pigments is due to their absorption of visible light. The absorption rate can reach 99.8%. The black color can take on a bluish or brownish tone, depending on light scattering, wavelength, the type of carbon black, and the system into which the carbon black is incorporated. Infrared and ultraviolet light is also absorbed. Therefore, some carbon blacks are used as UV stabilizers in plastics (Figure 4.3).

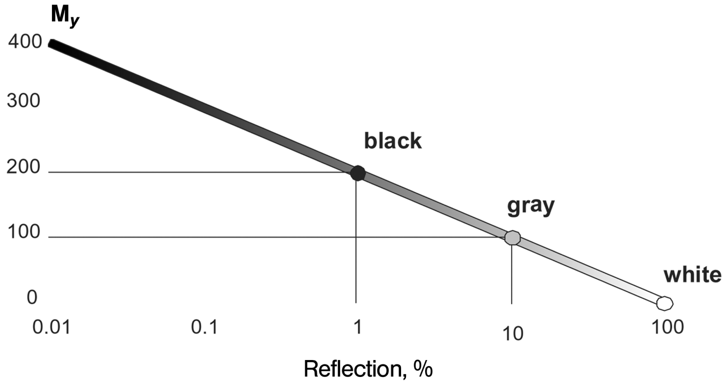

Fig. 4.3 Jetness M_y as a function of reflection.

4.2
Chemical Properties

The general chemical composition of carbon black according to elemental analysis is within the following limits:

Element	Content (wt.%)
Carbon	95–99.5
Hydrogen	0.2–1.3
Oxygen	0.2–0.5
Nitrogen	0–0.7
Sulfur	0.1–1.0
Residual ash	<1

The composition depends on the manufacturing process, the raw material, and the chemical aftertreatment. The ash content of most furnace blacks is <1 wt.% .The ash components can result from the raw material, the salts that are injected to control the structure, and the salts of the process water. The ash content of gas blacks is less than 0.02%.

The surface of carbon blacks contains certain amounts of polynuclear aromatic substances. These are strongly adsorbed and can only be isolated by continuous extraction with solvents, e.g., boiling toluene. For most industrial carbon blacks, the amount of extractable material is below the limit defined by the food laws.

The oxygen content of carbon blacks is of the greatest importance for their application. Oxygen is bound to the surface in the form of acidic or basic functional groups. The amount of surface oxides and their composition depend on the production process and an eventual aftertreatment. Furnace blacks and thermal blacks, which have been produced in a reducing atmosphere, contain about 0.2–2 wt.% oxygen in the form of almost pure, basic surface oxides. Gas and channel blacks, which are manufactured in the presence of air, contain up to 8 wt.% oxygen. In this case, the greater part of the oxygen is contained in acidic surface oxides and only a small portion in basic oxides. The amount of acidic surface oxides can be increased by oxidative aftertreatment. Oxygen contents of up to 15 wt.% may be obtained.

The surface oxides are destroyed at high temperatures. Due to this fact the weight loss at 950 °C ("volatiles") is a rough indication of the oxygen content of a carbon black. The pH value measured in aqueous slurry is another indication of the degree of oxidation. In general, the pH value is >7 for furnace blacks (low oxygen content, basic surface oxides), 4–6 for gas blacks, and 2–4 for oxidized carbon blacks (high oxygen content, acidic surface oxides with a high amount of polar functional groups). Further organic reactions, e.g., alkylation, halogenation, esterification, can be carried out with the surface oxides to modify the surface properties.

Concerning their oxidation behavior, industrial carbon blacks do not spontaneously ignite when stored in air at 140 °C according to the IMDG Code [4.5]. When ignited in air, carbon black glows slowly. In contrast to coal, dust explosions are not observed under normal test conditions [4.6]. However, ignition sources of extremely high energy, e.g., a gas explosion, may induce a secondary dust explosion in air.

4.3
Raw Materials

The preferred feedstocks for most carbon black production processes, especially the furnace process, are heavy oils, which are composed mainly of aromatic hydrocarbons. The aromatic form of carbon gives the highest carbon to hydrogen ratio, thus maximizing the available carbon, and is the most efficient one in terms of carbon black yields. In theory, the greater the aromaticity the more efficient is the process. Unfortunately as the number of combined rings increases, the substances move from viscous liquids to solid pitches. Therefore, in reality, the most suitable oils are those in which the majority of the carbon is in the form of substances comprising three or four-membered rings.

Distillates from coal tar (carbochemical oils), or residual oils that are created by catalytic cracking of mineral oil fractions and olefin manufacture by the thermal cracking of naphtha or gas-oil (petrochemical oil) can also be used as a source of raw material. Quality is the main criteria to favor a specific feedstock. Here a variety of properties are important: density, distillate residue, viscosity, carbon/ hydrogen ratio, asphaltene content, specified impurities, etc. All these play a role for the desired feedstock specifications. The BMCI (Bureau of Mines Correlation Index) provides a measure of aromaticity based on either density and average boiling point or viscosity and API gravity [4.7]. Economically a suitable feedstock should have an index above 120.

However, the BMCI is really only applicable to feedstocks derived from petroleum. In the case of carbochemical oils, the BMCI may not reflect the true aromaticity of the product. For this reason, the carbon/hydrogen ratio is more favored for carbochemical products. However, as this measurement is also superior to BMCI, even for petrochemical products, the carbon/hydrogen ratio or the carbon content are becoming the preferred criteria for all carbon black feedstocks.

Additional quality requirements involve impurities from foreign matter. Alkaline metals, for instance, are important because they have a direct effect on a specific carbon black property. The sulfur content of the oil can also play a significant role in production operations since, in many countries, producing sites have to meet rigorous environmental standards. Sulfur emissions from combustion processes are restricted by law. Furthermore, carbon blacks having high sulfur contents might be prohibitive for certain applications. When describing the various production methods we will also address the different raw materials that can be used to produce carbon black.

4.4
Production Processes

A summary of the most important production processes is given in Table 4.2.

Tab. 4.2: Production methods for carbon black pigments.

Chemical process	Manufacturing methods	Main raw materials
Thermal-oxidative decomposition	Furnace black process	Aromatic oils on coal tar basis or mineral oil, natural gas
	Degussa gas black process	Coal tar distillates
	Lamp black process	Aromatic oils on coal tar basis or mineral oil
Thermal decomposition	Thermal black process	Natural gas or mineral oils
	Acetylene black process	Acetylene

In the past decades, the rapidly expanding automobile industry has required increasing numbers of tires, black pigmented plastics and black paints with various characteristics. This has led not only to the development of new rubber grades, but also to the development of new carbon blacks required by refined application processes and to the development of a new and better manufacturing process, the furnace-black-process. This process allows the production of nearly all types of carbon black required from the industries using rubber, plastics, paints and inks. It also meets the high economic and ecological requirements of the present times.

4.4.1
Furnace Black Process

The furnace black process was developed in the United States in the 1920s, and since then, it has been greatly refined. It is a continuous process, carried out in closed reactors, so that all reactants can be carefully controlled [4.8]. Today most semi-reinforcing rubber blacks (carcass or soft blacks) with specific surface areas of 20–60 $m^2\ g^{-1}$ and the active reinforcing blacks (tread or hard blacks) with specific surface areas of 65–150 $m^2\ g^{-1}$ are manufactured by this process, as well as to an increasing extent, pigment-grade carbon blacks with much greater specific surface areas and smaller particle sizes. In addition to the specific surface area, other quality specifications such as structure, measured as DBP absorption, and application properties of rubber such as abrasion resistance, modulus, and tear strength or jetness and tinting strength for color blacks can also be systematically varied in the furnace black process by adjusting the operating parameters. This flexibility is necessary to meet the very narrow specifications required by customers.

The heart of a furnace black production plant is the furnace in which the carbon black is formed. The feedstock is injected, usually as an atomized spray, into a high-temperature and high-energy density zone, which is achieved by burning a fuel (natural gas or oil) with air. The oxygen, which is in excess with respect to the fuel, is not sufficient for the complete combustion of the feedstock, which therefore is, for the most part, pyrolyzed to form carbon black at temperatures of 1200–1900 °C. After the reaction mixture is quenched with water and further cooled in heat exchangers, the carbon black is collected from the tail gas by using a filter system.

Figure 4.4 shows a schematic drawing of a furnace black plant. The feedstock, preferably petrochemical or carbochemical heavy oils, which usually begins to crystallize near the ambient temperature, is stored in heated tanks equipped with circulation pumps to maintain a homogeneous mixture. Oil is conducted to the reactor by means of rotary pumps via heated pipes and a heat exchanger, where it is heated to 150–250 °C to obtain a viscosity appropriate for atomization. Various types of spraying devices are used to introduce the feedstock into the reaction zone. An axial oil injector with a spraying nozzle at its tip, producing a hollow-cone spray pattern, is a frequently used device. One- and two-component atomizing nozzles [4.9] are in use, air and steam being the preferred atomizing agents in the latter case. However, the feedstock is injected into other reactors as a plurality of coherent or atomized streams into the accelerated combustion gases perpendicular to the direction of stream [4.10].

As the carbon black structure may be reduced by the presence of alkali metal ions in the reaction zone [4.11], alkali metal salts, preferably aqueous solutions of potassium hydroxide or potassium chloride, are often added to the oil in the oil injector. Alternatively, the additives may be sprayed separately into the combustion chamber. In special cases, other additives, e.g., alkaline-earth metal compounds, which increase the specific surface area, are introduced in a similar manner.

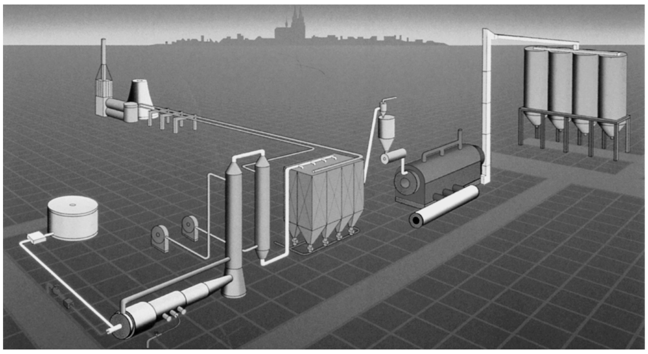

Fig. 4.4 Furnace black production installation.

The high temperature necessary for pyrolysis is obtained by burning fuel in excess air in a combustion chamber. Natural gas is still the fuel of choice, but other gases, e.g., coke oven gases or vaporized liquid gas, are occasionally used. Various oils including the feedstock are used as fuel for economic reasons. Special burners, depending on the type of fuel, are used to obtain fast and complete combustion (Figure 4.5).

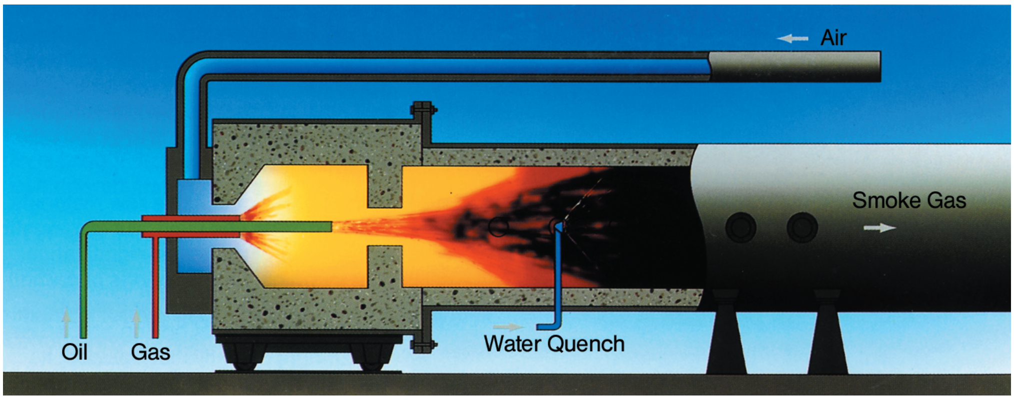

Fig. 4.5 Furnace reactor.

The air required for combustion is compressed by rotating piston compressors or turbo blowers. It is preheated in heat exchangers by hot gases containing carbon black leaving the reactor. This conserves energy and thus improves the carbon black yield. Preheated air temperatures of 500–700 °C are common.

Important progress has been made on the reactor throughput. A production plant with a capacity of 20,000 t a^{-1} (2.5 t h^{-1}) was previously run with 12 furnaces, which in the last decades have been replaced by only one high-performance reactor for the same capacity. Modern plants are one-stream units with only one aggregate for each process step (reactor, collecting system, beading device, dryer). From a technical point of view, even larger units could be built. However, due to the great variety of carbon black types required, the capacity of one unit is economically limited by the frequency of switching over to other types and the amount of off-grade carbon black produced during this procedure.

The reactors of modern furnace plants vary considerably in internal geometry, flow characteristics, and the manner in which fuel and feedstock are introduced. Nevertheless, they all have the same basic process steps in common, producing hot combustion gases in a combustion chamber, injecting the feedstock and rapidly mixing it with the combustion gases, vaporizing the oil, pyrolyzing it in the reaction zone, and rapidly cooling the reaction mixture in the quenching zone to temperatures of 500–800 °C.

Most furnace black reactors are arranged horizontally. They can be up to 18 m long with an outer diameter of up to 2 m. Some vertical reactors are used especially for the manufacture of certain semi-reinforcing blacks (Figure 4.5) [4.12]. Further reactors are described in Ref. [4.13].

The properties of carbon blacks are dependent on the ratios of fuel, feedstock, and air, which therefore must be controlled carefully [4.14]. The particle size of the carbon black formed decreases, in most cases, with increasing amounts of excess air relative to the amount needed for the complete combustion of the fuel. Since the excess air reacts with the feedstock, a greater amount of air leads to higher oil combustion rates, resulting in rising temperatures in the reaction zone. As a consequence, the nucleation velocity and the number of particles formed increases, but the mass of each particle and the total yield decreases. This allows semi-reinforcing carbon blacks to be manufactured with better yields than active reinforcing carbon blacks. The yields, which depend on the carbon black type and the type of feedstock, range between 50 and 65% for semi-reinforcing blacks and 40 and 60% for reinforcing blacks. Pigment blacks with large surface area and markedly smaller particle sizes than rubber blacks gives lower yields.

Other parameters influencing the carbon black quality are the manner in which the oil is injected, atomized, and mixed with the combustion gases, the type and amount of additives, the preheating temperature of the air, and the quench position. As long as the carbon black is in contact with the surrounding gases at the high reaction temperature, several reactions on the carbon surface occur (e.g., Boudouard reaction, water gas reaction), so that the chemical nature of the carbon black surface is modified with increasing residence time. When quenched to temperatures <900 °C, these reactions are stopped and a certain state of surface activity is frozen. Carbon black surface properties can also be adjusted by varying the pelletizing and drying conditions.

The mixture of gas and carbon black leaving the reactor is cooled to temperatures of 250–350 °C in heat exchangers by counter flowing combustion air and then conducted into the collecting system.

Generally, the collecting system consists of only one high-performance bag filter with several chambers, which are periodically purged by counter-flowing filtered gas or by pulsejets. Occasionally, an agglomeration cyclone is installed between the heat exchanger and the filter [4.15]. Depending on the capacity of the production unit, the filter may contain several hundred bags with a total filter area of several thousand square meters.

The fluffy carbon black coming out of the filter is pneumatically conveyed into a first storage tank. Small amounts of impurities ("grit", e.g., iron, rust, or coke particles) are either removed by magnets and classifiers or milled to an appropriate consistency.

Freshly collected carbon black has an extremely low bulk density of 20–60 g L^{-1}. To facilitate handling and further processing by the customer, it must be compacted. Densification by "put gassing", a process by which the carbon black is conducted over porous, evacuated drums, is the weakest form of compacting which allows the carbon black to retain its powdery state [4.16]. This form of compacting is used for certain pigment blacks for the paint, ink and plastic applications in which good dispersibility must remain.

The carbon black leaving the beading machine contains ca. 50 wt.% water. It is dried in dryer drums, indirectly heated by burning tail gas. The dried carbon black is transported via conveyor belts and elevators to the storage tank or packing station. Bulk densities of wet-pelletized carbon blacks are between 250 and 500 g L^{-1}.

4.4.2
Gas Black and Channel Black Processes

The channel black process, used in the United States since the late 19th century, is the oldest process for producing small-particle-size carbon blacks on an industrial scale. In 1961, the production of channel black was about 120,000 t. The last production plant in the United States was closed in 1976, due to low profitability and environmental difficulties. Natural gas was used as the feedstock. The carbon black yield was only 3–6%.

The gas black process was developed in the 1930s. It is similar to the channel black process, but uses coal tar oils instead of natural gas. Yields and production rates are much higher with oil-based feedstock. Degussa has used the gas black process on an industrial scale since 1935. Today, almost all grades are used as color blacks in printing inks, plastics, and coatings. High-quality oxidized gas blacks are of special interest, e.g., in deep black coatings.

In the gas black process (Figure 4.6) the feedstock is partially vaporized. The residual oil is continuously withdrawn. The oil vapor is transported to the production apparatus by a combustible carrier gas (e.g. hydrogen, coke oven gas, or methane). Air may be added to the oil-gas mixture for the manufacture of very small particle size carbon black. Although this process is not as flexible as the furnace black process. Varying the relative amounts of carrier gas, oil, and air can lead to various types of gas black.

A gas black apparatus consists of a burner pipe approximately 5 m long, which carries 30–50 diffusion burners. The flames burn in contact with a water-cooled drum, where about half of the formed carbon black is deposited. This black is scraped off and transported by a screw to a pneumatic conveying system. A steel box, open at

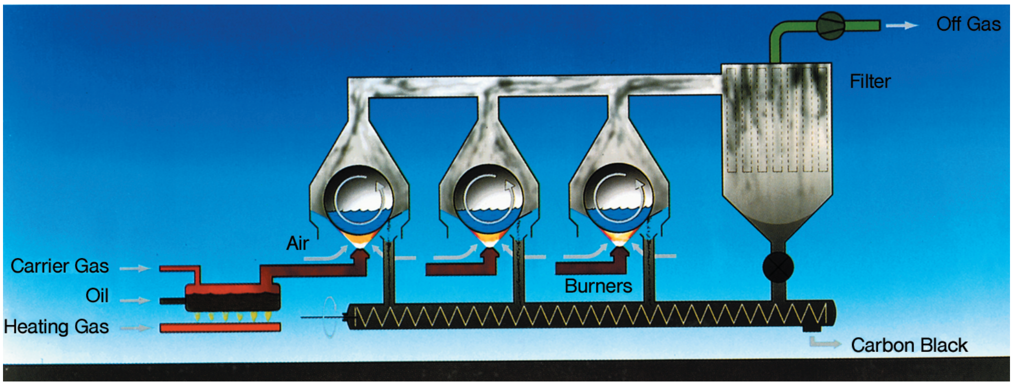

Fig. 4.6 Scheme of gas black production plant.

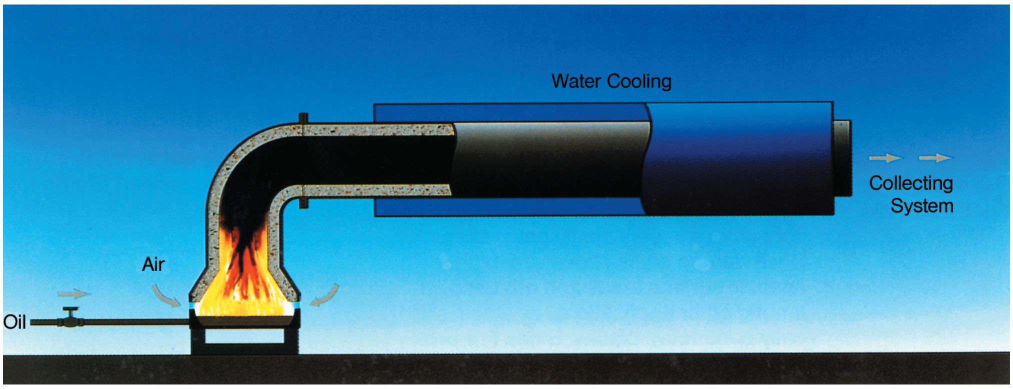

Fig. 4.7 Scheme of lamp black production plant.

the bottom, surrounds the gas black apparatus. At the top of it, fans suck the off-gas into filters, which collect the carbon black suspended in the gas.

The amount of air entering the apparatus can be regulated by valves in the exhaust pipes. Several gas-black apparatuses are combined to form one production unit. One oil vaporizer feeds the whole "group". The production rate and the yield of an apparatus depend on the type of carbon black produced. For a typical RCC black, the production rate is 7–9 kg h^{-1} and the yield is 60%. The yield for high-quality color blacks is considerably lower (10–30%).

As a result of the contact with oxygen at high temperatures during production, acidic oxides are formed on the surface of the carbon black particles. In contrast to furnace blacks, gas blacks thus display an acidic reaction when suspended in water.

4.4.3
Lamp Black Process

The lamp black process (Figure 4.7) is the oldest commercially used carbon black production process [4.8, 4.15].

However, besides the general principle, today's lamp black production units have very little in common with the ancient carbon black ovens. Smoking chimneys and settlement chambers have been replaced by highly sophisticated filtering systems.

The lamp black apparatus consists of a cast-iron pan that holds the liquid feedstock, which is surmounted by a fireproof flue hood lined with refractory bricks. The air gap between the pan and the hood, as well as the vacuum present in the system, help to regulate the air supply and thus enable the manufacturer to fine-tune the carbon black's ultimate properties. Though radiant heat from the hood causes the raw material to vaporize and partially combust. Most of it is converted into carbon black.

In order to separate the solids, process gases containing carbon black are passed through a filter after the cooling stage. Onward processing is similar to that of the furnace black manufacture.

These carbon blacks are characterized by a broad primary particle size distribution, ranging from approximately 60 to over 200 nm and are widely used in a number of specialized applications.

4.4.4
Thermal Black Process

This method of producing carbon black is a non-continuous or cyclic process, with natural gas as the most commonly used feedstock, although higher-grade hydrocarbon oils are used. A thermal black plant delivers maximum efficiency when operating in a tandem mode. It consists of two reactors operating alternately in cycles lasting between 5 and 8 min, one of which is heated with a natural gas or oil/air mixture while the other one is fed with pure feedstock, which undergoes thermal decomposition.

One could also include the thermal black method in the group of thermal-oxidative processes, with the distinction that energy generation and decomposition reaction are not simultaneous. However, the fact that the actual carbon black formation takes place in the absence of oxygen and at decreasing temperatures results in carbon black properties that are markedly different from those achieved with thermal-oxidative processes.

Thermal blacks are formed relatively slowly, resulting in coarse particles in sizes ranging from 300 to 500 nm, referred to as medium thermal. However, formerly, when using natural gas only as feedstock, it was possible to dilute it with inert gases and produce a thermal black consisting of particles in the range of 120 to 200 nm. This was referred to as fine thermal although it has virtually disappeared from the market.

Thermal blacks are used for mechanical rubber goods with high filler contents. Cheaper products (clays, milled coals, and cokes), however, have gained increasing importance as substitutes in recent years. The total production of thermal blacks is, therefore, decreasing.

4.4.5
Acetylene Black Process

Acetylene and mixtures of acetylene with light hydrocarbons are the raw materials for a process that has been used since the beginning of the 20th century. Unlike other hydrocarbons, the decomposition of acetylene is highly exothermic.

The discontinuous explosion process is the oldest technical process for acetylene black. It was mainly used for the production of color blacks. Continuous processes were developed later with production rates up to 500 kg h^{-1} [4.17]. Acetylene or acetylene-containing gases are fed into a preheated, cylindrical reactor with a ceramic inner liner. Once ignited, the reaction is maintained by the decomposition heat that is evolved. The carbon black is collected in settling chambers and cyclones. Approximately 95–99 % of the theoretical yield is obtained.

The primary particles of acetylene black have different shapes compared with those of other carbon blacks. As the increased order in the c-direction of the crystalline regions indicates, folded sheets of carbon layers are the main structural components. The application of acetylene blacks is limited to special uses, e.g., in dry cells, because of their relatively high price. The total worldwide production today is approximately 40,000 t a^{-1}.

4.4.6
Other Production Processes

Hydrocarbon vapors may be almost quantitatively decomposed in a plasma into carbon and hydrogen [4.18]. This process can be used to make small-particle carbon blacks with new properties. However, an economical plasma-based commercial process is not yet known.

The Huels-electric-arc process was the only large-scale process using plasma reactions where large quantities of carbon black were produced as a by-product in the production of acetylene. However, this type of carbon black is no longer used as a pigment.

Since the price of both feedstocks and fuels is highly dependent on the petrochemical industry, several attempts have been made to find new raw materials. Processes for the manufacture of carbon black directly from coal [4.19] or for isolating carbon black from old tires have been studied. None of them, however, has achieved commercial importance up to now. On the other hand, clay, milled coal, and coke have found limited use as substitutes for very coarse carbon blacks, primarily thermal blacks and some SRF blacks. The increasing use of precipitated silicas in tires and mechanical rubber goods, mostly in combination with organo-silane coupling agents, which originally was indicative of an increasing search for new non-oil-based fillers, has led to new features of rubber properties.

4.4.7
Oxidative Aftertreatment of Carbon Black

Oxygen-containing functional groups on the surface of carbon blacks strongly influence their application properties (Figure 4.8). High contents of volatiles, i.e., high concentrations of surface oxides, decrease the vulcanization rate and improve the flow characteristics of inks. The gloss of coatings is increased, the color tone is shifted from brownish to bluish, and jetness often increases.

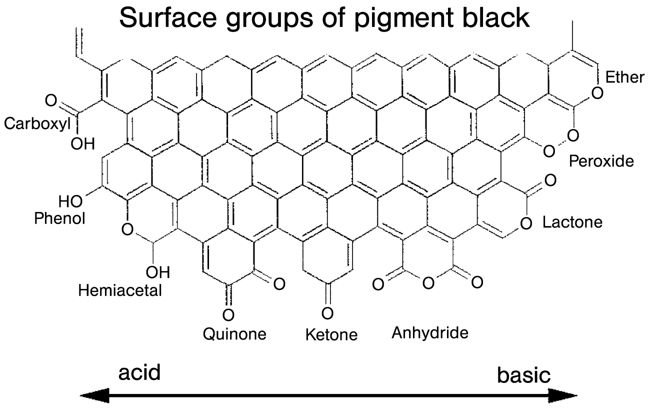

Fig. 4.8 Surface groups of pigment black.

Some color blacks receive oxidative aftertreatment on a commercial scale to amend their color properties. Depending on the oxidizing agent and the reaction conditions selected, different types of surface oxides are formed in varying quantities.

The simplest method of oxidizing the carbon black surface is by aftertreating it with air at 350–700 °C. However, the degree of oxidation is limited. Higher contents of surface oxides and better process control are achieved with nitric acid [4.20], mixtures of NO_2 and air [4.21], ozone, or sodium hypochlorite solutions [4.22] as oxidizing agents. As a rule, all strongly oxidizing agents may be used, either as a gas or in solution. Most surface oxidation of carbon black is carried out at elevated temperature.

Oxidized carbon blacks may contain up to 15 wt.% oxygen. They are strongly hydrophilic. Some of them form colloidal solutions spontaneously in water. In polar printing ink systems and coatings, a better wettability and dispersibility is achieved by surface oxidation, thus reducing binder consumption [4.23].

Surface oxidation of carbon black with nitric oxide and air can be carried out industrially in a fluidized-bed reactor [4.24]. A suitable aftertreatment unit consists of a preheating vessel, in which the carbon black is fluidized and heated, a reaction vessel to carry out the surface oxidation, and a desorption vessel, in which adsorbed nitric oxide is removed. Typical reaction temperatures are in the range 200–300 °C. Depending on the degree of oxidation, the residence time can amount to several hours. The nitric oxide acts primarily as a catalyst, the oxygen in the air being the genuine oxidizing agent.

Another common method of surface oxidation is carried out during pelletization. Nitric acid, instead of water, is used as a pelletizing agent. The surface is oxidized while the wet pellets are dried at elevated temperature [4.25]. Oxidation of powdery black with ozone is also carried out on a commercial scale.

4.5
Testing and Analysis

For a long time, characterization of carbon blacks was a question of determining different shades of black with the human eye. Precise data on the reinforcing effect were available only to a limited degree.

The composition described below refers to all carbon black grades, regardless of the production method. Process-related variances have already been addressed in the description of the various methods used today for the manufacture of carbon black. The specific surface area of carbon black is a function of its primary particle size. The structure designates the three-dimensional arrangement of primary particles in the aggregates. Extensive interlinking or branching characterizes a “high-structure”, whereas less pronounced interlinking or branching indicates a “low-structure”. The structure of a carbon black particle can only be determined indirectly. The most commonly accepted method is based on DBP (dibutyl-phthalate) absorption. DBP is added to a specified quantity of carbon black in a Brabender kneader. The measurement consists of registering the amount of added DBP to reach a predetermined level of torque generated by the kneading machine during titration.

The method is based on the premise that all interstices, known as void volumes, in the carbon black aggregates are filled with DBP. The surface of the carbon black is considered to be “wetted” and this new surface state is translated into a change in the torque required for the kneading machine. The DBP requirement thus allows conclusions on the degree of aggregation of individual carbon blacks. The rule: the greater the DBP absorption, measured in ml g^{-1}, the higher the carbon black structure.

High-resolution electron microscopy shows the primary particles of carbon blacks in detail. This technology, combined with X-ray structural analysis, shows that the primary particles consist of concentrically arranged, graphite-like crystallites. By partially fusing together, the graphite layers are often twisted into each other, exhibiting a non-ordered state. One single primary particle can contain up to 1500 of such crystallites.

Scanning tunneling microscopy leads to the supposition that the primary particles consist of superimposed, scale-like layers of graphite. For this reason, the L-values determined by X-ray diffraction have to be regarded as a median overlap surface of graphite layers and not as the average size of individual crystallites.

The chemical analysis of carbon blacks detects in many cases minute quantities of oxygen, hydrogen, nitrogen and sulfur besides the carbon. Carbon blacks also contain traces of metals, the amounts and type being feedstock dependent. The type and the content of metals in pigment blacks can be summarized as follows:

Element	**Content**
Antimony	<10 ppm
Arsenic	<5 ppm
Barium	<10 ppm
Cadmium	<1 ppm
Chrome	<5 ppm
Cobalt	<10 ppm
Copper	<5 ppm
Lead	<50 ppm
Nickel	<10 ppm
Mercury	<1 ppm
Selenium	<10 ppm

Most of these elements are concentrated on the surface of the carbon black. Removal of traces of organic elements is possible with the use of special solvents. The carbon black extraction based on toluene, the toluene extract, results in values of mostly less than 0.1%. Further analysis of the material shows, among other substances, minute quantities of PAHs (polycyclic aromatic hydrocarbons), which are tightly bound to the carbon black surface.

Hydrogen is, to a certain degree, directly fused to the carbon. However, together with oxygen, another part forms surface-bound functional groups that can be identified by analysis, both qualitative and quantitative. Here, carbonyl, carboxyl, pyrone, phenol, quinone, lactol and ether groups have been identified as the oxygen-containing groups bound to the surface of the carbon black particles. Heating the substance to 950 °C in the absence of oxygen, however, results in separation. This explains their designation as "volatile matter".

Oxygen-containing functional groups on the carbon black surface can also be created through specific oxidative aftertreatment. Oxygen content levels of 15% and higher are possible.

Sulfur is present in a variety of forms, in its elementary form, as a bound molecule, but also in an oxidized state. High sulfur contents import certain acidity to industrial carbon blacks. Nitrogen, when present, is usually included in the graphite grid. One thing to bear in mind is that sulfur and nitrogen content are contingent primarily on feedstock type and quality.

Among the physical properties of carbon blacks, the density and the electrical conductivity are the most important.

4.5.1
Density

The density of carbon black powders is difficult to determine. It can vary between 1.82 and 1.89 g cm^{-3}.

4.5.2
Electrical Conductivity

This property is usually not measured for the carbon black itself, but in the system containing the carbon black, i.e. in a polymer or binding agent. Conductivity of a filled polymer increases with the specific surface area and the structure of the carbon black being incorporated into the system. It is also a function of carbon black concentration and dispersion and of the type of polymer or binding agent used.

Test methods that resemble certain physicochemical measurements and give information on application properties for carbon black are summarized in Table 4.3.

Tab. 4.3: Standardized analytical test methods for carbon black.

Description	ISO	ASTM	DIN
Surface			
Iodine adsorption	S-1304	D-1510	53 582
Nitrogen surface	S-4652	D-3037/4820	66 132
CTAB number	6810	D-3765	
Tinting strength	S-5435	D-3265	
Structure/rheology			
DBP absorption	S-4656	D-2414	53 601
24M4-DBP	6894	D-3493	
Oil absorption	787/5		DIN/ISO method
Coloristics			
Jetness (blackness)			55979
Tinting strength	787/16 -/24		
Chemical analyses			
Volatile content			53552
Moisture	787/2	D-1509	DIN/ISO method
Ash residue	S-1125	D-1506	53 586
Sieve residue	787/18	D-1514	DIN/ISO method
Toluene extract			53 553
Photelometer	S-3858	D-3392	
pH	787/9	D-1512	DIN/ISO method
External appearance and handling properties			
Bulk density	S-1306	D-1513	53 600
Individual pellet hardness		D-3313	
Pellet size distribution		D-1511	

4.6
Transportation and Storage

The majority of the carbon black produced is shipped as bulk material (up to 80%); the rest is handled in bags. Generally, the large stocks of pelletized furnace blacks for the rubber industry are stored, by the producers as well as the customer, in plastic-coated steel storage tanks consisting of one or more cells with a capacity of 100–1000 t (300–3000 m^3). Carbon black is shipped in containers or tank trucks with a capacity of up to 20 t. In recent times big bags and steel bins with a capacity of up to 1 t have received increasing interest. Smaller amounts of rubber blacks and especially pigment blacks are stored and shipped in paper or plastic bags stacked on palettes.

4.7
Uses

Table 4.4 gives an overview of the most important carbon black applications.

Tab. 4.4: Major carbon black applications.

Area	Application
Rubber	Reinforcing filler in tires and mechanical rubber components
Printing inks	Pigmentation, rheology
Coatings	Full black and tinting application
Plastics	Black and gray pigmentation, tinting, UV protection, conductivity, conductor coatings
Fibres	Pigmentation
Paper	Black and gray pigmentation, conductivity, decorative and photo-protective papers
Construction	Cement and concrete pigmentation, conductivity
Power	Carbon brushes, electrodes, battery cells
Metal reduction, compounds	Metal smelting, friction compound
Metal carbide	Reduction compound, carbon source
Fire protection	Reduction of mineral porosity
Insulation	Graphite furnace, polystyrene and PU foam

4.7.1
Rubber Blacks

About 90% of the carbon black produced is used in the rubber industry as reinforcing filler in tires, tubes, conveyor belts, cables, rubber profiles, and other mechanical rubber goods. Furnace blacks are predominantly used in rubber processing.

The following widely acknowledged typology of carbon blacks based on reinforcing properties has stood the test of time.

4.7.1.1
Active Blacks

High reinforcing capability, fine carbon blacks, tire tread blacks (particle size: 18–28 nm)

4.7.1.2
Semi-Active Blacks

Lower reinforcing capability, carcass blacks (particle size: 40–60 nm).

4.7.1.3
Inactive Blacks

Negligible reinforcing capability, high filling rates (particle size: >60 nm). Though the preceding typology is still widely respected, the internationally recognized ASTM designations are those generally used (Table 4.5). The first character in the nomenclature system for rubber-grade carbon blacks is a letter indicating the effect of the carbon black on the cure rate of a typical rubber compound containing the black. The letter "N" is used to indicate a normal curing rate of typical furnace blacks that have received no special modification to alter their influence on the rate of cure of rubber. The letter "S" is used for channel blacks or for furnace blacks that have been modified, usually by oxidative methods, to effectively reduce the curing rate of rubber. Channel blacks characteristically impart a slower rate of cure to rubber compounds. Thus, the letter "S" designates a slow cure rate. Blacks may vary considerably in "curing rate" within each of the two letter classifications. The second character in the system is a 3-digit number the first digit of which designates the average surface area of the carbon black as measured by nitrogen surface area. The surface area range of the carbon blacks has been divided into six arbitrary groups, and each has been assigned a digit to describe that group.

Tab. 4.5: Rubber blacks typology (ASTM).

Designation	Particle size range (nm)
N 110	11–19
N 220	20–25
N 330	26–30
N 550	40–48
N 660	49–60
N 770	61–100

The N 300 series is characterized by a wide variety of rubber blacks, covering about 10 different types. As mentioned above, fine-particle active blacks are used for rubber components that need to withstand significant levels of mechanical stress, e.g. tire treads. Semi-active blacks, on the other hand, are used in the tire carcass but also in technical rubber components, from screen and door seals to floor mats. Tires also contain other special carbon blacks, for instance, so-called adhesion blacks for improving radial steel belt adhesion, conductive blacks or inactive blacks for higher filler load rates [4.26].

4.7.2
Pigment Blacks

Quantitatively, the pigment blacks are substantially less important than the rubber blacks. Qualitatively, pigment blacks belong to the group of highly sophisticated pigments. These carbon blacks are used for a variety of applications such as printing, paints and coatings manufacture, plastics, fibre, paper and others (printing blacks, coating blacks, plastic blacks). But here as well, the industry works with a widely accepted typology based on particle size.

4.7.2.1
Pigment Properties

Pigment blacks have a number of advantages compared to other black pigments and black organic dyes:

- Color stability
- Solvent resistance
- Acid and alkaline resistance
- Thermal stability
- Hiding power

Though not considered as an international standard, the following classification system serves as the main reference for most manufacturers. This system contains four groups:

High Color (HC), Medium Color (MC), Regular Color (RC) and Low Color (LC).

A third letter refers to the manufacturing process: (F) for furnace black and (C) for channel or gas black. Finally, oxidative aftertreatment is indicated by the suffix (o) for “oxidized” (Table 4.6).

The most important coloristic properties of carbon blacks are jetness and tinting strength. The jetness refers to the achievable intensity of blackness. A method for

Tab. 4.6: Pigment black classification.

Designation		**Particle size range (nm)**
Gas blacks	*Furnace blacks*	
HCC	HCF	10–15
MCC	MCF	16–24
RCC	RCF	25–35
	LCF	>36
Gas blacks oxidized		
HCC (o)		10–17
MCC (o)		18–24
RCC (o)		>25

measuring residual refraction (<0.5%) invented by Degussa became a standard as DIN 55979. Here, a carbon black sample mixed with linseed oil and measured with a spectral photometer results in a M_y-value. The finer the carbon black particles, the higher the M_y-value, corresponding to a higher blackness. A refined version of the paste method described above consists of determining the M_y-factor in an alkyd/melamine resin system (PA 1540). The jetness achieved is mapped against various group standards and indicated as a relative blackness value M_y for optimum reproducibility and consistency [4.27, 4.28].

Measuring of the blackness:
Without colored undertone

$$M_y = 100 \log (100/y)$$

Contribution of the colored undertone

$$d_M = 100 (\log X_n/X - \log Z_n/Z)$$

blue $d_M > 0$
brown $d_M < 0$

Tinting strength is the coloring ability of a carbon black as measured against a white pigment (titanium dioxide, zinc oxide). However, tinting strength is not only influenced by particle size and structure but also to some extent by particle size distribution. The finer the carbon black particles, the greater the tinting strength, an indirect indicator of surface or particle size specification.

In addition to the particle size expressed in the jetness (M_y-value), the surface chemistry of the pigment blacks has a decisive influence on their processing behavior. The effect of surface treatment on the performance of pigment black in coatings was shown in Section 4.4.7.

4.7.2.2
Pigment Blacks for Printing Inks

The printing ink industry places many requirements on pigment blacks. Several properties are expected for pigment blacks, both in printing inks and for the printed products. Printing inks: good wettability, easily dispersible, high concentration, optimum viscosity, good flow characteristics, storage stability, and economy. Printed products: jetness, hiding power, blue hue, gloss, rub resistance.

The use of suitable pigment blacks makes it possible to achieve various effects:

Dyeing, tinting

Almost 100% of the pigment black applications in the printing ink industry involve the “dyeing” of black inks. Pigment blacks are also used to tint gray and colored inks (brown, olive, etc.), but this amount is relatively small compared with the entire consumption.

Dyeing, thickening

Bearing in mind the effects which may be achieved by pigment blacks in printing inks, one can distinguish between the color giving (inking) component and the rheological component. The inking component comprises jetness, undertone and gloss, whereas the rheological component includes the parameters viscosity flow properties and tack.

Color density, undertone

The inking component depends largely on the particle size of the pigment black. The finer the particle size of the pigment black, the higher the color density or jetness of the printing ink:

Decreasing the particle size, increasing jetness and brown undertone
Increasing the particle size, decreasing jetness and bluer undertone

Rheology

The rheological component is likewise dependent on the particle size and the resulting surface area, but also on the structure and the surface chemistry. Finely divided pigment blacks have a relatively high surface area and therefore a strong thickening effect. If the particle size increases, the surface area decreases and the thickening effect is reduced. This means:

Decreasing particle size: high viscosity
Increasing particle size: low viscosity

Structure: The structure of the pigment black is an important parameter for the production of printing inks. A number of quality attributes depend on the structure: dispersion properties, viscosity, flow properties, color density, gloss, rub resistance, and conductivity:

High-structure: high yield value, high viscosity and reduction in gloss
Low-structure: good flow properties, low viscosity and increased gloss

Electrical conductivity

Pigment blacks are electrically conductive as a function of their structure. The higher the structure, the better the conductivity of the pigment black. Electrically conductive printing inks are manufactured with special high-structured pigment blacks. Due to the special nature of these pigment blacks, conductive printing inks have a relatively high viscosity. In order to achieve good electrical conductivity on the printed article, it is an advantage to have a high pigment black concentration in the printing ink and a high inkfilm thickness when printing.

UV-application

UV curing printing inks are becoming more and more popular. However, black UV curing printing inks can only be a compromise, since pigment black strongly absorbs the incident light, both in the invisible and ultraviolet range. Hence, the blacker the printing ink, the greater the delay in curing. Special carbon blacks are available for this application.

Substrate

The substrate, which is to be printed upon, is an important criterion for the choice of pigment blacks. Low-structure pigment blacks can achieve a high quality of jetness and gloss on coated papers. High-structure pigment blacks produce higher levels of jetness on uncoated papers. Generally, better results can be expected with coated papers.

Offset inks, letterpress inks

The surface roughness and the absorbence of the printing substrate determine the composition of the printing inks. Inks with a high yield value are suitable for this application where less penetration into the uncoated paper and a greater degree of jetness can therefore be reproduced. Flow properties and structural viscosity can be adjusted according to the structure of the pigments. Pigment blacks with a particle size from 56 nm up to 25 nm are possible.

Newspaper printing inks

These are manufactured with medium to high-structure pigment blacks. An unpleasant characteristic of conventional newspaper inks is their low rub resistance. This can be influenced by the structure of the pigment black. Low-structure pigment blacks improve the rub resistance, those with a higher structure promote smudging. A combination of both pigment blacks is usually the solution to this problem. More carbon blacks in beaded form are now used in newspaper printing inks. Beaded carbon blacks generate little dust and therefore improve the handling necessary for an automatic ink production. The most popular of the beaded versions, including oil beads, dry beads and wet beads, is the oil-beaded carbon black, due to its relatively easy dispersibility.

Gravure printing inks for magazines

Due to the very high printing speeds involved in the processing of magazine gravure inks, a low viscosity is essential. Low-structure pigment blacks with medium-sized particles are used to produce printing inks, which can fulfill these conditions and, at the same time, display excellent hiding power, jetness and gloss.

Decoration and packaging printing inks

In decorative and packaging printing (flexographic and gravure printing), the most varied printing substrates are encountered. Printing substrate and binder are chosen to suit one another. For this reason, a selection of binder systems is available for use in these printing inks. Pigment blacks manufactured according to the gas and furnace methods are applied here, both in an oxidized and non-oxidized form.

Aqueous or water-based printing inks play an important role in the field of packaging inks. High levels of jetness are generally achieved with high-structured pigment blacks. For the most part, this involves the printing of uncoated papers. However, the high-structure impairs the flow properties of the printing ink. If coated paper or cardboard and non-absorbent surfaces are to be printed upon, preference should be given to oxidized pigment blacks with a low-structure. Low-structured pigment blacks provide better flow properties and can be used in higher concentrations [4.29].

4.7.2.3
Pigment Blacks for Paints

Thanks to its excellent properties, pigment black is the most frequently used black pigment in the paint and coatings industry. The following special behavior of these pigments makes it suitable for nearly all coatings applications, from deco systems to the highly sophisticated automotive topcoats:

- Outstanding coloristic, from just black to deep black with blue or brown undertone
- High tinting strength, special tinting blacks show no flooding
- Good alkaline- and acid resistance, makes them suitable in water-based coatings
- Excellent weathering resistivity
- Wide range of comparable products, specialities e.g. conductive black pigments

One technical application parameter, which is important for evaluating the right quality for the right application, is the average primary particle size, expressed in nanometers or microns. A second parameter is the surface chemistry expressed in the value of volatile matter determined by 7 min at 950 °C in % (DIN 52552).

In most cases, the pigment blacks are chosen from a coloristic point of view. In this regard, the most important differentiating property for pigment blacks is the average particle size. The attainable jetness of a coating is determined in principal by the average size of the primary particles. Hence, the smaller the particle size the deeper the jetness. Figure 4.9 explains the coloristic properties of pigment black as a function of primary particle size.

By means of an oxidative aftertreatment to which the pigment blacks are subjected, the processing and technical application behavior is improved compared to non-oxidized products. They fulfill the practical demands to a greater extent. The following properties are improved: dispersion behavior, rheology (especially in the millbase), jetness, undertone, flocculation stability, gloss, and resistance to weathering.

Because of their small particle size and their resulting large surface area, pigment blacks are classed as pigments, which are more difficult to disperse. Depending on the supplied form, pigment blacks can be dispersed with all grinding machines, for example sand mill, pearl mill, ball mill, triple roll mill and others.

Of decisive importance for the efficiency of dispersion is the formulation of the mill base of a coating, which must be composed differently for the various dispersing machines. Depending on the wetting properties of the resin, the preferred binder concentration used is 30–50% and the pigment black concentration, calculated on

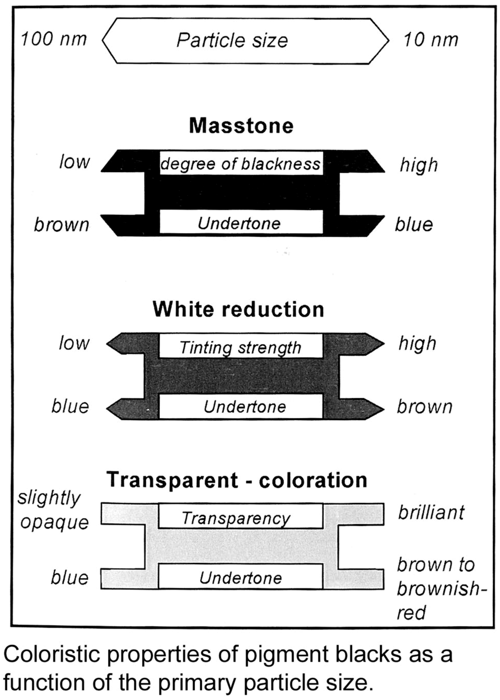

Fig. 4.9 Coloristic properties of pigment blacks as a function of the primary particle size.

resin solid is 12–20% for fine particle size carbon blacks and up to 100% for typical tinting pigment blacks.

The final pigment black concentration to produce a good opacity is 2–5%, for base coats up to 10%, calculated on resin solid. Pigment blacks with extremely high-structure and surface area can be used for electro-conductive coatings [4.27, 4.29]. The carbon black content in this case is 30–50% on resin solid.

4.7.2.4
Pigment Blacks for Plastics

Unlike other pigments, carbon black used in plastics does not only yield coloristic effects but also modifies the electrical properties, provides heat and UV resistance, and may act as a filler to modify mechanical properties.

Tinting of Plastics

Carbon black is used in large amounts for the black and gray tinting of plastics, including polyethylene, polypropylene, polyvinyl chloride, polystyrene, ABS polymers, and polyurethanes. The largest application in tonnages is in polyolefins. Pelletized black is usually employed.

Carbon black concentrations of 0.5–2% are required for full-tone tinting. For crystal-clear plastics, the addition of up to 1% carbon black is generally sufficient. Plastics with marked intrinsic color, e.g. ABS, are tinted with blacks of higher tinting strength at concentrations of 1–2%. Transparent tints have black contents of 0.02–0.2%.

The color depth (blackness) increases as the primary particle size and the degree of aggregation decline. The blackness achieved by a given carbon black, however, also depends on the polymer. Optically critical deep black tinting is achieved with HCC and HCF gas and furnace blacks. For general black tinting, where optimal brilliance and color depth are not essential, lower-priced blacks of moderate fineness belonging to classes MCC, RCC, and MCF are employed. Coarse furnace blacks and flame black are suitable for tinting.

Most of the carbon black used in the plastics industry is produced by the furnace black process. Fine furnace blacks often appear more bluish in incident light (full-tone tinting) than coarse ones, but more brownish in transmitted light (transparent tinting) and in gray tints. By controlling the conditions of black manufacture, however, substantial shifts in hue can be achieved. Bluish carbon blacks are commonly preferred to achieve the impression of greater color depth.

Blacks for tinting of products used for food packaging and storage must comply with relevant legal provisions.

Dispersion is crucial for tinting quality. In order to develop its full coloristic properties, carbon black requires much greater shear forces for dispersion than other pigments. Optimal dispersion, i.e., complete disintegration of agglomerates into discrete particles (carbon black aggregates), and coating with the polymer is more difficult as the finer the black is and the lower its degree of aggregation (black structure). Unsatisfactory distribution of the black has a negative effect on the tinting strength and becomes a problem, especially in gray tints and in the black tinting of opaque plastics. The depth of color in black-tinted transparent plastics, on the other hand, is only slightly affected by a small proportion of poorly dispersed black. Poor dispersion can also cause surface defects (specks) in plastic parts and mechanical defects, especially in films and fibres.

Good distribution of the black in the plastic is achieved by incorporating it in two stages. In the first step, a carbon black–plastic concentrate (master batch) is prepared, for example in kneaders. This contains approximately 20–50% carbon black, depending on the binder absorption of the black. In a second operation, the concentrate is diluted with the appropriate polymer to give the final black content. Dispersion of the black takes place during the preparation of the concentrate. The high black concentration increases the viscosity and enables the medium to transmit higher shear forces than it would be possible if 1–2% black were incorporated directly.

The carbon black–plastic concentrates are often not prepared by the plastics processor. They may be purchased, from the pigment black manufacturer in the form of chips, pellets, or powders. Black plasticizer pastes (e.g., black/DOP pastes for tinting plastisols) and water- and solvent-based dispersions (e.g., for fiber manufacture) are also commercially available.

Conductive Fillers

The incorporation of sufficiently large amounts of blacks can impart antistatic (resistivity 10^6–10^9 Ω) or conductive (<10^6 Ω) properties to plastics. The conductivity of a plastic with carbon black filler increases with decreasing particle size and increasing degree of aggregation of the black, and increasing carbon black concentration. Surface oxides and hydrogen-containing surface groups of the black diminish the conductivity. The distribution of the black in the plastic is also crucial for the conductivity. As the black is incorporated into the plastic, the conductivity initially increases, passes through a maximum, and, if the black is subject to excessive shear force, it decreases. Conditions are optimal when the black is uniformly distributed in the polymer but is not so widely dispersed that the black particles are completely surrounded by the medium. Only under these conditions, can bridges be formed between the particles, thus promoting the flow of current. Orientation of the black particles (e.g., in extrusion or injection molding) permits anisotropic conductivity. Conductivity also depends on the polymer system, due to variations in wettability or local concentration by partial crystallization of the polymer. For example, to obtain the same conductivity, nonrigid PVC requires roughly double the black concentration that polypropylene does.

Blacks used to produce conductive and antistatic plastics are chiefly high-structure furnace blacks with relatively fine particles and low contents of volatile components. Black concentrations for conductive systems are around 10–40%. Antistatic plastics (e.g., cable sheathing and floor coverings) contain 4–15% carbon black.

Relatively coarse-grained oxidized gas blacks with high volatile contents are especially suitable for plastics with good electrical insulation (e.g., cable sheathing compounds, plastics for high-frequency welding, toners).

UV Stabilization

Many polymers, especially polyethylene, are degraded by UV radiation under atmospheric conditions. Blacks can confer long-term stability to such polymers, firstly by absorbing the UV radiation and secondly by acting as free-radical acceptors to inactivate the active intermediate species formed in the degradation process. The stabilizing effect is improved with decreasing particle size and with increasing black concentration up to about 2–3%. Blacks with primary particle sizes of 20–25 nm are commonly used. The radical-accepting ability of blacks used as stabilizers can interfere with the free radical cross-linking of polymers [4.30].

4.8
Toxicology and Health Aspects

4.8.1
Carbon Black, Soot, and Black Carbon

Carbon black is not soot or black carbon, which are the two most common, generic terms applied to various unwanted carbonaceous by-products resulting from the incomplete combustion of carbon-containing materials, such as oil, fuel oils or gasoline, coal, paper, rubber, plastics and waste material. Most soot and black carbon species are ubiquitous in the environment as aerosols, sediments, and soils and have low available surface areas due to their large particle size and small carbon content. They also contain large quantities of dichloromethane and toluene extractable materials and can exhibit an ash content of 50% or more.

Carbon black is chemically and physically different from soot and black carbon, with greater than 97% of carbon black consisting of elemental carbon arranged as aciniform (grape-like cluster) particles. On the contrary, less than 60% of the total particle mass of soot or black carbon is composed of carbon, depending on the type of soot or black carbon, the relative amount and type of carbon, and the characteristics of the particles (shape, size, and heterogeneity).

In the case of commercial carbon blacks, organic contaminants such as polycyclic aromatic hydrocarbons (PAHs) can only be extracted under very rigorous laboratory analytical procedures (soxlet extraction using organic solvents and high temperatures). These extracts are similar to those derived from soot. Both extracted mixtures demonstrate mutagenic and carcinogenic activity. In the case of carbon black, however, extracts exist only in extremely small quantities for transient time periods in laboratories. Water and body fluids are ineffective in removing them from the surface of carbon black and, therefore, they are not considered to be biologically available. There is no scientific evidence that normal exposures to manufactured carbon blacks share the same potential adverse effects for humans, that is, mutagenesis and carcinogenesis, as with soot or black carbon.

Two other commercial carbonaceous products often confused with carbon black are activated carbon and bone black. Each is produced by processes different from commercial carbon black and possesses unique physical and chemical properties.

4.8.2
Safety: Fire and Explosion

Carbon blacks will burn slowly (smoulder) and sustain combustion that may not be visible in the powder or pellet form (no visible flames or smoke). A direct water spray or stream may spread the fire due to the burning carbon black powder floating on the water. A fog spray is recommended when water is used as an extinguishing agent. Foam is also an acceptable extinguishing agent. Carbon black that has been on fire (or suspected of being on fire) should be observed for at least 48 h to ensure that smouldering material is not present. Combustion gases include carbon monoxide, carbon dioxide, sulfur dioxide, and organic products of decomposition.

4.8.3
Storage and Handling

Carbon black should be stored in a clean, dry, uncontaminated area away from exposure to high temperatures, open flame sources and strong oxidizers. Since carbon black will adsorb moisture and chemical vapors, it should be stored in closed containers.

4.8.4
Confined Space Entry

Entry into bins, silos, rail tank cars, tank trucks, or other confined spaces used to ship or store carbon black should only be done following correct confined space entry procedures. Confined space entry procedures should include testing for carbon monoxide, carbon dioxide, and oxygen.

4.8.5
First Aid

There is no evidence to suggest that acute exposure to carbon black may result in life threatening injury or illness. Carbon black is not a respiratory irritant and does not produce respiratory or dermal sensitization.

Inhalation: Short-term exposures above 3.5 mg m^{-3} (total) may produce temporary discomfort to the upper respiratory tract that may result in coughing and wheezing. Removal from carbon black exposure normally is sufficient to cause symptoms to subside with no lasting effects.

Skin: Carbon black dust or powder may cause drying of the skin with repeated and prolonged contact. Skin drying may also result from frequent washing of carbon black contaminated skin.

Ingestion: No adverse effects are expected from carbon black ingestion.

4.8.6
Health

Carbon black is classified by the International Agency for Research on Cancer (IARC) as a Group 2B carcinogen (possibly carcinogenic to humans) based on “sufficient evidence” in animals and “inadequate evidence” in humans. Recent evidence indicates that the phenomenon of carcinogenicity in the rat lung is species-specific, resulting from persistent lung overload to carbon black particles in a size range (<1.0 μm) that is not found in the carbon black manufacturing environment. Mortality studies of carbon black manufacturing workers do not show an association between carbon black exposure and elevated lung cancer rates.

4.8.7
Environmental Disposal

Carbon black, with the exception of chemically treated and water dispersible carbon black grades, is appropriately and most often disposed of in landfills. It is nontoxic and will not leach or release any constituents to the groundwater from a landfill. Carbon black, like activated carbon, has a very high surface area and a strong adsorptive capacity. Organic materials that come in contact with carbon black can be adsorbed and are not easily liberated thereafter. Carbon black is not biodegradable. Water discharges containing carbon black must comply with applicable requirements for solids and oxygen demand. Carbon black is not soluble in water and has a specific gravity of 1.7 to 1.9 (water = 1). Gravity settling is effective and the most common.

Spills should be cleaned immediately to prevent the spread of carbon black. If it is necessary to clean up a remote or small spill by dry sweeping, great care should be taken not to disperse the carbon black into the air.

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5
Specialty Pigments

5.1
Magnetic Pigments

5.1.1
Iron Oxide Pigments

Ferrimagnetic iron oxide pigments are used in magnetic information storage systems such as audio and videocassettes, floppy disks, hard disks, and computer tapes. Cobalt-free iron(III) oxide and non-stoichiometric mixed-phase pigments (so called Berthollide $FeO_xFe_2O_3$, with $0<x<1$) have been used since the early days of magnetic tape technology. Currently, γ-Fe_2O_3 [*1309-37-1*] and Fe_3O_4 [*1317-61-9*] (the latter in small amounts) are mainly used in the production of low-bias audio cassettes (iron oxide operating point IEC I standard (International Electrotechnical Commission), and studio, broadcasting, and computer tapes.

5.1.1.1
Production

The shape of the pigment particle is extremely important for ensuring good magnetic properties. Isometric iron oxide pigments produced by direct precipitation are seldom used. Since 1947, needle-shaped γ-Fe_2O_3 pigments have been prepared with a length to width ratio of ca. 5 : 1 to 20 : 1 and a crystal length of 0.1–1 µm [5.1].

Anisometric forms of Fe_3O_4 with the spinel structure or γ-Fe_2O_3 with a tetragonal superlattice structure do not crystallize directly. They are obtained from iron compounds that form needle-shaped crystals (usually α- and γ-FeOOH, see Section 3.1.1 Iron Oxide Pigments) [5.2–5.4]. An alternative method for the production of the α-FeOOH precursor starts from an aqueous suspension of $Fe(OH)_2$, oxidizing that suspension to needle-shaped particles of α-FeOOH with an oxidizing gas while maintaining the pH greater than 11 at a temperature between 30 and 45 °C under intensive stirring [5.5, 5.6]. The oxide hydroxides are converted to Fe_3O_4 by dehydration and reduction. Reducing agents may be gases (hydrogen, carbon monoxide) or organic compounds (e.g., fatty acids). The particle geometry is retained during this process.

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Since the pigments are subjected to considerable thermal stress during this conversion, the FeOOH particles are stabilized with a protective coating against sintering (usually silicates [5.7], phosphates [5.8], chromates [5.9], or organic compounds such as fatty acids [5.10]).

Finely divided stoichiometric Fe_3O_4 pigments are not stable to atmospheric oxidation. They are therefore stabilized by partial oxidation or by complete oxidation to γ-Fe_2O_3 below 300 °C.

In an alternative process, the starting material consists of needle-shaped particles of α-Fe_2O_3 instead of FeOOH pigments [5.11, 5.12]. The synthesis is carried out in a hydrothermal reactor, starting from a suspension of $Fe(OH)_3$ and crystal growth is controlled by means of organic modifiers.

5.1.1.2
Properties

Magnetic pigments with very different morphological and magnetic properties that depend on the field of application and quality of the recording medium are used. The largest particles (length ca. 0.6 µm) are used in computer tapes. The noise level of the magnetic tape decreases with decreasing particle size. Fine pigments are therefore being used increasingly for better quality compact cassettes. The magnetic properties may be determined by measurement of hysteresis curves on the powder or magnetic tapes.

Table 5.1 shows some quality requirements for the most important applications of magnetic pigments. Column 4 gives the coercive field strength (H_c) required for information storage materials. The coercive field is the magnetic field required to demagnetize the sample.

The saturation magnetization M_s is a specific constant for the material. For magnetic iron oxides M_s is principally determined by the Fe^{2+} ion content. The ratio of remanent magnetization to saturation magnetization (M_r/M_s) for the tape depends mainly on the orientation of the pigment needles with respect to the longitudinal direction of the tape, and should approach the theoretical maximum value of unity as closely as possible. In Figure 5.1, transmission electron micrographs are shown giving the morphology of the magnetic pigments listed in Table 5.1.

Apart from the morphological and magnetic properties, usual pigment properties such as pH value, tap density, soluble salt content, oil absorption, dispersibility, and chemical stability are of great importance for the manufacture of magnetic recording materials.

Producers of magnetic iron oxides include Toda Kogyo and Titan Kogyo (Japan), 3M, Magnox, ISK Magnetics (USA), Saehan Media (South Korea), and Herdilla (India). World production of cobalt-free magnetic iron oxides in 2002 was ca. 10,000 t, of which ca. 96% were used in compact cassettes and audiotapes, and ca. 4% in computer tapes.

Tab. 5.1: Some quality requirements for iron oxide and metallic iron magnetic pigments.

Field of application	Pigment type	Approximate particle length, μm	Specific surface area, $m^2\ g^{-1}$	Coercive field strength H_c, $kA\ m^{-1}$	Saturation magnetization, M_s, $\mu T \cdot m^3/kg$	M_r/M_s
Computer tapes	γ-Fe_2O_3	0.60	13 –17	23–25	86–90	0.80–0.85
Studio radio tapes	γ-Fe_2O_3	0.40	17–20	23–27	85–92	0.80–0.85
IEC I compact cassettes						
standard (iron oxide operating point)	γ-Fe_2O_3	0.35	20–25	27–30	87–92	0.80–0.90
high grade	Co-γ-Fe_2O_3	0.30	25–37	29–32	92–98	0.80–0.90
IEC II compact cassettes (CrO_2 operating point)	Co-γ-Fe_2O_3, Co-Fe_3O_4	0.30	30–40	52–57	94–105	0.85–0.92
IEC IV compact cassettes (metal operating point)	metallic iron	0.35	35–40	88–95	130–160	0.85–0.90
Digital audio (R-DAT)*	metallic iron	0.25	50–60	115–127	130–160	0.85–0.90
$\frac{1}{2}''$ Video	Co-Fe_3O_4	0.26	30–40	52–57	98–105	0.80–0.90
Super-VHS video	Co-γ-Fe_2O_3	0.20	45–50	64–72	94–96	0.80–0.85
8 mm video and broadcasting media	metallic iron	0.25	50–60	115–127	130–160	0.85–0.90
Data storage tape (S-DLT)	metallic iron	0.06	50–70	190–210	119–130	0.85–0.90

*R-DAT: rotary digital audio tape.

5.1.2
Cobalt-Containing Iron Oxide Pigments

Cobalt-containing iron oxides form the largest proportion (ca. 71%) of magnetic pigments produced in 2002. Due to their high coercivity, they can be used as an alternative to chromium dioxide for the production of videotapes, high-bias audiotapes (CrO_2 operating point, IEC II), and high-density floppy disks.

5.1.2.1
Production

The iron oxide pigments described in Section 5.1.1 are either doped or coated with cobalt:

1. Body-doped pigments contain 2–5 wt.% cobalt that is uniformly distributed throughout the bulk of the pigment particles. It is either incorporated during production of the FeOOH precursor or precipitated as the hydroxide onto one of the intermediate products [5.13] using cobalt(II) salts as the cobalt source.

2. Cobalt-coated pigment particles (1.6–4 wt.% Co) consist of a core of γ-Fe_2O_3 or non-stoichiometric iron oxide phase, and a 1–2 nm coating of cobalt ferrite with a

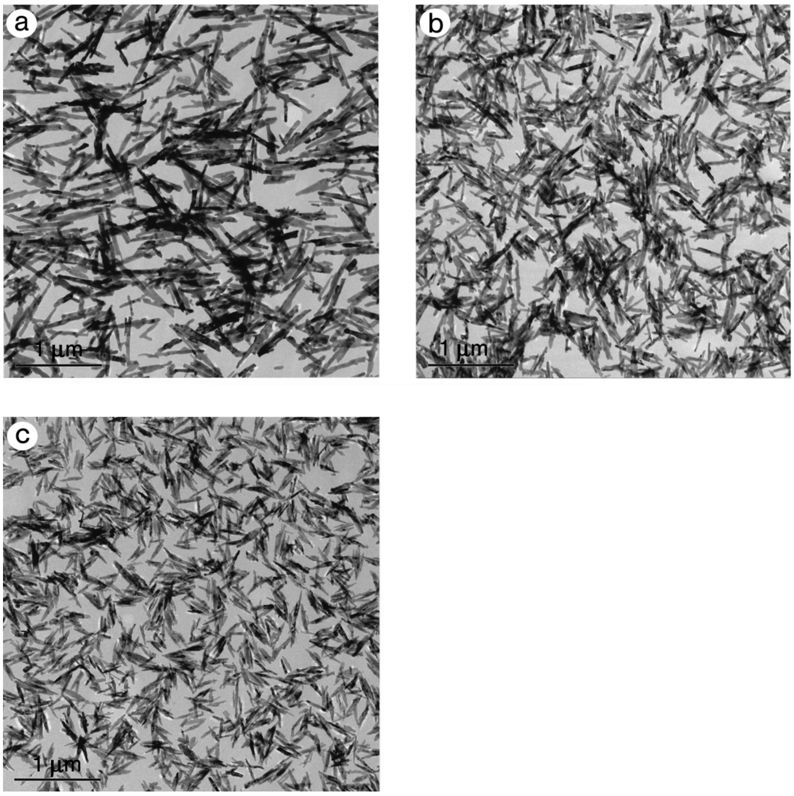


Fig. 5.1 TEM-photographs showing typical morphology of magnetic iron oxide pigments from Toda Kogyo (Table 5.1) Magnification ×30000. A) γ-Fe_2O_3QX-440®, for computer tapes and studio radio tapes; B) Co- γ-Fe_2O_3TX-3045®, for IEC I compact cassette tapes, standard, iron oxide operating point, high grade; C) Co-Fe_3O_4 CSB-195®, for IEC II compact cassette tapes, CrO_2 operating point, $\frac{1}{2}$″ video tape, super-VHS video tape.

high coercivity [5.14]. The coating can be produced by adsorption of cobalt hydroxide, or epitaxial precipitation of cobalt ferrite in a strongly alkaline medium [5.15, 5.16]. Surface coated pigments show better magnetic stability than doped pigments.

5.1.2.2
Properties

Pigments with a coercive field strength of 50–57 kA m^{-1} are used in videocassettes, high-bias audiocassettes (chromium dioxide operating point IEC II), and high-density floppy disks. Depending on the quality of the tape, the particle size varies between 0.2 and 0.4 µm (see Section 5.1.1, Table 5.1, and Figure 5.1).

Pigments with a higher coercive field strength (ca. 70 kA m^{-1}) and smaller particle size (particle length ca. 0.15–0.2 µm) are used for super VHS cassettes.

Pigments treated with only small amounts of cobalt (0.5–1 wt.% Co, coercive field strength ca. 31 kA m^{-1}) are used as an alternative to cobalt-free γ-Fe_2O_3 pigments for high-quality low-bias audiocassettes. The other parameters described in Section 5.1.1 are also of importance for cobalt-treated pigments.

Cobalt-containing pigments are mainly produced by the magnetic iron oxide producers Toda Kogyo, Titan Kogyo (Japan), 3M, Magnox (USA), Saehan Media (South Korea). World production in 2002 was about 25,000 t, of which the highest amount (ca. 85%) was used for videotapes.

5.1.3
Chromium Dioxide

In the course of the development of pigments for magnetic information storage, CrO_2 was the first widely used pigment material that gave a higher recording density than γ-Fe_2O_3. In the field of audio recording this led to the IEC II standard or "chrome position".

5.1.3.1
Physical Properties

Chromium dioxide [*12018-01-8*], chromium(IV)oxide, CrO_2, is a ferromagnetic material with a specific saturation magnetization M_S/ρ of 132 A m^2 kg^{-1} at 0 K, corresponding to the spin of two unpaired electrons per Cr^{4+} ion. The M_S/ρ value of CrO_2 at room temperature is ca. 100 A m^2 kg^{-1} [5.17]; CrO_2 magnetic pigments reach values of 77–92 A m^2 kg^{-1}. The material crystallizes with a tetragonal rutile lattice in the form of small needles, which have the desired magnetic shape anisotropy. The morphology of the particles can be varied with several dopants, particularly antimony and tellurium [5.18]. The coercive field strength can be controlled between ca. 30 and 75 kA m^{-1} (in addition to shape) by doping with transition metal ions, which modify the magneto-crystalline anisotropy of the material; the Fe^{3+} ion being industrially important [5.19].

5.1.3.2
Production and Chemical Properties

The conversion of an intimate mixture of Cr(III) and Cr(VI) compounds into CrO_2 under hydrothermal conditions has been developed into an industrial process in autoclaves at ca. 350 °C and 300 bar [5.18].

Pure CrO_2 slowly disproportionates in the presence of water. The CrO_2 crystal surface of commercial pigments is therefore topotactically converted to β-CrOOH, which serves as a protection layer [5.20]. In the absence of moisture, CrO_2 is stable up to ca. 400 °C, above this temperature it decomposes to form Cr_2O_3 and oxygen.

5.1.3.3
Uses and Economic Aspects

Chromium dioxide is used exclusively for magnetic recording media. It may also be used in combination with cobalt-modified iron oxides (see Section 5.1.2) in the production of magnetic recording media. The world consumption of CrO_2 is decreasing continuously as compact disc and digital videodisc are taking over the audio and video market. The sole producer is DuPont.

5.1.4
Metallic Iron Pigments

The magnetization of iron is more than three times higher than that of iron oxides. Metallic iron pigments can have a coercive field strength as high as 150 kA m^{-1}, depending on the particle size. These properties are highly suitable for high-density recording media. Oxidation-resistant products based on metallic pigments first became available in the late 1970s.

5.1.4.1
Production

Metallic iron pigments are commercially produced by the reduction of acicular (needle-shaped) iron compounds [5.21]. As in the production of magnetic iron oxide pigments, the starting materials are iron oxide hydroxides (see Section 3.1.1) or iron oxalates, which are reduced to iron in a stream of hydrogen either directly or via oxidic intermediates.

Due to their high specific surface area, metallic pigments are pyrophoric, so that passivation is necessary. This can be achieved by slow, controlled oxidation of the particle surface [5.22].

5.1.4.2
Properties

The coercive field strength of metallic iron pigments is primarily determined by their particle shape and size, and can be varied between 30 and 210 kA m^{-1}. Pigments for analog music cassettes ($H_c \approx 90$ kA m^{-1}) usually have a particle length of 0.35 μm (see Section 5.1.1, Table 5.1). The length to width ratio of the pigment needles is ca. 10 : 1. Finely divided pigments (particle length ca. 0.12 μm) with a coercive field strength of 130 kA m^{-1} are used for 8 mm video and digital audiocassettes (R-DAT), tapes used by television organizations (ED Beta, Betacam SP MP, M II, Digital Video D2), and for master videocassettes (mirror master tapes). In the field of data storage, a small quantity is used in micro floppy disks and backup cassettes.

Metallic pigments have a higher specific surface area (up to 60 $m^2 g^{-1}$) and a higher saturation magnetization than oxidic magnetic pigments. Their capacity for particle alignment corresponds to that of the oxides (see Table 5.1). Figure 5.2 shows the morphology of the metallic particles as TEM photographs.

5.1.4.3
Economic Aspects

The largest producers of metallic iron pigments are Dowa Mining and Toda Kogyo (Japan). World consumption in 2002 was ca. 1800 t, of which ca. 65% were used in the manufacture of broadcasting media, 2% for audiotapes, and 33% for data storage applications; this last being expected to increase later.

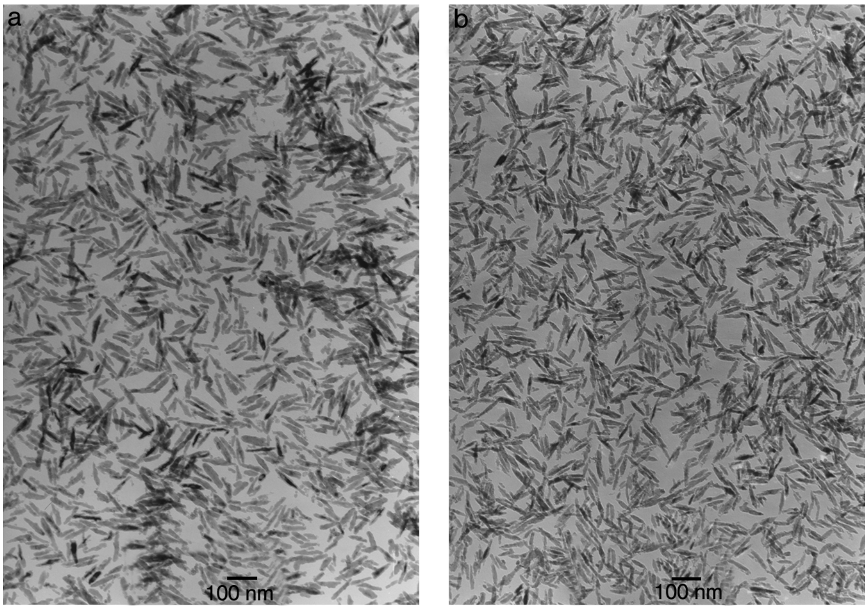


Fig. 5.2 TEM-photographs showing typical morphology of metallic iron pigments (Table 5.1). A) Iron pigment for IEC IV compact cassettes (metal operating point). B) Iron pigment, for digital audio (R-DAT) 8 mm video tape, data storage.

5.1.5
Barium Ferrite Pigments

Barium ferrite pigments have been considered for several years for high-density digital storage media [5.23, 5.24]. They are very suitable for preparing unoriented (e.g., floppy disks), longitudinally oriented (conventional tapes), and perpendicularly oriented media. In the latter the magnetization is oriented perpendicular to the coating surface. They are required for perpendicular recording systems, which promise extremely high data densities especially on floppy disks. Barium and strontium ferrites are also used to prevent forgery of magnetic stripes, e.g., in cheque and identity cards.

5.1.5.1
Properties

Hexagonal ferrites have a wide range of structures distinguished by different stacking arrangements of three basic elements known as M, S, and Y blocks [5.25]. For magnetic pigments, the M-type structure (barium hexaferrite [*12047-11-9*] $BaFe_{12}O_{19}$) is the most important. The magnetic properties of M-ferrite can be controlled over a fairly wide range by partial substitution of the Fe^{3+} ions, usually with combinations of di- and tetravalent ions such as Co and Ti. Barium ferrite crystallizes in the form of small hexagonal platelets. The preferred direction of magnetization is parallel to the c-axis and is therefore perpendicular to the surface of the platelet. The specific saturation magnetization of the undoped material is ca. 72 A m^2 kg^{-1} and is therefore somewhat lower than that of other magnetic oxide pigments. In barium ferrite, the coercive field strength is primarily determined by the magneto-crystalline anisotropy and only to a limited extent by particle morphology. This is the reason why barium ferrite can be obtained with extremely uniform magnetic properties. Barium ferrite pigments have a brown color and chemical properties similar to those of the iron oxides. Typical values of physical properties of barium ferrite pigments used in magnetic recording are given in Table 5.2. Figure 5.3 shows the TEM photograph of barium ferrite pigments listed in Table 5.2.

Tab. 5.2: Typical properties of barium ferrite pigments.

Application	**Specific surface area, m^2 g^{-1}**	**Platelet diameter, nm**	**Platelet thickness, nm**	**H_c, kA m^{-1}**	**M_s/ρ, A m^2 kg^{-1}**
Unoriented (floppy disk)	25–40	40–70	15–30	50–65	50–65
Oriented	25–60	40–120	10–30	55–100	50–65
Magnetic stripes	12–15	100–300	50–100	220–440	60–70
Magnetic cards	3–7	300–600	100–400	130–320	50–65

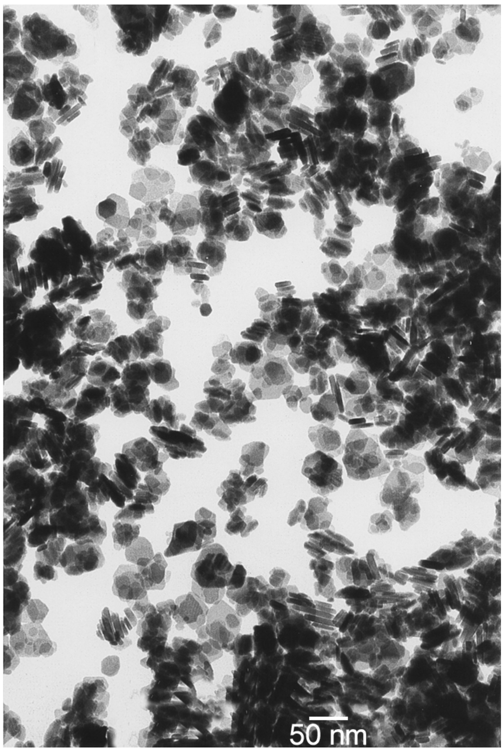


Fig. 5.3 TEM-photograph showing typical morphology of barium ferrite pigments (Table 5.2).

5.1.5.2
Production

There are three important methods for manufacturing barium ferrite on an industrial scale: the ceramic, hydrothermal, and glass crystallization methods. The main producers were Toshiba and Toda in 1995. Actual data were not disclosed.

Ceramic Method

Mixtures of barium carbonate and iron oxide react at 1200–1350 °C to produce crystalline agglomerates, which are ground to a particle size of ca. 1 µm. This method is only suitable for the high-coercivity pigments required for magnetic stripes [5.26].

Hydrothermal Method

Iron (Fe(III)), barium, and the dopants are precipitated as their hydroxides and react with an excess of sodium hydroxide solution (up to 6 mol l^{-1}) at 250–350 °C in an autoclave. This is generally followed by an annealing treatment at 750–800 °C to obtain products with the desired magnetic properties. Many variations of the process have been described [5.27–5.31], the earliest report being from 1969 [5.32]. In later processes, hydrothermal synthesis is followed by coating with cubic ferrites, a process resembling the cobalt modification of iron oxides (see Section 5.1.2). The object is to increase the saturation magnetization of the material [5.33–5.35].

Glass Crystallization Method

This process was developed by Toshiba [5.36]. The starting materials for barium ferrite production are dissolved in a borate glass melt. The molten material at ca. 1200 °C is quenched by pouring it onto rotating cold copper wheels to produce glass flakes. The flakes are then annealed to crystallize the ferrite in the glass matrix. In the final stage the glass matrix is dissolved in acid. In a variation of this process, the glass matrix is produced by spray drying [5.37].

5.1.5.3
Magnetic Recording Properties

Barium ferrite is highly suitable for high-density digital recording, mainly because of its very small particle size and its very narrow switching field distribution. It also has a high anhysteretic susceptibility and is difficult to overwrite [5.38]. This is partly explained by positive interaction fields between particles in the coating layer [5.39]. The high anhysteretic susceptibility makes barium ferrite media particularly suitable for the anhysteretic (bias field) duplicating process [5.40].

Besides the thermal magnetic duplication process [5.41] used for CrO_2 tapes, this is the second faster-than-real-time videotape duplicating process. The signal is transferred from the mirror master tape to the copy tape by applying a high-frequency bias field while the two tape coatings are in close contact with each other. The amplitude of the bias field is equal to the maximum coercivity of the copy tape. Under the influence of both the bias field and the field of the master tape, the magnetic particles in the copy tape are magnetized in exactly the opposite pattern to that of the mirror tape.

The current copy speed is ca. 100 times standard playing speed for VHS videotapes. Figure 5.4 shows the principle of the method [5.42].

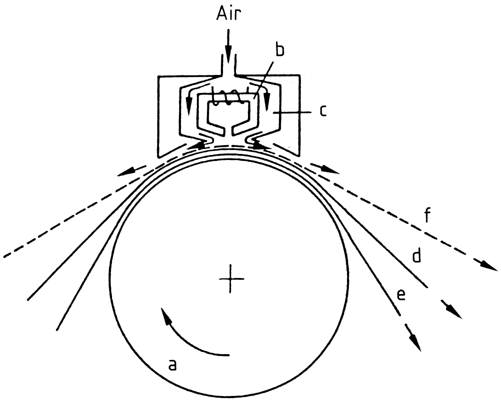


Fig. 5.4 Anhysteretic duplication process [5.42]. a) Transfer drum; b) Transfer magnetic field head; c) Air chamber; d) Mirror master tape; e) Copy tape; f) Drive tape.

Unlike many other magnetic materials used in high-density recording, barium ferrite, being an oxide, is not affected by corrosion [5.43]. Processing of the pigment can be problematic, e.g., applying orienting fields can easily lead to unwanted stacking of the particles, which has adverse effects on the noise level and the coercive field strength of the magnetic tape. A marked temperature dependence of the magnetic properties was a problem in the early days, but this can be overcome by appropriate doping [5.44].

5.1.6
Toner Pigments

Many toners used in photocopiers and laser printers contain black magnetic iron oxide pigments (magnetite Fe_3O_4). The heart of a copier or laser printer is a cylinder coated with an organic photoconductor coating (OPC). Before the actual copying or printing process, the cylinder is electrostatically charged by a high-voltage corona, and then exposed to light from a laser or projection system (Figure 5.5). The areas of the coating subjected to light give up a varying portion of the charge, while the unexposed areas, corresponding to the black dots of the original, retain their charge. Xerography then makes use of the effect that electrostatically charged objects attract dust. What happens is that a fine, black thermoplastic powder, the so-called toner, is sprinkled over the cylinder, and the charged areas become covered by the black toner dust. This produces a mirror image of the original on the roller. The particles are then transferred electrostatically to paper and fixed by heat exposure or pressure to make the image permanent [5.45].

A magnetic brush development system serves for the transportation of the toner powder. In a Dual Component System a rotating bar magnet is covered with a magnetizable ferrite powder, the so-called carrier (component 1), giving it the appearance of a brush. The carrier is dipped into a bath of toner powder (component 2) and

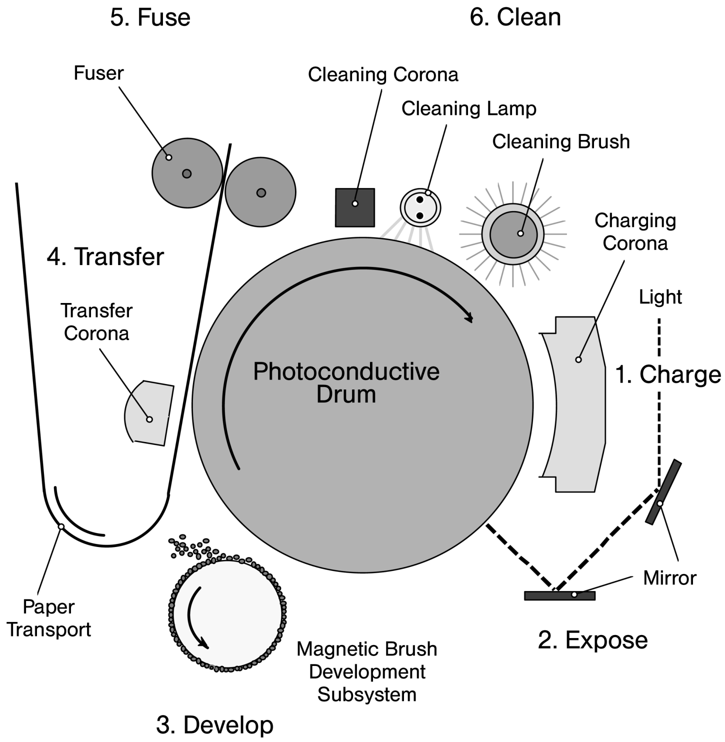


Fig. 5.5 Scheme of a photocopier.

transported past the cylinder at a specifically defined distance away from it. The powder becomes attracted to the areas that are electrostatically charged.

Laser printers and many copiers work by the one-component process, which allows the design of particularly compact machines. The principle of the magnetic brush is retained, however, the toner itself is magnetizable. This can be done by dispersing ca. 30–50 wt.% of black, magnetizable iron oxide particles in thermoplastic resins. Apart from the iron oxide, various additives are generally also incorporated to control the electrostatic chargeability, the flow characteristics and the color. The particle size of these toners is ca. 5–15 μm.

5.1.6.1
Production

Black magnetite pigments are typically produced either by precipitation from iron salt solutions or by the Laux process. The production processes are described in detail in Section 3.1.1 (Table 3.2, especially Eqs. (3.10), (3.11) and (3.12)).

5.1.6.2
Iron Oxide Properties

A particle size between 0.2 and 0.5 µm is preferred. High quality toners contain oxides with a narrow particle size distribution as demonstrated in Figures 5.6 and 5.7.

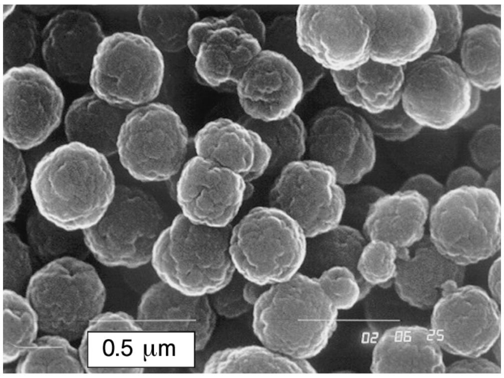


Fig. 5.6 Magnetite pigment for use in laser printer toners.

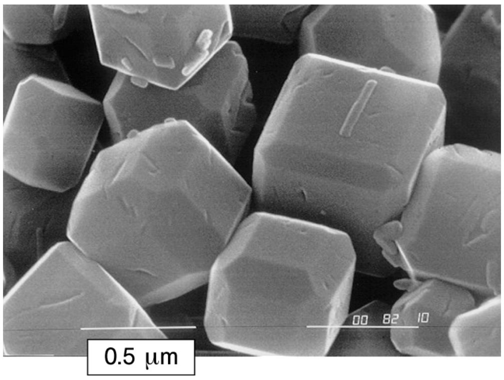


Fig. 5.7 Magnetite pigment for use in copier toners.

The coercivity and remanent magnetization [5.46] of a toner is, to a certain extent, dependent on the type of system used in the copying machine or printer. Many copier toners contain oxides with a coercivity of 7–9 kA m^{-1} while laser printer toners typically contain oxides with a lower coercivity in the region of 5 kA m^{-1}. The coercivity of magnetite is governed by the production process, particle shape and particle size, and increases in the order spherical<cubical<octahedral particles [5.47]. Therefore, high quality laser printer toners contain spherical oxides (Figure 5.6) while most copier toners contain octahedral or cubical particles (Figure 5.7).

Producers of magnetic iron oxides for use in toners include Lanxess (Germany), Elementis, Magnox, Rockwood (USA), Kanto Denka K., Mitsui, Titan K., Toda K, (Japan) and Saehan (South Korea). World production in 2003 was ca. 30,000 t.

5.2
Anticorrosive Pigments

5.2.1
Introduction

Corrosion protection of metallic materials has, for a long time, been one of the key roles performed by organic coatings. The costs of damage incurred by corrosion of metals can be anything up to 5% of the gross domestic product in leading industrial nations [5.48]. Calculations over the past 50 years have shown that from 1800 million tons of iron used for structures, objects, etc., about 800 million tons have been lost through corrosion [5.49]. It is well known, that the performance of a protective coating can distinctly be affected by incorporation of anticorrosive pigments. Therefore the choice of anticorrosive pigments used in conjunction with suitable binder systems plays a major role when trying to protect metals from corrosion by means of protective coatings. The most important role of anticorrosive pigments in protective coating technology is probably the control of corrosion, even though the degree of corrosion protection of a coating depends not only on the kind of the anticorrosive pigment used. One of the most important factors besides the pigment used is the resin system selected in order to formulate the coating. Before discussing anticorrosive pigments in detail, it is helpful to review what is actually meant by the term corrosion.

5.2.2
Corrosion Mechanism

Corrosion leads to deterioration of metals by chemical or electrochemical reactions resulting from exposure to weathering, moisture, chemicals or other agents in the environment into which they are placed [5.50].

Often corrosion is described as an electrochemically driven process of energy exchange. Within this process, the metals, which were originally found in nature as ores, are reconverted back to their ores [5.51].

The required energy for the iron production from iron ore to cast iron and later to steel is enormous [5.52]:

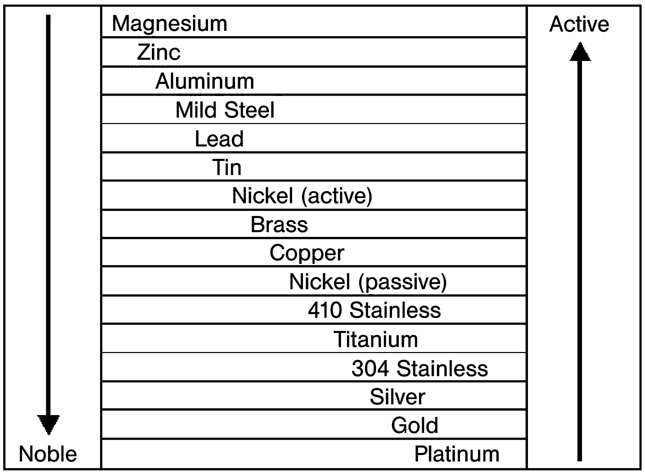
$$172.6\ \text{kJ} + CO_2 + C \rightarrow 2\ CO$$

$$2\ FeO + 2\ CO \rightarrow 2\ Fe + 2\ CO_2 + 34.4\ \text{kJ}$$

$$138.2\ \text{kJ} + 2\ FeO + C \rightarrow 2\ Fe + CO_2.$$

In accordance with the rule of Lenz, the same energy will be released when iron is reconverted back to its ore. So, iron is not a thermodynamically stable metal. Because of this property it is a non-stable metal affected by corrosion, corrosion being the natural tendency of metals to move to their most stable form, for example as the oxide, sulfide and so on [5.51, 5.52].

Metals differ in the way by which they can be obtained from the ore. So, each metal shows a different readiness to react with oxygen or other elements and to return to its lower energy state [5.51]. The more energy that is needed for the metal production, the more readily the energy is released in the form of corrosion. Figure 5.8 shows that the most active metals are those with ready release of energy, which means these metals are most susceptible to corrosion [5.51].



		Active
	Magnesium	
	Zinc	
	Aluminum	
	Mild Steel	
	Lead	
	Tin	
	Nickel (active)	
	Brass	
	Copper	
	Nickel (passive)	
	410 Stainless	
	Titanium	
	304 Stainless	
	Silver	
	Gold	
Noble	Platinum	

Fig. 5.8 Electromotive series of metals [5.51].

Any metal shows slight heterogeneities in its composition, for example from surface contamination or grain structure [5.51]. If such heterogeneous areas on a metal substrate come into contact with an electrolyte (an electrical conductor, such as moisture), these contiguous areas, having a slightly higher or lower tendency to corrode, will act as anodes and cathodes of an active electrochemical cell, as demonstrated in Figure 5.9 where iron is used as an example [5.51, 5.53].

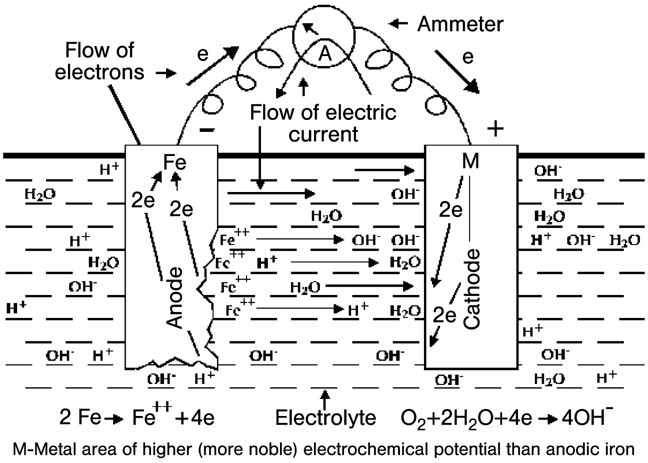


Fig. 5.9 Electrochemical corrosion cell [5.51].

At the anode, the metal passes into solution as metal ions, which release electrons. Due to the presence of the electrolyte these electrons are able to migrate to the cathode and will be consumed by reactions with the environment [5.51]. Some electrochemical reactions are summarized in Figure 5.10.

Anodic reactions

- Examples

$Fe \longrightarrow Fe^{2+} + 2e^-$
$Zn \longrightarrow Zn^{2+} + 2e^-$
$Al \longrightarrow Al^{3+} + 3e^-$
$H_2 \longrightarrow 2H^+ + 2e^-$
$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

- Oxidation reactions
- Produce electrons

Cathodic reactions

- Examples

$O_2 + H_2O + 4e^- \longrightarrow 4\,OH^-$
$2\,H_2O + 2e^- \longrightarrow H_2 + 2\,OH^-$
$Fe^{3+} + e^- \longrightarrow Fe^{2+}$

- Reduction reactions
- Consume electrons

Fig. 5.10 Electrochemical reactions.

As the main part of this section deals with anticorrosive pigments as such, we shall not go into more detail on the discussion of corrosion processes in this section. However, it should be mentioned that one key feature of the electrochemical process of corrosion is the presence of an electrolyte. This electrolyte is made up of rain, snow and dew, leading to ionogenic surface contamination. The electrolyte contains material coming from airborne pollution, such as dirt, water-soluble chloride and sulfate salts. Chlorides and sulfates are well known as so-called corrosion stimulators, which have a distinct influence on the course of the corrosion reactions [5.51, 5.54].

5.2.3
Classification of Anticorrosive Pigments

Anticorrosive pigments can affect the performance of protective coatings in several ways, such as

- Prevention of underfilm corrosion
- Protection of the metal substrate where the paint film is discontinued due to mechanical damage
- Prevention of undercutting in damaged areas
- Improvement of durability per unit of film thickness
- Improvement of durability in thin films making application errors less damaging [5.55].

Anticorrosive pigments may be classified by their mode of action, for example chemical and/or electrochemical (Active Pigments), physical (Barrier Pigments), and electrochemical/ physical (Sacrificial Pigments) [5.54–5.56].

1. *Active pigments* are anticorrosives with a chemical and/or electrochemical action. They are also described in the literature as inhibitive pigments. These pigments interact chemically, either directly or via intermediates with the metal substrate to reduce the rate of corrosion. Such intermediates can, for example, be formed by reaction with the resin system.

   The ability to render a metal surface passive is termed passivation. Those pigments that prevent corrosion of the metal by forming a protective layer on the surface of the substrate are regarded as being active in the anodic areas (anodic passivation). Pigments, which prevent rust formation due to their high oxidation potential, are said to be active in the cathodic areas (cathodic passivation). In general active pigments are able to inhibit one or both of the two electrochemical partial reactions.

   Another mechanism of active pigments is neutralization of corrosive substances such as sulfates, acids and chlorides resulting in maintaining a constant pH value in the coating.

2. *Barrier pigments* act by physically reinforcing the barrier properties of the paint film, which means that they reduce the permeability of the paint film to agents that support corrosion. Normally, they are chemically inert and are said to be inactive or passive.

   The barrier effect can be achieved, for example, by using pigments with a platelet-like or lamellar particle shape. This allows them to form a wall of flat particles within a paint film and therefore water and electrolytes have to take an extended/less direct route through the paint film to the substrate.

3. *Sacrificial pigments* are a special group of active pigments. They are metallic pigments, which act by cathodic protection when applied to ferrous substrates. Such pigments must contain a metal that is higher in the electromotive series of metals (Figure 5.8) than the metal of the substrate to be protected. Under corrosive conditions, the sacrificial pigment, being more reactive than the substrate, becomes the anode in an electrochemical corrosion cell (Figure 5.9) in which the substrate is the cathode. This is the meaning of the term cathodic protection. The only sacrificial pigment of commercial importance is metallic zinc, supplied either as zinc dust or zinc flakes [5.55]. In addition to the electrochemical action of a sacrificial pigment, the chemical reaction of the pigment with the atmosphere results in the formation of insoluble zinc compounds which protect the paint by filling in voids (“cementation”).

There are also anticorrosive pigments described in the coatings literature that are called “film reinforcers” showing “good film forming properties”. The intended meaning of this term might be that some pigments can be incorporated into a coating to improve the overall integrity of the film, because in all cases an inorganic pigment is not capable of forming films. For example iron oxide red pigments are described as “film reinforcers”. It is discussed that, in addition to their optical properties, iron oxide pigments show excellent resin/pigment bonding properties resulting in an enhancement of the barrier effect of the coating. A second example of a so-called “film reinforcer” is zinc oxide. In the past, zinc oxide was used in oil-based anticorrosive primers to improve hardness. In the protective coatings area it is usually applied in combination with active pigments. It may also protect the coating by acting as an ultraviolet absorber [5.55]. The protective action of zinc oxide is also based on its ability to react with corrosive substances and to maintain an alkaline pH value in the coating [5.56].

5.2.4
Traditional Lead and Chromate Pigments

5.2.4.1
Lead Pigments

Corrosion inhibition by protective coatings can trace its origins to the earliest days of civilization. Red lead, as an anticorrosive pigment used in linseed oil coatings, established itself as the standard for corrosion inhibitive coatings [5.57]. Over the years, lead pigments have been proven to be outstanding anticorrosives, which perform particularly well when used in coatings for application on insufficiently prepared surfaces [5.53]. However, the increasing awareness for human health protection (see Section 5.2.16) has led to a distinct curtailment concerning the usage of lead pigments.

Red lead (Pb_3O_4) was the most popular lead-based anticorrosive. It was produced industrially by oxidizing lead monoxide (PbO) at about 480 °C with agitation in a stream of air for 15–24 h [5.56]. Red lead is a cathodic passivator (reduction of Pb(IV) to Pb(II)), that means an oxidizing agent, but its inhibitive mechanism is much more complicated. The main use of red lead has been in linseed oil based paints. Red lead can form soaps with the fatty acids present in the oil. These soaps can also inhibit rust formation. In addition, the lead soaps can improve the mechanical properties of the paint film and give good mechanical strength, water resistance and adhesion to the substrate. Furthermore, it is discussed in the literature that red lead and other lead-based pigments precipitate corrosion, promoting chloride and sulfate ions by Pb(II) ions [5.55, 5.56].

Basic lead silicochromate ($4(PbCrO_4 \cdot PbO) + 3(SiO_2 \cdot 4\ PbO)$) reached certain industrial importance. It was developed to replace red lead. The pigment is a so-called core pigment, in which the active pigment substance ($PbCrO_4$) is precipitated onto an inert core (SiO_2). Because this anticorrosive contains both lead and hexavalent chromium, it has lost its previous economic importance as well [5.53, 5.56].

For very specific and limited applications the following lead-based products have been used: lead suboxide, lead carbonate and lead cyanamide (mirror coatings), lead silicate (electro disposition primers), dibasic lead phosphate, tribasic lead phosphate silicate, and calcium plumbate [5.51, 5.53].

5.2.4.2
Chromate Pigments

Chromates have long been utilized as anticorrosives. The anticorrosive action of chromates is based on the content of a certain amount of water-soluble chromate within these pigments (Table 5.3).

Tab. 5.3: The solubility of chromates in water at 25 °C [5.51].

Pigment	Formula	Grams of CrO_3/ 1000 ml of H_2O
Calcium chromate	$CaCrO_4$	17
Zinc potassium chromate	$4\ ZnO \cdot K_2O \cdot 4\ CrO_3 \cdot 3\ H_2O$	1.1
Zinc tetrahydroxychromate	$ZnCrO_4 \cdot 4\ Zn(OH)_2$	0.6
Strontium chromate	$SrCrO_4$	0.02
Barium chromate	$BaCrO_4$	0.001

Chromates have been widely successful because most paint films are permeable to water. If the rate of moisture permeability is matched to the solubility of the chromate pigment used then enough chromate ions may migrate to the metal surface to initiate and sustain the formation of passive layers [5.51]. The effectiveness of chromates in both the cathodic and anodic areas is simplified and illustrated in Figure 5.11 [5.58].

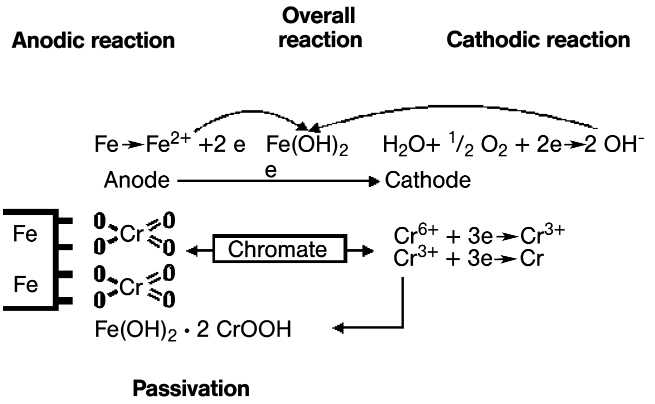


Fig. 5.11 Atmospheric corrosion of iron and inhibitive effects of chromate pigments [5.58].

The anticorrosive properties of chromate pigments are related to

- the content of water-soluble chromate ions.
- the neutralizing and pH-stabilizing effect of zinc hydroxide present in zinc-based chromate pigments.
- the active pigment surface in the coating (particle shape and size, particle size distribution, dispersibility).

ISO 1249 – Zinc chromate pigments – Basic zinc potassium chromate pigments and zinc tetrahydroxychromate pigments – specifies the requirements, and corresponding test methods for zinc chromate pigments suitable for use in paints and/or corrosion-inhibiting coatings [5.59].

The requirements on strontium chromate pigments are specified in ISO 2040 – Strontium chromate pigments for paints [5.60]. Required characteristics for zinc potassium chromate, zinc tetrahydroxychromate and strontium chromate are summarized in Table 5.4.

Tab. 5.4: Quality requirements for zinc chromates and strontium chromate.

Characteristic	Unit	Zinc potassium chromate	Zinc tetrahydroxy-chromate	Strontium chromate
Zn as ZnO	%	35 to 40	68.5 to 72	
Strontium as SrO	%			min. 48
Chromium as CrO_3	%	min. 42	17 to 19	min. 46
Water-soluble chromate as CrO_3*	g/100 ml	0.06 to 0.15		0.04 to 0.1
Water-soluble sulfate as SO_4	%	max. 0.1	max. 0.1	
Water-soluble chloride as Cl	%	max. 0.1	max. 0.1	max. 0.1
Water-soluble nitrate as NO_3	%	max. 0.1		max. 0.1
Matter volatile at 105 °C	%	max. 1.0	max. 1.0	max. 1.0
Color		yellow	yellow	yellow

*10 g pigment in 100 ml water.

Zinc Potassium Chromate

This pigment, also called zinc yellow, is produced by reacting an aqueous slurry of zinc oxide or hydroxide with dissolved chromate ions, followed by neutralization, or by precipitation of dissolved zinc salts with dissolved chromate salts, followed by washing, filtration, drying, and milling processes [5.56]. Previously zinc yellow used to hold a major share of the anticorrosive pigment market.

Zinc Tetrahydroxychromate

This is obtained by reaction of an aqueous slurry of zinc oxide with potassium dichromate, and sulfuric acid. It is also washed, filtered, dried and ground [5.56]. Zinc tetrahydroxychromate has been mainly used for the formulation and production of wash and shop primers based on polyvinylbutyrale resins.

Strontium Chromate

This anticorrosive is precipitated from solutions of sodium dichromate, and strontium chloride, also followed by filtration, washing, drying and grinding [5.56]. One of the most important uses for strontium chromate has been in primers for application on aluminum. This pigment still maintains much commercial importance because it is considered to be the most effective anticorrosive pigment for application in Aircraft and Coil Coating primers.

Other Chromate Pigments

Barium chromate, and calcium chromate were also utilized in the past as anticorrosives. Even then, their usage was limited, and therefore does not merit any detailed discussion in this section [5.53].

In general the usage of chromate anticorrosive pigments has reduced significantly, compared to previous times, due to the fact that they are now classified as either confirmed or suspected human carcinogens (see Section 5.2.16.) [5.53, 5.55].

5.2.5
Phosphate Pigments

5.2.5.1
Zinc Phosphate

In order to replace lead and chromate pigments, much attention has been focused upon zinc phosphate. Today, zinc phosphate is one of the most commonly used phosphate-containing anticorrosive pigments. The formulation versatility, due to the extremely lower solubility compared with chromate and other pigments, and therefore the lower reactivity, has led to its economic importance in the market. Zinc phosphate can be used in a wide variety of resin systems [5.53, 5.55].

ISO 6745 - Zinc phosphate pigments for paints - Specifications and methods of test- defines a zinc phosphate pigment as a white corrosion-inhibiting pigment consisting either predominantly of zinc phosphate dihydrate ($Zn_3(PO_4)_2 \cdot 2\,H_2O$) or of a mixture of zinc phosphate dihydrate and zinc phosphate tetrahydrate ($Zn_3(PO_4)_2 \cdot 4\,H_2O$) or predominantly of zinc phosphate tetrahydrate. Regarding the influence on the corrosion protection behavior, ISO 6754 notes that the corrosion-inhibiting properties of the various types of zinc phosphate pigments may differ [5.61]. The main requirements of the product properties of zinc phosphate pigments are summarized in Table 5.5.

Tab. 5.5: Quality requirements of zinc phosphate.

Characteristic	Unit	Requirement
Zinc as Zn	%	50.5 to 52.0
Phosphorus as PO_4	%	47.0 to 49.0
Conductivity	$\mu S\ cm^{-1}$	max. 154
pH		6.0 to 8.0
Density	$g\ cm^{-3}$	3.0 to 3.6
Sieve Residue (45 μm)	%	max. 0.5
Color		white

Zinc phosphates are normally produced on an industrial scale by a wet-chemical reaction involving zinc oxide (ZnO) and orthophosphoric acid (H_3PO_4), followed by filtration, washing, drying and milling processes. Numerous technical publications have gone into detail regarding the mode of action of zinc phosphate [5.62–5.66].

The performance properties of zinc phosphate pigments are attributed to chemical effectiveness, and the ability to form adhesion and inhibitor complexes on the surface of the substrate. In addition, in the case of zinc phosphate, electrochemical effectiveness, preferably in anodic areas, is also of note, since small amounts of the zinc phosphate will hydrolyze under moist conditions. The result of this reaction is argued to be the formation of zinc hydroxide and secondary phosphate ions, which are able to build protective layers on the metal surface in anodic areas [5.67, 5.68].

It is also discussed in the literature that, under moist conditions, basic complexes can be formed by reaction of zinc phosphate with inorganic ions or with carboxylic groups of the resin used, which lead, by reaction with metal ions, to so-called adhesion, cross-linking and inhibitor complexes [5.67–5.69]. Under the assumption, that the hydrolyzation process is the prerequisite for the effectiveness of zinc phosphates, this means that such pigments need a certain time before becoming active [5.69]. This leads to the conclusion that zinc phosphates do not have the well-recognized electrochemical effectiveness of chromate pigments [5.69].

The formation of hydrolysis products, in the case of zinc phosphate, depends on the permeability of the protective coating. The permeability of the protective coating itself is influenced by the type of resin used, and in particular, by the PVC (Pigment Volume Concentration). This means that the choice of resin, pigments and fillers and the complete formulation have an important influence on the corrosion protection behavior of protective coatings containing zinc phosphate [5.69].

Maybe, the proposed mechanism of the action of zinc phosphate is more related to theoretical considerations than to fully proven knowledge. However, practical experience has shown that zinc phosphate is an active anticorrosive pigment, but the protective effect of lead and chromate pigments can only be achieved in certain systems [5.70].

5.2.5.2
Modified Orthophosphates

As mentioned in Section 5.2.5.1, zinc phosphate, while having many desirable properties as an anticorrosive pigment, does not demonstrate the degree of corrosion protection offered by lead and chromate pigments [5.55]. Therefore the pigment industry has concentrated on developing phosphate-based pigments with improved properties.

By controlled chemical modifications under consideration of different points of view with suitable elements and compounds connected with the optimization of the manufacturing processes, it has become possible to improve the effectiveness of zinc phosphate for many applications [5.68, 5.70].

An overview of modified orthophosphate pigments that have gained economic importance is given in Table 5.6. When looking at Table 5.6, it becomes obvious that the pigment industry has developed several variations of zinc phosphate to improve the performance properties. These developments have been possible by taking account the effect of synergistic values [5.54]. For example, the development of basic zinc phosphates, based on the knowledge that when the hydroxyl ion concentration is increased, the equilibrium of the local cathodic reaction will be stabilized, resulting in prevention or inhibition of the emission of electrons [5.78]. In addition, a pH-stabilizing effect in the coating due to the presence of basic compounds in the pigment is also discussed [5.54].

The aim of phosphate borate combinations was to accelerate the readiness to hydrolyze [5.78] because,e as discussed in Section 5.2.5.1, the hydrolyzation process is one prerequisite for the effectiveness of zinc phosphates but these pigments need a certain time for activation. The improved anticorrosive activity of zinc phosphate molybdates is attributed to the inhibitive effect of water-soluble molybdate ions [5.55].

Tab. 5.6: Anticorrosive pigments based on orthophosphates [5.71]

Product	Modification	Reference
Zinc aluminum phosphates	with aluminum phosphate	[5.72–5.74]
Basic zinc phosphates	containing basic components (e.g. zinc hydroxide)	[5.72, 5.73]
	partly with differently treated organic compounds	[5.72, 5.75]
	partly with zinc molybdate and/or calcium molybdate	[5.76–5.78]
	partly with basic zinc borate	[5.75, 5.78]
	partly with iron phosphate	[5.79]
	partly with calcium phosphate	[5.77]
	partly with potassium phosphate	[5.73]
	partly with barium phosphate	[5.77]
	partly with aluminum phosphate and zinc molybdate	[5.80]
	partly with treated inorganic compounds	[5.75]
Zinc-free phosphates	variation of the cations e.g. with calcium phosphate and/or magnesium phosphate	[5.54, 5.81]
Zinc phosphate silicates	partly with calcium silicate and strontium phosphate	[5.54, 5.80, 5.82]
	partly with barium phosphate	[5.83]
	partly with calcium carbonate	[5.84]
	partly with differently treated organic compounds	[5.54, 5.83]
Zinc-free phosphate silicates	variation of the cations, e.g. with calcium phosphate silicate	[5.83]
	partly with barium phosphate	[5.83]
	partly with strontium phosphate	[5.83]

An aluminum zinc phosphate is produced by coprecipitation of primary aluminum phosphate ($Al(H_2PO_4)_3$) with zinc oxide. Such pigments have a higher phosphate content than standard zinc phosphate. The improved performance properties are attributed to this higher phosphate content [5.85].

In the case of the organically treated modified phosphate pigments, a closer bonding between pigment and binder, and also between coating, and substrate are discussed [5.86].

As a further example, phosphate silicates that are often termed as mixed phase or core pigments, may also be mentioned. By fixing the active components onto the surface of wollastonite (calcium silicate-core) and adjusting the pH value near neutral, these pigments show a relatively universal applicability [5.86].

5.2.5.3
Modified Polyphosphates

During research for anticorrosive pigments with improved performance properties compared to zinc phosphate, the development of so-called modified polyphosphate pigments was a further focus.

Orthophosphates are manufactured using the reaction of orthophosphoric acid with basic and/or amphoteric substances. Polyphosphates are obtained by condensation of acidic orthophosphates at higher temperatures [5.54]:

- Orthophosphates
  e.g. $3\ ZnO + 2\ H_3PO_4 \rightarrow Zn_3(PO_4)_2 + 3\ H_2O$
- Polyphosphates
  e.g. $Al(H_2PO_4)_3 \rightarrow AlH_2P_3O_{10} \cdot 2\ H_2O$

Modified polyphosphate pigments, which are of practical importance today, are predominantly reaction products of acidic aluminum tripolyphosphate with compounds based upon zinc, strontium, calcium, and magnesium (Table 5.7).

Development activities in conjunction with polyphosphate pigments have been focused on the high chelate building potential of acidic aluminum tripolyphosphate with metal ions [5.87].

Furthermore the accentuation of specific properties of certain substances within one product (synergistic effects) was tried [5.54]. Although the utilization of synergistic effects is not new for the pigment and coatings industry, it leads to very interesting results in the area of anticorrosive pigments [5.54]. Recent research work reports that special synergistic effects can be observed when using a phosphate-based pigment in combination with an organic corrosion inhibitor. Due to the utilization of such a combination, there might be the possibility to improve the substrate protection during the initial phase of exposure, resulting in improved long-term protection in special applications [5.54]. As discussed before, the development of modified orthophosphates, and polyphosphates was possible by taking effect of synergies. A key feature of the most modified phosphate-based pigments is their compatibility with a wide range of resins. Although the modified phosphate anticorrosives show wide

Tab. 5.7: Anticorrosive pigments based on polyphosphates [5.71].

Product	Modification	Reference
Zinc aluminum phosphates	with aluminum phosphate	[5.75, 5.87]
	partly with calcium silicate	[5.75]
	partly with strontium chromate	[5.75]
	partly with silicon dioxide	[5.78]
	partly with differently treated organic compounds	[5.75, 5.87]
Zinc-free aluminum phosphates	with strontium phosphate	[5.75]
	with calcium silicate	[5.75]
	with magnesium phosphate	[5.87]
	partly with barium phosphate	[5.77]
	partly with treated inorganic compounds	[5.75]

compatibility, it is advisable to select those pigments, which are recommended by the pigment supplier for any particular application [5.54].

This is one of the reasons why the pigment industry has been working on the development of phosphate-based pigments for universal applications. The typical properties of two modified orthophosphate based anticorrosive pigments, which have been available on the market since 2003 for universal applications, are summarized in Table 5.8.

Tab. 5.8: Typical properties of two modified orthophosphate pigments for universal application [5.80].

Characteristic	Unit	Zinc aluminum molybdenum phosphate	Zinc calcium strontium aluminum phosphate silicate
Zn as ZnO	%	62	37
Phosphorus as P_2O_5	%	27	18
Aluminum as Al_2O_3	%	2	3
Molybdenum as MoO_3	%	1	
Calcium as CaO	%		14.5
Silicon as SiO_2	%		15.5
Strontium as SrO	%		5
Conductivity	$\mu S\ cm^{-1}$	max. 300	max. 100
pH		7.0	7.5
Density	$g\ cm^{-3}$	3.7	3.5
Oil absorption value	g/100 g	18	30
Average particle size	µm	3	3
Color		white	white

5.2.5.4
Other Phosphates

Recently, there has been reference in the literature has to further phosphate-based pigments, such as barium phosphate, manganese phosphate, lead phosphate, and chromium phosphate. Utilization of such products has been limited, due to economical aspects [5.71].

5.2.6
Other Phosphorus-Containing Pigments

5.2.6.1
Zinc Hydroxyphosphite

In US 4,386,059, a zinc hydroxyphosphite anticorrosive, is described with the theoretical formula $[2\ Zn(OH)_2 \cdot ZnHPO_3] \cdot x\ ZnO$, wherein $x = 0$ to 17 [5.88]. This pigment is produced by reacting zinc oxide slurry with phosphorous acid in the presence of a zinc hydroxyphosphite complex promoter [5.88]. It is a white pigment with basic character [5.56].

The effectiveness of this anticorrosive is attributed to the ability of phosphite ions to inhibit anodic corrosion reactions by formation of iron phosphites and phosphates. In addition, the ability to form zinc soaps in oleoresinous resins that also inhibit corrosion, is referred, too [5.55].

5.2.6.2
Iron Phosphide

Commercial iron phosphide anticorrosive pigments consist of Fe_2P, with traces of FeP and SiO_2. These pigments are powders with a metallic gray color [5.56]. They are described as conductivity enhancers that are designed as a partial substitute for zinc dust in zinc-rich organic and inorganic coatings. When replacing zinc dust by up to 50% in a coating, there will be the possibility of improving the weldability. The partial use of iron phosphide leads to a reduction in price [5.89]. Compared to the utilization of zinc dust and lamellar zinc flakes, iron phosphides have not reached such an economic importance in the market.

5.2.7
Borate Pigments

In general borates are alkaline. This alkalinity plays a major role in their inhibitive properties [5.51]. Due to the utilization of borate-based anticorrosive pigments, there is the possibility to maintain a high pH value in the coating [5.56]. Borate pigments may also form soaps (mainly calcium or barium, depending on the pigment) with acidic products derived from the film [5.51]. It is also being discussed, that borates act as anodic passivators, forming a protective film on the metallic substrate [5.56]. Borates are said to be most effective in the initial phase of corrosion protection [5.56].

5.2.7.1
Calcium Borate Silicates

These pigments, also termed core pigments, such as phosphate silicates (see Section 5.2.5.3), consist of a complex composite of alkaline earth silicates, like calcium silicate. Available commercial grades differ primarily in their B_2O_3-content and oil absorption value (Table 5.9) [5.53].

Tab. 5.9: Typical properties of calcium borate silicates [5.53].

Characteristic	Unit	Grade 1	Grade 2	Grade 3
Boron as B_2O_3	%	11	11	16
pH		10	10	10
Oil absorption value	g/100 g	36	27	41
Color		white	white	white

They are mainly recommended for application in protective coatings based on solvent-borne alkyd resins [5.83].

5.2.7.2
Barium Metaborates

Commercially available pigments are characterized as modified barium metaborates. In this case, the meaning of the term modified is a silicon modification, which is used to reduce the solubility of the barium metaborate. Unmodified barium metaborates would not be suitable as pigments due to their high solubility [5.55]. Barium metaborate pigments can be produced by precipitation of a mixture of barium sulfide (BaS) and borax ($Na_2B_4O_7 \cdot 5\,H_2O$) in the presence of sodium silicate (Na_2SiO_3) [5.90]. Modified barium metaborates have a neutral white color and are mainly recommended for use in industrial solvent-borne coatings [5.55].

5.2.8
Molybdate Pigments

The inhibitive properties of molybdate-based anticorrosive pigments are attributed to the ability of molybdate ions to pass into solution, and to migrate to the metal surface resulting in the formation of a protective layer on the substrate, which insulates (passivates) the metal from attack and prevents corrosion [5.91].

The use of the pure molybdate-based pigments available on the market is limited due to their cost [5.53, 5.56]. To overcome this disadvantage, molybdate, and phosphate pigments are combined (see Section 5.2.5.2.) or molybdate compounds are applied to inorganic fillers like calcium carbonate and/or zinc oxide [5.56, 5.91].

Compared to the pure modified molybdates, those combinations are difficult to disperse [5.53]. Micronized versions of combined molybdate based pigments that are available today as easily dispersible grades are summarized in Table 5.10 [5.91].

Tab. 5.10: Typical properties of molybdate-based pigments [5.91].

Characteristic	Unit	Calcium zinc molybdate	Calcium zinc phosphate molybdate	Zinc molybdate	Zinc phosphate molybdate
Core material		Calcium carbonate	Calcium carbonate	Zinc oxide	Zinc oxide
Color		white	white	white	white
Specific gravity	g cm^{-3}	3.0	3.0	5.1	4.1
Oil absorption value	g/100 g	18	18	11	13.5
pH		8.5	8.0	6.5	7.0
Recommended for		Water- and solvent based coatings		Solvent based coatings	

5.2.9
Ion-Exchange Pigments

Ion-exchange pigments are based on calcium ion exchanged silica gel. These anticorrosives are described as slightly porous pigments with a basic, calcium-exchanged silica surface, and a relatively high surface area. Therefore these pigments have a different chemical and physical identity compared to other types of anticorrosive pigments [5.92]. The typical properties of two commercially available ion-exchange pigments are shown in Table 5.11.

Tab. 5.11: Typical properties of ion-exchange pigments [5.93].

Characteristic	Unit	Pigment 1	Pigment 2
Calcium content	%	6	6
Moisture		3	3
Oil absorption value	g/100 g	60	80
Density	g cm^{-3}	1.8	1.8
pH		9	9
Average particle size		3	5

Figure 5.12 demonstrates the corrosion protection afforded by using calcium-exchanged silica [5.92].

It is reported in the literature that, when a corrosion-causing ion enters the film and comes into contact with the silica, an ion exchange occurs. The aggressive ion is locked onto the silica and the corresponding calcium ion migrates to the metal surface. The ion-exchange process should be continuous. Whenever an aggressive ion enters the paint film, the correspondingly released calcium ions form a protective layer at the metal coating interface with barrier properties, which prevents corrosion

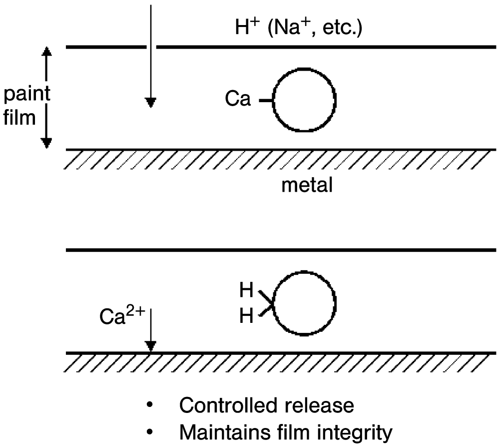


Fig. 5.12 Corrosion protection by ion-exchanged pigments [5.92].

causing ions from contacting the metal surface [5.92]. As a result of the ion exchange process a neutralizing effect is also discussed [5.56].

Maybe, the most important real application of ion-exchange pigments is their use in coil coating primers, mostly in combination with other anticorrosive pigments.

5.2.10
Titanium Dioxide-Based Pigments

Since 1999, there has been a new anticorrosive pigment on the market, combining the hiding power of a white pigment with anticorrosive properties. This pigment is based on a titanium dioxide carrier material, which provides physical properties like light scattering [5.94, 5.95]. The surface of this titanium dioxide is treated with phosphate-containing anticorrosive substances (manganese aluminum phosphates) by a precipitation process comparable to the procedure used in order to reduce the photoactivity of titanium dioxide pigments. In addition this pigment is organically treated to provide good dispersing properties in both polar inorganic and organic media, which might be of importance for use in water- and solvent borne protective coatings [5.94, 5.95].

This pigment is said to be bifunctional. It combines corrosion protection and light scattering in a single pigment [5.95]. It is recommended for application in water- and solvent-borne primers as well as in cathodic electrodeposition coatings and coil coatings [5.95]. The typical properties of this anticorrosive are summarized in Table 5.12.

Tab. 5.12: Typical properties of treated titanium dioxide pigment [5.96].

Characteristic	Unit	1
Lightness *L**		ca. 95
*b**-value		ca. 5
Relative scattering power		ca. 100
pH		ca. 8
Conductivity	$\mu S\ cm^{-1}$	ca. 150
Specific surface area	$m^2\ g^{-1}$	10
Average particle size	µm	0.4
Moisture	%	0.24
Rutile content	%	>99
Oil absorption value	g/100 g	20

5.2.11
Inorganic Organic Hybrid Pigments

It was mentioned in Section 5.2.5.3, that special synergistic effects in the field of anticorrosives could be observed when using inorganic anticorrosive pigments in combination with organic corrosion inhibitors. Following this theoretical and in practice proven knowledge, there are pigments on the market referred to as synergistic hybrid pigment grade corrosion inhibitors. For example in US 6,139,610, a corrosion-inhibiting pigment is described based on a stable unitary hybrid which contains organic and inorganic solid phase constituents [5.97]. The inorganic phase includes a cation selected from Zn, Mg, Ca, Sr, Ti, Zr, Ce, Fe and as anion a phosphate, polyphosphate, phosphite, molybdate or silicate [5.97]. The organic phase may include zinc or alkyl-ammonium salts of organic mercapto- and thio-compounds or their derivates [5.97].

As a second example of inorganic organic hybrid pigments, anticorrosives based on oxyaminophosphate salts of magnesium or magnesium and calcium should be mentioned. It is reported, that these pigments, when used in protective coatings, build a layer of magnesium oxide on the metal substrate. In the case of steel this layer is said to be a passive layer, and in the case of aluminum to be a barrier layer [5.98].

Many of the phenomena involved in the inhibition of corrosion provided by means of the application of protective coatings using new inorganic anticorrosive pigments in combination with organic corrosion inhibitors or so-called inorganic organic hybrid pigments have still not been fully explained [5.51].

However, when looking at the recent developments in the field of modified inorganic anticorrosive pigments (see previous Sections) and inorganic organic hybrid pigments, it becomes obvious that one of the main driving forces within this development process has been the possibility to take advantage of synergistic properties [5.54].

The terms synergy or synergism are defined as a “property by which two or more agents act together more effectively than either does alone. A phenomenon, where the mixed effect of two influences is greater than the sum of the two influences acting separately, i.e., the unexpected interaction of parts in combination” [5.99].

5.2.12
Zinc Cyanamide Pigments

Zinc cyanamide ($Zn(CN)_2$) was developed as a replacement for lead cyanamide (see Section 5.2.4.1) mainly for application in mirror coatings. The electrochemical effectiveness of cyanamides is attributed to a passivation action under alkaline conditions [5.56].

Zinc cyanamide is produced on an industrial scale from pure calcium cyanamide in an aqueous medium with zinc salts or a slurry of zinc oxide [5.56]. The pigment has, until now, not reached the importance of lead cyanamide for application in mirror coatings.

5.2.13
Micaceous Iron Oxide Pigments

Anticorrosive pigments have been divided in Section 5.2.3 according to whether they act as active pigments, barrier pigments or sacrificial pigments. Micaceous iron oxide pigments have been one of the most popular barrier pigments for nearly a century and have been proven in intermediate and topcoats for long-term corrosion protection of structural steel work [5.100]. Probably the best-known example of the use of micaceous iron oxide (MIO) is the protection of the Eiffel Tower in Paris. MIO has been used in maintenance paints on this tower since its erection in 1889 [5.55]. MIO is a naturally occurring form of hematite (α-Fe_2O_3), which crystallizes as either granular or, more often ,mainly lamellar and is also known as specular hematite. The term micaceous is used because of the more common lamellar particle shape of these pigments, but it does not contain mica (a special potassium aluminum silicate), the well-known filler used in coatings [5.55, 5.100]. MIO differs in particle size from the well-known red iron oxide color pigments (Figure 5.13).

MIO is dark gray in color with a metallic sheen. When viewed under an optical microscope by transmitted light, the thin-flake MIO particles appear as red translucent platelets and thicker and granular particles appear in a black shade [5.100]. The main function when using MIO in protective coatings is as a physical barrier, formed by the overlap of lamellar particles in the coating resulting in an elongation of the diffusion path for moisture and other corrosion stimulating substances through the coating (Figure 5.14) [5.100].

A comparative investigation of MIOs with different shapes, i.e. granular or a more lamellar shape (carried out within a study for the “Deutsche Bahn AG”) has shown no difference in the application of either grade in protective coatings with regard to the anticorrosive effect. This has been confirmed not only by accelerated laboratory tests but also by means of outdoor exposure in a coastal climate [5.103].

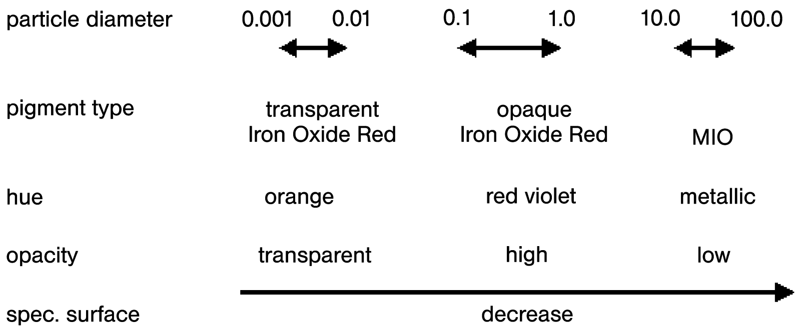


Fig. 5.13 Particle size and properties of iron oxide pigments based on a α-Fe_2O_3 [5.101].

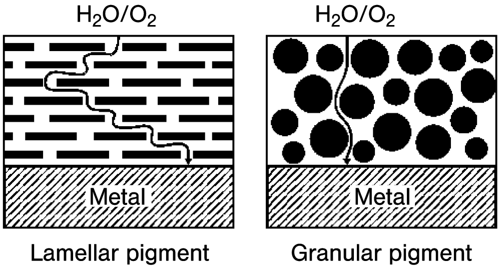


Fig. 5.14 Demonstration of the barrier effect when using lamellar pigments [5.102].

This result leads to the conclusion, that there are other important product properties besides the particle shape that have an influence on the barrier effect. In this connection, it is discussed that effective MIO pigments should have a very high Fe_2O_3 content and very low water-soluble salt (i.e. chlorides and sulfates) content.

An ideal MIO pigment should not contain very fine particles in order to keep the wettable pigment surface small. High PVC in the coating can only be achieved when the oil absorption value of the MIO pigment is low [5.103]. In addition to the barrier mechanism, MIOs are recommended for use in topcoats as a protection against ultraviolet degradation [5.55].

MIO has also reached its importance as an anticorrosive pigment due to its properties such as very good thermal and chemical stability, good hardness (abrasion resistance) and good electrical resistivity [5.55]. The requirements and corresponding test methods on MIO-pigments are specified in ISO 10601 - Micaceous iron oxide pigments for paints - Specifications and test methods. ISO 10601 differentiates MIO-pigments into three grades depending on the lamellar particle content:

- Grade 1: thin-flake content >50%
- Grade 2: thin-flake content 10 to 50%
- Grade 3: thin-flake content <10% [5.104].

Synthetic MIO-pigments are also available, but these have not achieved the economic importance of the processed natural pigments (see Section 3.1.1). The currently available MIO-pigments on the market consist mostly of more lamellar particles. Other barrier pigments of a certain economical importance are aluminum flakes, steel flakes, phlogopite and muscovite mica.

5.2.14
Zinc Pigments

Zinc dust is the only sacrificial anticorrosive pigment (see Section 5.2.3) on the market with significant economical importance. Zinc dust is a blue–gray free-flowing powder composed of spheroidal particles [5.56]. In the past, the zinc dust for use in protective coatings was a by-product of zinc metal production. Today, zinc dust pigments for application in protective coatings are specifically produced to offer different qualities for varying uses [5.105].

Zinc dust is produced from primary or secondary zinc metal by evaporation. The generated zinc vapor is condensed under controlled conditions under exclusion of air followed by sieving processes in order to obtain different particle size fractions [5.105]. The particle sizes of zinc dust are normally in the range 2 to 8 μm [5.105]. A product classed as fine quality shows a typical particle size of 3 μm whereas standard quality has particle size 8 μm [5.105].

The anticorrosive properties of zinc dust in protective coatings are based upon sealing effects and electrochemical reactions. Due to the high reactivity of zinc, it reacts with atmospheric components (water, oxygen, carbon dioxide), that diffuse into the binder, resulting in the formation of voluminous water-insoluble zinc salts, mainly basic zinc carbonates. The increase in volume connected with the filling of existent voids in the paint film decreases the permeability, and hence increases the barrier properties [5.56, 5.105]. The electrochemical effectiveness of zinc dust arises because zinc has a high position in the electromotive series of metals (see Section 5.2.3). Zinc becomes a sacrificial anode under corrosive conditions when in contact with ferrous metals. The sacrificial anode protects the ferrous cathode, as described before. This protection can be efficient as long as the zinc is able to go into solution. Weathering, together with zinc removal, should be avoided in any case by application of a topcoat [5.105].

While the correct loading level of zinc dust in primers is still a matter of debate, these primers normally have a zinc dust content of more than 80% in the dry paint film [5.53, 5.105]. The requirements of test methods for zinc dust pigments suitable for use in protective coatings are specified in ISO 3549 - Zinc dust pigments for paints - Specifications and test methods [5.106].

Zinc dust coatings are utilized in large quantities for the protection of structural steel, also including underwater steel construction and ship building [5.56]. Zinc dust is used in organic and inorganic binder systems (alkali silicates, ethyl silicates) [5.56, 5.105].

Zinc as a pigment for application in protective coatings is also available in the form of zinc flakes with a lamellar particle shape. Zinc flakes are mainly used in so-called micro-layer corrosion protection systems. These systems are accepted in the industry as standard surface protection for threaded parts [5.107].

5.2.15
Corrosion Control of Metals by Protective Coatings

Protective coatings are specified in numerous national and international standards. For example, the extensive control description, ISO 12944 - Paints and varnishes - Corrosion protection of steel structures by protective paint systems - deals with the protection of steel by paint systems and covers in eight parts more or less all features, which are important to achieve good corrosion protection [5.108]:

- Part 1: General Introduction
- Part 2: Classification of environments
- Part 3: Design considerations
- Part 4: Types of surface and surface preparations
- Part 5: Protective paint systems
- Part 6: Laboratory performance test methods
- Part 7: Execution and supervision of paintwork
- Part 8: Development of specifications for new work and maintenance

Part 5 gives, in the primer area, information about the type of primer to be used for the different corrodibility categories (classification of environment according to Part 2) and indicates whether the primer is zinc-rich or based on other anticorrosive pigments. For example, ISO 12944-5 requests for a zinc-rich primer a zinc dust content of 80% by mass (m/m) related to the non-volatile content of the primer [5.108].

Resin systems for primers according to ISO 12944-5 are alkyds, chlorinated rubbers, acrylics, polyvinyl chlorides, epoxies, ethyl silicates and polyurethanes [5.108].

In ISO 12944-6, a method is described for evaluating the quality of a protective paint system by means of laboratory tests, which enables the user to select the most suitable test methods [5.108].

ISO 12944 gives planners, consultants and companies working on corrosion protection state-of-the-art information in concise form [5.108].

5.2.16
Toxicology and Occupational Health

The changes in the toxicological classification of lead- and chromate-based anticorrosive pigments have resulted in reappraisal of the formulation of anticorrosive coatings.

5.2.16.1
Occupational Health

Precautions have to be taken and workplace concentration limits have to be observed when handling the various anticorrosive pigments. General regulations exist for all lead-containing materials like Red Lead or lead silicochromate. Concentration limits are as follows:

MAK value (lead)	<0.1 mg m^{-3}
BAT values	
Lead (blood)	<70 µg dL^{-1}
Lead (blood – women <45 years)	< 30 µg dL^{-1}
δ-aminolevulinic acid	
urine, Davies method	<15 mg L^{-1}
women <45 years	<6 mg L^{-1}
TLV-TWA value (lead)	<0.15 mg m^{-3}

It is accepted that the BAT limit has been complied with if the blood lead level does not exceed 50 µg dL^{-1} (or for women of <45 years, 30 µg dL^{-1}).

Council Directive 82/605/EEC specifies maximum lead concentrations in the air of < 150 µg m^{-3} and permitted blood lead levels of 70–80 µg dL^{-1}, with δ-aminolevulinic acid values of 20 mg/g creatinine [5.109, 5.110].

For chromate-containing anticorrosive pigments like zinc chromate, zinc potassium chromate, zinc tetraoxichromate and strontium chromate, the TRK value/TLV-TWA value for chromium(VI) compounds of 0.05 mg m^{-3} calculated as CrO_3 in total dust has to be complied with [5.111].

Lead- and chromate-containing anticorrosive pigments are classified for chronic toxicity as follows [5.109, 5.112, 5.113]:

Lead-containing anticorrosives (Red Lead, lead silicochromate)

Toxic for reproduction (unborn child):	Rep. Cat. 1 / category R_E 1
Fertility:	Rep. Cat. 3 / category R_F 3
Zinc chromate, zinc potassium chromate, zinc tetraoxichromate	
carcinogenic:	Carc. Cat. 1 / category C 1
Strontium chromate	
carcinogenic:	Carc. Cat. 2 / category C 2

5.2.16.2
Environmental Aspects

Air: Dust emissions from approved manufacturing plants must not exceed the following total mass flows or mass concentrations (TA-Luft) [5.114]:

Lead:	mass flow 2.5 g h^{-1} or mass concentration 0.5 mg m^{-3}
Chromium:	mass flow 5 g h^{-1} or mass concentration 1 mg m^{-3}.

Water: According to German wastewater legislation [5.115] for inorganic pigment manufacturing processes discharging directly into public streams of water, the mass limits for lead and chromium related to approved tonnes of annual production capacity (t_{prod}) and the concentration limits for zinc are:

Lead	0.04 kg t_{prod}^{-1}
Chromium (total)	0.03 kg t_{prod}^{-1}
Zinc	2 mg L^{-1}
Fish toxicity dilution index	2

Local or regional authorities, even for “non-direct” discharges into municipal sewer systems, might set lower limits.

The European Community classifies lead-containing anticorrosive pigments like Red Lead as well as zinc chromate, zinc potassium chromate, zinc tetraoxichromate, strontium chromate and, since 2000, also zinc phosphate as N, Dangerous for the environment (dead fish / tree) with the risk (R) and safety phrases (S) [5.112]:

R50/53 Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

S60	This material and its container must be disposed of as hazardous waste.
S61	Avoid release to the environment. Refer to special instructions/safety data sheets.

Waste: Waste containing lead-, zinc- and chromate-containing anticorrosive pigments that cannot be recycled must be taken to a special waste disposal site under proper control.

5.2.16.3
Classification and Labeling

In the EC lead-, chromate- and zinc phosphate-containing anticorrosive pigments must be appropriately labeled. Such substances must carry the following symbols and indications of danger [5.112]:

Lead-containing anticorrosives (Red Lead, lead silicochromate)
T, Toxic (skull and cross bone)
N, Dangerous for the environment (dead fish/tree)
R-phrases: R61-20/22-33-50/53-62, S-phrases S53-45-60-61
Zinc chromate, zinc potassium chromate, zinc tetraoxichromate
T, Toxic (skull and cross bone)
N, Dangerous for the environment (dead fish/tree)
R-phrases: R45-22-43-50/53, S-phrases S53-45-60-61
Strontium chromate
T, Toxic (skull and cross bone)
N, Dangerous for the environment (dead fish/tree)
R-phrases: R45-22-50/53, S-phrases S53-45-60-61
Zinc phosphate
N, Dangerous for the environment (dead fish/tree)
R-phrases: R50/53, S-phrases S60-61.

According to Council Directive 1999/45/EC on Classification, Packaging and Labeling of Dangerous Preparations (Preparations Directive) [5.116] in conjunction with the 28th Adaption to Council Directive 67/548 on Classification, Packaging and Labeling of Dangerous Substances [5.112], such preparations have to be labeled in accordance with the limits set for the single R-phrases.

With respect to improved protection of public health, special restrictions on cancerogenic and teratogenic substances and their corresponding preparations have been established by the Council Directive 94/60/EC (14th amendment of Council Directive 76/769/EEC) [5.117].

In accordance with the 14th amendment of Council Directive 76/769/EEC [5.117] and revised ChemVerbV [5.118], lead- and chromate-containing anticorrosive pigments are no longer permitted to be used by private consumers and have to be labeled with the phrase "Only for industrial purposes".

For road transport in accordance with GGVSE [5.119] and ADR 2003 [5.120], lead-, chromate- and zinc phosphate-containing anticorrosive pigments are assigned to the following classes:

Lead-containing anticorrosives (Red Lead, lead silicochromate)
6.1 (T5), III (UN-No. 2291), hazard symbol 6.1 (Toxic),
Zinc chromate, zinc potassium chromate, zinc tetraoxichromate
9 (M7), III (UN-No. 3077), hazard symbol 9
Strontium chromate
9 (M7), III (UN-No. 3077), hazard symbol 9
Zinc phosphate
9 (M7), III (UN-No. 3077), hazard symbol 9.

For maritime transport, in accordance with the IMDG code [5.121], such anticorrosive pigments have to be labeled additionally as marine pollutants.

5.3
Effect Pigments

The class of effect pigments (luster pigments) comprises the two main groups of special effect pigments including pearl luster pigments (pearlescent pigments, nacreous pigments, interference pigments) and metal effect pigments. All these pigments consist of small thin platelets that show strong lustrous effects when oriented in parallel alignment in application systems (e.g. in paints, plastics, printing inks, cosmetic formulations). Special effect pigments are described in Section 5.3.1, metal effect pigments in Section 5.3.2).

5.3.1
Special Effect Pigments

5.3.1.1
Introduction

Special effect pigments, which can be natural or synthetic, show outstanding qualities of luster, brilliance and iridescent color effects based upon optically thin layers [5.122–5.125]. This visual impression develops by reflection and scattering of light on thin multiple layers. In nature this is not limited to pearls and mussel shells alone; there are a multitude of birds, fish, precious stones and minerals, even insects, that demonstrate a luster effect. Experiments to understand the optical principles of natural pearl luster demonstrate that the brilliant colors are based upon structured biopolymers and upon layered structures, which are developed by biomineralization.

Figure 5.15 illustrates the various optical principles of conventional pigments (A) (absorption pigments), metal effect pigments (B), and pearls (C) and pearl luster pigments (D), the most important group of special effect pigments. In the case of absorption pigments, the interaction with light is based upon absorption and/or diffuse scattering. A completely different optical behavior can be observed with the group of effect pigments including pearl luster and metal effect pigments. Metal effect pigments consist of small metal platelets (for example aluminum, titanium, copper), which operate like little mirrors and almost completely reflect the incident light.

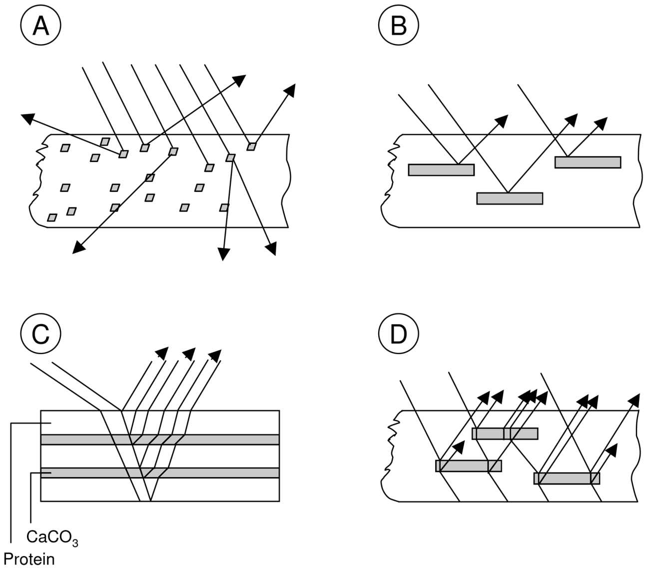


Fig. 5.15 Optical properties of absorption pigments, effect pigments and natural pearls.
A) conventional pigment; B) metal effect pigment; C) natural pearl; D) pearl luster pigment.

Pearl luster pigments simulate the luster of natural pearls. They consist of alternating transparent layers with differing refractive indices. The layers consist of $CaCO_3$ (high refractive index) and proteins (low refractive index).

This difference in refractive indices, arising equally on the interface between an air/oil film or oil film/water, is a prerequisite for the well-known iridescent color images in these media. Small highly refractive platelets of pearl luster pigments align themselves parallel in optically thin systems such as paints, printing inks, or plastics. Interference effects develop when the distances of the various layers or the thicknesses of the platelets have the right values.

Synthetic pearl luster pigments are either transparent or light-absorbing platelet-shaped crystals. They can be monocrystalline, as in $Pb(OH)_2 \cdot 2\,PbCO_3$ and BiOCl, or possess a multi-layered structure in which the layers have differing refractive indices and light absorption properties.

The use of pearls and nacreous shells for decorative purposes goes back to ancient times (e.g., in Chinese wood intarsia). The history of pearl pigments dates back to 1656, when French rosary maker Jaquin isolated a silky lustrous suspension from fish scales (pearl essence) and applied this to small beads to create artificial pearls. It took more than 250 years to isolate the pearl essence material (guanine platelets) and understand the pearl effect. Attempts were made to create synthetic pearl colors as organic or inorganic, transparent, highly refractive coatings and pearl pigments as crystalline platelets. From 1920 onwards, hydroxides, halides, phosphates, carbonates, and arsenates of zinc, calcium, barium, mercury, bismuth, lead, and other cations were produced for this purpose. Only the traditional natural pearl essence, basic lead carbonate and bismuth oxychloride, is still of importance.

The strong demand for pearl effects came from the growing coatings and plastics industries, which wanted to improve the acceptance and popularity of their products. Furthermore, pearl luster pigments also allowed artists and designers to create new visual effects similar to those found in nature. The breakthrough for pearl luster pigments came with the invention of mica coated with metal oxides. Mica-based pearl luster pigments now account for >90% of the world market. Important manufacturers of pearl luster pigments are Merck KGaA, Germany (with overseas subsidiaries EMD Chemicals Inc., USA and Merck Ltd., Japan) and Engelhard Corp., USA.

Pearl luster pigments are used to obtain pearl, iridescent (rainbow), or metallic effects, and in transparent color formulations to obtain brilliance or two-tone color, luster flops, and color travel effects (changing with viewing angle). The most important applications are plastics, industrial coatings, printing inks, cosmetics, and automotive paints.

Table 5.13 shows an overview of inorganic pigments with luster effects. Effect pigments can be classified with regard to their composition as metal platelets, oxide-coated metal platelets, oxide-coated mica platelets, oxide-coated silica, alumina and borosilicate flakes, platelet-like monocrystals, comminuted PVD films (PVD = physical vapor deposition), and liquid crystal polymer platelets (LCP-pigments, the only industrially relevant organic effect pigment type) [5.124–5.126]. The aims of new developments are new effects and colors, improvement of hiding power, more intense interference colors, increased light and weather stability, and improved dispersibility. Of special interest are pigments which are toxicologically safe and which can be produced by ecologically acceptable processes.

The total market for effect pigments can be estimated to be about 50,000 tons per year. Half of this amount can be calculated to be special effect pigments, the other half to be metal effect pigments.

5.3.1.2
Optical Principles of Pearl Luster and Interference Pigments

The physical background of optical interference effects has been the subject of many publications [5.122–5.125, 5.127–5.130]. The optical principles of pearl luster (interference) pigments are shown in Figure 5.16 for a simplified case of nearly normal

Tab. 5.13: Overview of inorganic effect pigments.

Pigment type	Examples
Metallic platelets	Al, Zn/Cu, Cu, Ni, Au, Ag, Fe (steel), C (graphite)
Oxide coated metallic platelets	Surface oxidized Cu-, Zn/Cu-platelets, Fe_2O_3 coated Al-platelets
Coated mica platelets*	non-absorbing coating: TiO_2 (rutile), TiO_2 (anatase), ZrO_2, SnO_2, SiO_2 selectively absorbing coating: FeOOH, Fe_2O_3, Cr_2O_3, TiO_{2-x}, TiO_xN_y, $CrPO_4$, $KFe[Fe(CN)_6]$, colorants totally absorbing coating: Fe_3O_4, TiO, TiN, $FeTiO_3$, C, Ag, Au, Fe, Mo, Cr, W
Platelet-like monocrystals	BiOCl, $Pb(OH)_2 \cdot 2\ PbCO_3$, α-Fe_2O_3, α-$Fe_2O_3 \times n\ SiO_2$, $Al_xFe_{2-x}O_3$, $Mn_yFe_{2-y}O_3$, $Al_xMn_yFe_{2-x-y}O_3$, Fe_3O_4, reduced mixed phases, Cu-phthalocyanine
Comminuted thin PVD-films	Al, Cr (semitransp.)/SiO_2/Al/SiO_2/Cr (semitransp.)

*Instead of mica other platelets such as silica, alumina, or borosilicate can be used.

incidence without multiple reflection and absorption. At the interface P_1 between two materials with refractive indices n_1 and n_2, part of the beam light L_1 is reflected (L_1') and part is transmitted (i.e., refracted) (L_2). The intensity ratios depend on n_1 and n_2. In a multilayer arrangement, as found in pearl or pearl luster and iridescent materials (Figure 5.15D), each interference produces partial reflection. After penetration through several layers, depending on the size of and difference between n_1 and n_2, virtually complete reflection is obtained, provided that the materials are sufficiently transparent.

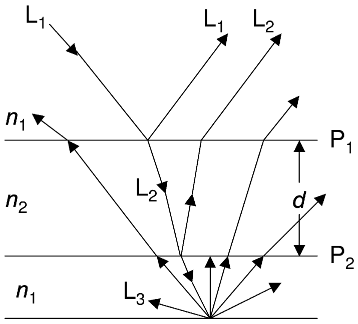


Fig. 5.16 Simplified diagram showing nearly normal incidence of a beam of light (L_1) from an optical medium with refractive index n_1 through a thin solid film of thickness d with refractive index n_2. L_1' and L_2' are regular reflections from phase boundaries P_1 and P_2. L_3 represents diffuse scattered reflections from the transmitted light.

In pigments that simulate natural pearl effects, the simplest case is a platelet-shaped particle with two phase boundaries P_1 and P_2 at the upper and lower surfaces of the particles, i.e., a single, thin, transparent layer of a material with a higher refractive index than its surroundings. For small flakes with a thickness of ca. 100 nm, the physical laws of thin, solid, optical films apply.

Multiple reflection of light on a thin solid film with a high refractive index causes interference effects in the reflected light and in the complementary transmitted light. For the simple case of nearly perpendicular incidence, the intensity of the reflectance (I) depends on the refractive indices (n_1, n_2), the layer thickness (d), and the wavelength (λ):

$$I = \frac{A^2 + B^2 + 2AB\cos\Theta}{1 + A^2B^2 + 2AB\cos\Theta}$$

$$\text{Where } A = \frac{n_1 - n_2}{n_2 + n_1},\quad B = \frac{n_2 - n_1}{n_2 + n_1},\quad \Theta = 4\,\pi\frac{n_2\,d}{\lambda}$$

With given n_1 and n_2 the maximum and minimum intensities of the reflected light, seen as interference colors, can be calculated and agree well with experimental results. Values for the refractive indices of the most important materials for pearl luster pigments are shown in Table 5.14.

Tab. 5.14: Refractive indices of materials.

Material	Refractive index
Vacuum/air	1.0
Water	1.33
Proteins	1.4
Organic polymers (plastics, lacquers, etc.)	1.4–1.7
Mica	1.5
$CaCO_3$ (aragonite)	1.68
Natural pearl (guanine, hypoxanthine)	1.85
$Pb(OH)_2 \times 2\ PbCO_3$	2.0
BiOCl	2.15
TiO_2 (anatase)	2.5
TiO_2 (rutile)	2.7
Fe_2O_3 (hematite)	2.9

In practice, platelet crystals are synthesized with a layer thickness *d* calculated to produce the desired interference colors (iridescence). Most pearl luster pigments now consist of at least three layers of two materials with different refractive indices. Thin flakes (thickness ca. 500 nm) of a material with a low refractive index (mica, silica, alumina, glass) are coated with a highly refractive metal oxide (TiO_2, Fe_2O_3, layer thickness ca. 50–150 nm). This results in particles with four interfaces that constitute a more complicated but still predictable thin film system. The behavior of more complex multilayer pigments containing additional, thin, light-absorbing films can also be calculated if appropriate optical parameters are known.

Color effects depend on the viewing angle. Pearl luster pigment platelets split white light into two complementary colors that depend on the platelet thickness. The reflected (interference) color dominates under regular (maximum) reflection, i.e., when the object is observed at the angle of regular reflection. The transmitted part dominates at other viewing angles under diffuse viewing conditions, provided that there is a non-absorbing (white) or reflecting background. Variation of the viewing angle therefore produces a sharp gloss (reflectance) peak, and the color changes between two extreme complementary colors. The resulting complex interplay of luster and color is measured goniophotometrically in reflection and at different angles. A pearl luster pigment is characterized by a minimum of three L*a*b* data sets (CIE L*a*b*-system) measured under different conditions (e.g., 0°/45° black background, 22.5°/22.5° black background, 0°/45° white background). An analysis of these data specifies a pigment on the basis of its hiding power, luster, and hue [5.122, 5.131, 5.132].

Against a black background or in a blend with carbon black, the transmitted light is absorbed and the reflected interference color is seen as the mass tone (i.e., overall color) of the material. In blends of nacreous pigments with absorbing colorants, the particle size of the latter must be well below the scattering limit, i.e., they must be transparent. The nacreous effect or iridescent reflection is otherwise quenched by the hiding pigments. This also applies to blends with strongly reflecting metal effect pigments (e.g., aluminum). Blends of pigments with different interference colors obey an additive mixing law, (e.g., blue + yellow = green).

5.3.1.3
Substrate-Free Pearl Luster Pigments

Natural Pearl Essence

Natural pearl essence is isolated as a silky lustrous suspension from fish scales. The organic pigment particles in the suspension are platelet-shaped with a very high aspect ratio (0.05 µm × 1–10 µm × 20–50 µm), and consist of 75–97% guanine and 3–25% hypoxanthine (natural fish silver) [5.122, 5.123, 5.128, 5.130].

Today there is no commercial synthetic process for producing similar platelet-shaped products of such brilliance; one is limited to a process based on the natural supply. An aqueous suspension of white fish scales is treated with organic solvents in a complicated washing and phase-transfer process to remove proteins and irregular guanine crystals. One ton of fish yields less than 250 g of guanine. The pigment particles show a high tendency to agglomerate and are, therefore, only handled as dispersions.

Natural pearl essence is very expensive but shows some advantages over synthetic pearl luster pigments. For example, it shows a high but soft luster ($n_D = 1.79$ (parallel) to 1.91 (perpendicular)). It is not brittle and has a relatively low density of 1.6 g cm^{-3}, which reduces settling in liquid formulations. It is almost exclusively used in expensive cosmetic applications.

Basic Lead Carbonate

The first commercially successful synthetic pearl luster pigments were hexagonal lead salt crystals, especially basic lead carbonate $Pb(OH)_2 \cdot 2\ PbCO_3$. Basic lead carbonate is precipitated from aqueous lead acetate with carbon dioxide under carefully controlled reaction conditions.

$$3\ Pb(CH_3COO)_2 + 2\ CO_2 + 4\ H_2O \rightarrow Pb(OH)_2 \cdot 2\ PbCO_3 + 6\ CH_3COOH$$

The resulting platelets are less than 0.05 μm thick and show hexagonal dimensions of about 20 μm, yielding an aspect ratio of >200. Because of their high refractive index of 2.0 and their even surface, they exhibit a very strong luster. If the thickness of the platelets is increased by slightly modified reaction conditions, interference colors can be obtained [5.122, 5.123, 5.128, 5.130].

The crystals are very fragile and are handled only in dispersions. They settle very fast because of their density of 6.14 g cm^{-3}. The use of basic lead carbonate is also limited by its low chemical stability, the toxicity of its by-products, and toxicological concerns in its application areas.

Bismuth Oxychloride

Bismuth oxychloride is produced by the hydrolysis of very acidic (pH <1.0) bismuth solutions in the presence of chloride.

$$Bi(NO_3)_3 + HCl + H_2O \rightarrow BiOCl + 3\ HNO_3$$

The crystal quality can be varied by careful adjustment of bismuth concentration, temperature, pH, pressure, reactor geometry, and by addition of surfactants. The usually tetragonal bipyramidal structure can be flattened to platelets with a high aspect ratio. Products with an aspect ratio of 10–15 show low luster and a very good skin feel and are used as fillers in cosmetics. Crystals with higher aspect ratios show an exceptional luster and are mainly used for nail polish [5.122, 5.123, 5.128, 5.130].

The low light stability, the fast settling caused by the high density of 7.73 g cm^{-3}, and the lack of mechanical stability limit the use of BiOCl in technical applications. The pigment is mainly used in cosmetics, but also in buttons and jewelry. The light stability can be improved to some extent by cerium doping and UV absorbers.

Micaceous Iron Oxide

Micaceous iron oxide consists of pure or doped hematite (α-Fe_2O_3). Its density is 4.6–4.8 g cm^{-3}. Micaceous iron oxide can also be obtained by hydrothermal synthesis in alkaline media. However, the dull dark color is as unappealing as that of the natural product. If substantial amounts of dopants are incorporated, the aspect ratio can be increased up to 100, resulting in a much increased luster. The color can be also shifted to a more attractive reddish brown so that the products can be used for decorative purposes [5.126, 5.133].

The most important dopants are Al_2O_3, SiO_2, and Mn_2O_3. These can enforce a spinel structure. SiO_2 yields thin small platelets, Al_2O_3 yields thin larger platelets, and Mn_2O_3 reduces the thickness.

The starting material $Fe(OH)_3$ or better FeOOH is heated in an alkaline suspension together with the dopants to temperatures above 170 °C, typically 250–300 °C. After several minutes to hours, platelets of doped iron oxide are obtained. In a second reaction phase, the pH is further increased so that platelets grow and form flat basal faces.

Titanium Dioxide Flakes

Titanium dioxide flakes can be produced by breaking down a continuous film of TiO_2 [5.130, 5.134]. The most efficient process is a web-coating process involving thermal hydrolysis of $TiOCl_2$ on the web. Alternative procedures are the application of titanium alkoxide onto a smooth flat surface and cracking the resulting film into flakes by steam treatment or the application of a TiO_2 sol onto a glass surface and scratching off the resulting film [5.135, 5.136].

The titanium dioxide flakes produced by these methods are not single crystal but quite porous and, lacking the mechanical support of a substrate, hence brittle. Therefore, they are not yet used in technical applications in which mechanical stress is exerted.

5.3.1.4
Pigments Formed by Coating of Substrates

Metal Oxide–Mica Pigments

The dominant class of pearl luster pigments is based on platelets of natural mica coated with thin films of transparent metal oxides [5.122–5.125, 5.127–5.130, 5.137]. The mica substrate acts as a template for the synthesis and as a mechanical support for the deposited thin optical layers of the pearl luster pigments. Mica minerals are sheet layer silicates. Pearl luster pigments are usually based on transparent muscovite mica; only some are based on synthetic phlogopite. Although muscovite occurs worldwide, few deposits are suitable for pigments. Natural mica is biologically inert and approved for use as a filler and colorant.

Selection and pre-processing of the mica substrate is one of the key factors which determine the quality and appearance of nacreous pigments. The mica manufacturing process starts from rough mica blocks. These are ground and then classified into different particle size distributions affecting the quality of the pigments. The aspect ratio of the final pigments depends on the particle size distribution of the mica platelets, which have a thickness of 300–600 nm and various diameter ranges (e.g., 5–25, 10–50, 30–110 μm). Since light is regularly reflected from the planes of the metal-oxide-coated mica and scattered from the edges, brilliance and hiding power are inversely related to each other.

A mica pigment coated with a metal oxide (Figure 5.17) has three layers with different refractive indices and four phase boundaries P_1–P_4: P_1 / TiO_2 / P_2 / mica / P_3 / TiO_2 / P_4. Interference of light is generated by reflections of all six combinations of phase boundaries, some of which are equal: $P_1P_2 = P_3P_4$, $P_1P_3 = P_2P_4$, P_1P_4, and P_2P_3. The thickness of the mica platelets varies in accordance with a statistical distribution. Consequently, interference effects involving the phase boundaries between the mica substrate and the oxide coating add together to give a white background reflectance. The interference color of a large number of particles therefore depends only on the thickness of the upper and lower metal-oxide-coating layers.

The development of the mica-based pigments started with pearl luster colors (Figure 5.18(A), TiO_2–mica). This was followed by brilliant, mass-tone-colored, combination pigments (i.e., mica–TiO_2, and another metal oxide) with one color (interference

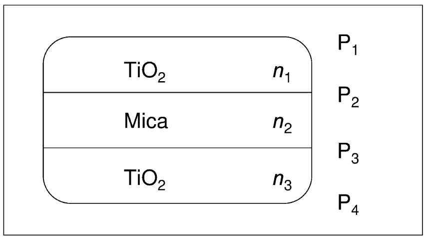


Fig. 5.17 Structure of a titanium dioxide mica pigment with the four existing interfaces.

color same as the mass tone) or two colors (interference and mass tone different) that depend on composition and viewing angle (Figure 5.18(B)). In the 1980s further development was made by coating mica particles with transparent layers of iron(III) oxide (Figure 5.18(C)).

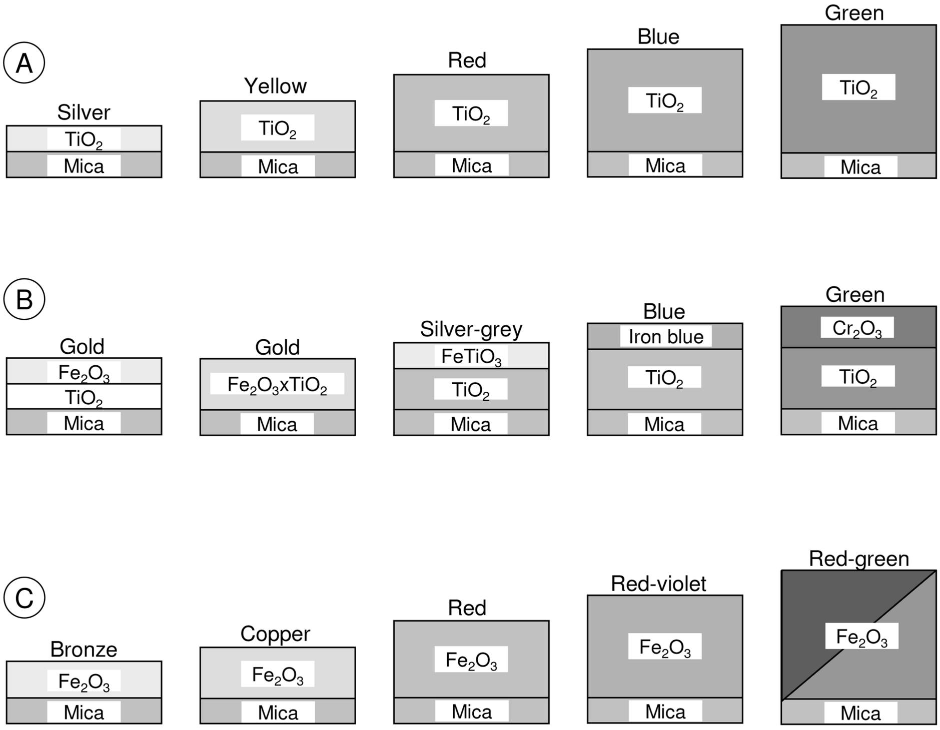


Fig. 5.18 Schematic illustration of different metal oxide mica pigments. A) interference colors; B) combination pigments; C) metallic colors. Only the upper half of the pigments is shown.

Titanium Dioxide–Mica

The first multilayer pigments were marketed in the 1960s as TiO_2-coated muscovite micas. Two different processes are used for coating mica in aqueous suspension on a commercial basis:

1. Homogeneous hydrolysis

   $$TiOSO_4 + Mica + H_2O \xrightarrow{100\ °C} TiO_2\text{–}Mica + H_2SO_4$$

2. Titration

   $$TiOCl_2 + 2\ NaOH + Mica \longrightarrow TiO_2\text{–}Mica + 2\ NaCl + H_2O$$

The pigments are then dried and calcined at 700–900 °C. The titration (chloride) process is preferred for interference pigments with thick TiO_2 layers because it is easier to control. Chemical vapor deposition in a fluidized bed has also been proposed:

$$TiCl_4 + 2\ H_2O + Mica \xrightarrow{>100\ °C} TiO_2\text{–}Mica + 4\ HCl$$

When TiO_2 is precipitated onto muscovite under reaction conditions unfavorable for side precipitation, e.g., pH >1.5, only the anatase modification is formed. Even after annealing at 1000 °C, no rutilization is found in the layer, whereas the free titania is transformed completely into rutile at about 700 °C.

Rutile has a higher refractive index than anatase. This yields a stronger reflectivity and pearlescence effect. Therefore, processes have been developed to create a rutile layer on mica. A thin layer of SnO_2 is precipitated as a continuous layer onto the substrate, and then the TiO_2 layer is created using the usual process. $SnCl_2$, or better $SnCl_4$, can be used as precursors for the SnO_2 precoating. SnO_2 acts as a template because its lattice parameters are close to those of rutile.

The desired interference color determines the thickness of the titania layer. For a silver white pigment 50 nm of anatase is needed and for a blue interference color about 120 nm. The sequence of interference colors obtained with increasing TiO_2 layer thickness agrees with theoretical calculation in the color space (Figure 5.19). A cross section of a TiO_2–mica pigment is shown in Figure 5.20.

Special effect pigments suitable for outdoor applications must meet the highest standards for color fastness and weather resistance. These pigments are coated additionally with thin layers of transparent and colorless oxidic compounds. These layers increase the light resistance by reducing the photoactivity of the titanium dioxide surface. In addition, the interaction between pigment and binder is optimized.

TiO_2–mica pigments are used in all color formulations of conventional pigments where brilliance and luster are required in addition to color, i.e., in plastics, coatings, printing, and cosmetics. Table 5.15 contains a comparative overview of TiO_2–mica, basic lead carbonate, bismuth oxychloride, and natural fish silver pigments. Some further physical data are summarized in Table 5.16.

Iron Oxide–Mica

Like titanium dioxide, iron(III) oxide is suitable for coating mica platelets. It combines a high refractive index (metallic luster) with good hiding power and excellent

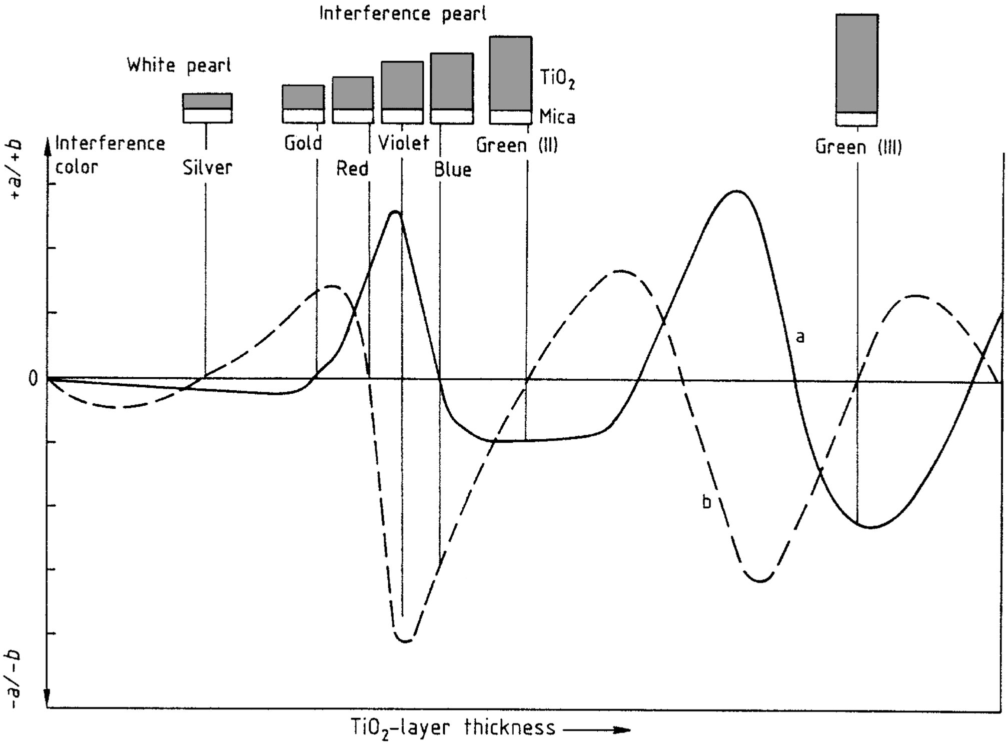


Fig. 5.19 TiO_2-mica pigments: the dependence of interference color on titanium dioxide layer thickness.

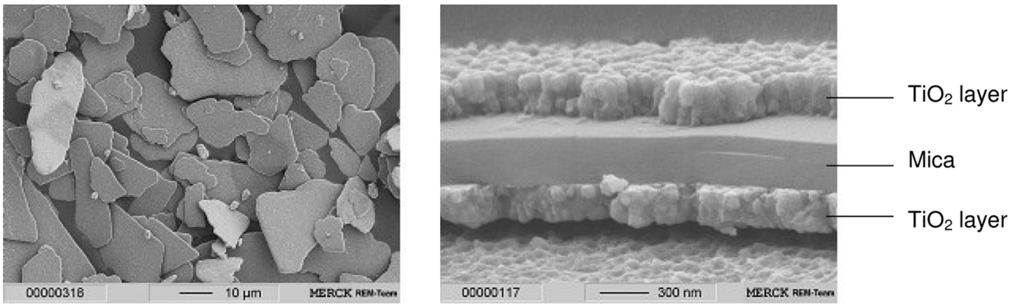


Fig. 5.20 SEM photographs of an anatase/mica pigment: left overview micrograph; right cross-section through one particle.

weather resistance. Commercial Fe_2O_3–mica pigments are produced by precipitation of iron(II) or iron(III) ions in aqueous mica suspensions and calcination of the resulting coated particles at 700–900 °C:

$$2\ FeCl_3 + Mica + 3\ H_2O \rightarrow Fe_2O_3\text{–}Mica + 6\ HCl$$

Tab. 5.15: Properties and applications of pearl luster pigments.

Pearl luster pigment	Advantages	Disadvantages	Main application field
Natural fish silver	very low density high luster nontoxic light stable	high price low hiding power limited availability	nail lacquers
Basic lead carbonate	very high luster good hiding power low price light stable	high density chemically and thermally of limited stability toxic	buttons bijouterie
Bismuth oxychloride	very high luster good hiding power nontoxic	limited light stability high density	decorative cosmetics buttons bijouterie
Titanium dioxide-mica	high luster good hiding power (depending on the particle size) highest thermal, chemical, and mechanical stability nontoxic low price low density	inferior luster in comparison with top qualities of basic lead carbonates and bismuth oxychloride	plastics lacquers cosmetics printing inks ceramic products

Tab. 5.16: Technical data of pearl luster pigments.

Pearl luster pigment	Shape	Particle size (µm)	Thickness (nm)	Density (g cm^{-3})
Natural fish silver	needles, longish platelets	10–40	40–50	1.6
Basic lead carbonate	hexagonal crystals	4–20	40–70	6.4
Bismuth oxychloride	flat tetragonal bipyramidal crystals	5–30	100–700	7.7
Titanium dioxide-mica	platelets	1–200	200–500	3

It is also possible to produce iron oxide–mica pigments by a direct CVD fluidized bed process in which iron pentacarbonyl is oxidized and Fe_2O_3 is deposited on the mica surface.

Independent of the synthesis route, iron(III) oxide crystallizes in the α-modification (hematite) after calcination. Brilliant, intense colors are obtained with 50–150 nm layers of Fe_2O_3 (hematite) on muscovite (see Figure 5.18 (c)). Absorption and interference colors are produced simultaneously and vary with layer thickness. The red shades are especially intense because interference and absorption enhance each other. An intense green–red flop with different viewing angles is possible at a Fe_2O_3 layer thickness, producing green interference.

Combination Mica-Based Pigments

Simple blending of transparent absorption pigments with pearl luster pigments is only one way to attain new coloristic effects. It is possible to produce pearl luster pigments coated with a layer of transparent absorption colorant to realize more pronounced brilliant colors with a sharper color flop. An additional advantage of such pigments is the elimination of dispersion problems associated with transparent absorption pigments due to their small particle size and high surface area.

One possibility for attractive combination pigments is the coating of TiO_2–mica pigments with an additional layer of an inorganic or organic colorant. The thickness of the TiO_2 layer is decisive for the brilliance or interference effect under regular viewing conditions, whereas the transparent colorant dominates at all other viewing angles. A deep, rich color with a luster flop at all angles is attained when the colorant and interference color are matched. If the interference color and the mass tone of the colorant are different, a color flop (two-tone pigments) is seen in addition to the luster flop.

Iron(III) oxide is the most important metal oxide for combination with titanium dioxide on mica flakes. Brilliant golden pigments result, which can be applied for several purposes. Two routes are used to synthesize these pigments, and different structures are formed. In the first, a thin layer of Fe_2O_3 is coated onto the surface of a TiO_2–mica pigment. The overall interference color is the result of both metal oxide layers. The mass tone is determined by the Fe_2O_3 layer, and interesting gold pigments (e.g., reddish gold) are possible. In the second case, co-precipitation of iron and titanium oxide hydroxides on mica particles followed by calcination leads to greenish gold pigments. Interference and mass tone can be explained as above. The mass tone in this case is, however, further modified because of the additional formation of the highly refractive yellowish iron titanate phase Fe_2TiO_5 (pseudobrookite).

Other inorganic colorants used instead of iron oxide for combination pigments are Cr_2O_3 (green), iron blue, cobalt blue, Fe_3O_4 (black), and $FeTiO_3$. In the case of black colorants, the interference color is seen as the mass tone. There is an analogy to blends with black pigments in a color formulation where the transmitted part of the light is absorbed. Coating of TiO_2–mica with an organic colorant for a mass-tone or two-tone pigment is performed by precipitation or deposition on the mica pigment surface in aqueous suspension, assisted by complexing agents or surfactants. Another method is to fix the colorant as a mechanically stable layer by using proprietary additives.

Mica platelets can be coated with a variety of other compounds to produce further pigments. Solid-state reactions and CVD processes extend the possibilities for the synthesis of mica pigments. In addition, the calcination of the materials in the presence of inert (e.g., N_2, Ar) or reactive gases (e.g., NH_3, H_2, hydrocarbons) allows the formation of phases, which cannot be produced by working in air. Table 5.17 contains a summary of mica-based effect pigments with special coloristic properties.

Initially, metal oxide–mica pigments were developed purely for their excellent coloristic properties. Since then, they have also become of interest for functional uses.

Tab. 5.17: Examples of mica-based effect pigments with special coloristic properties.

Pigment composition	Preparation	Remarks
TiO_{2-x}/TiO_2/mica [5.138, 5.139]	TiO_2/mica + H_2 (Ti, Si) $T > 900$ °C (solid state reaction)	gray, blue-gray
TiO_xN_y/TiO_2/mica [5.140]	TiO_2/mica + NH_3 $T > 900$ °C (solid state reaction)	gray, blue-gray
$FeTiO_3$/TiO_2/mica [5.141]	Fe_2O_3/mica + H_2 $T > 600$ °C (solid state reaction)	gray (ilmenite pigments)
Fe_3O_4/mica [5.140, 5.142]	Fe_2O_3/mica + H_2 $T \approx 400$ °C (solid state reaction) Fe^{2+} + O_2 + mica (preparation) $Fe(CO)_5$ + O_2 + mica (CVD-process)	black
TiN/mica [5.122]	$TiCl_4$ + NH_3 + mica (CVD-process)	gold
TiO_2/C/mica [5.143]	$TiOCl_2$ + C + mica (precipitation) calcination under N_2	silver-gray, interference colors (carbon inclusion pigments)
$BaSO_4$/TiO_2/mica [5.128, 5.144]	Ba^{2+} + $SO_4{}^{2-}$ + $TiOCl_2$ + mica (precipitation)	low luster pigments
Fe_3O_4/mica (mica surface only partially coated) [5.122, 5.145]	Fe^{2+} + O_2 + mica (precipitation)	transparent colors

In coatings with a high content of platelet fillers, an advantageous overlapping roof tile arrangement is possible that provides close interparticle contact, barrier effects, and dense covering. The composition and thickness of the oxide layer on the mica surface are always responsible for the physical properties like electrical conductivity, magnetism, IR reflectivity, and laser markability. Table 5.18 lists data on some functional metal oxide–mica pigments.

Silica Flake Pigments

Instead of mica, SiO_2 flakes can be used as a substrate for special effect pigments. The SiO_2 flakes are produced by a web-coating process. Synthetic SiO_2 flakes offer three advantages over the use of natural mica: 1. The thickness of the SiO_2 substrate can be controlled in the preparation so that a pigment with a true optical three-layer system is obtained. The interference color of these systems is stronger than that with the conventional mica pigments for which the effect of the mica is “wiped out” by a broad thickness distribution. 2. As synthetic substrates they do not have the small iron impurities that cause the slightly yellow mass tone of natural mica. 3. SiO_2 has a

Tab. 5.18: Functional metal-oxide pigments.

Pigment composition	Property	Application
$(Sn,Sb)O_2$/mica $Sn(O,F)_2$/mica [5.143, 5.146, 5.147, 5.148]	electrically conductive	conductive flooring, antistatic packaging materials, light colored primed plastic surfaces which can be electrostatically painted in further coating process, light colored conducting surfaces in clean room conditions for dust reduction
Fe_3O_4/mica [5.122]	magnetic	magnetic surfaces
TiO_2/mica [5.148, 5.149]	IR-reflective	IR-reflecting plastic sheets, e.g. for domed and continuous roof lights
TiO_2/mica [5.143, 5.148] $(Sn,Sb)O_2$/mica	laser sensitive	laser marking of plastics, coatings

lower refractive index (1.46) than mica (about 1.58) and, therefore, leads to a stronger interference effect [5.150–5.152]. Figure 5.21 shows a cross-sectional diagram of metal oxide coated on mica and metal oxide deposited on silica flake pigments. The new properties available with silica flake pigments can be summarized as follows:

- Improved substrate characteristics
  - Uniform and controllable substrate thickness
  - Smooth and uniform substrate surface
  - Transparent substrate with no mass tone color
- Improved reflection and refraction of light
- Improved chromatic strength and purity
- New color travel behavior

The silica flakes are manufactured by a web-coating process as shown in Figure 5.22. The web, moving at a controlled speed, is wet with an aqueous solution of a silica compound. The film on the web is dried to form a stable coating layer that can be selected to be between 50 nm and 1000 nm thick by adjustment of process parameters. The layer is then removed from the web and processed further to generate flakes that are fractioned and coated. The transparent flakes have a relatively low refractive index. However, they provide an excellent substrate for coating with the relatively high index metal oxides such as titanium dioxide and iron oxide. The metal oxides are applied in a standard precipitation-coating process producing high performance pearl luster pigments.

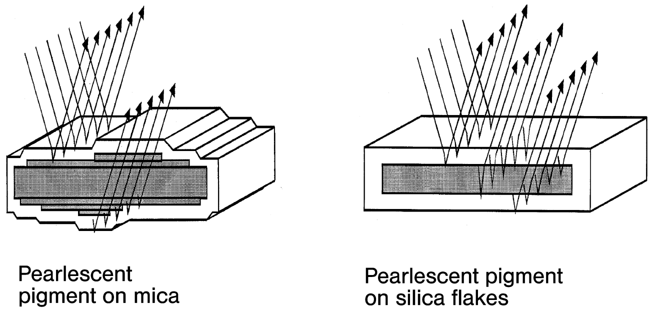


Fig. 5.21 Schematic cross-section of metal-oxide-coated pigments.

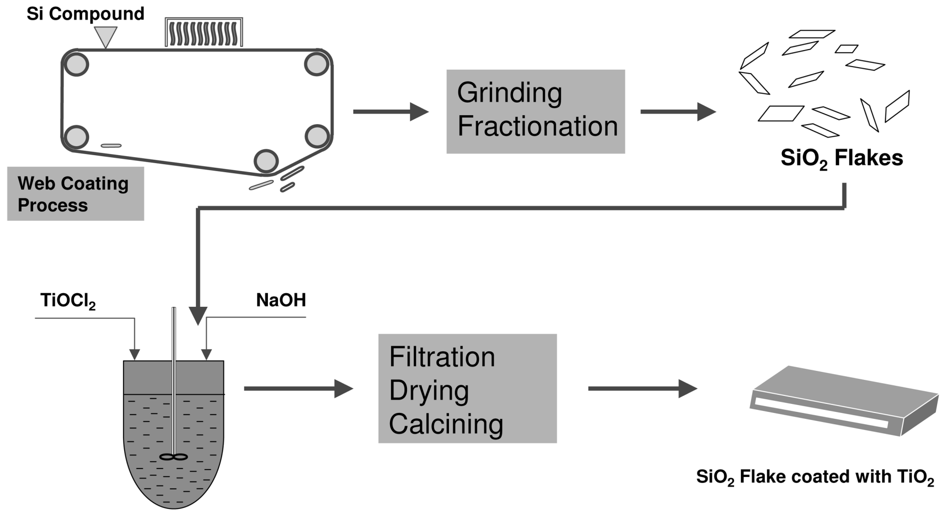


Fig. 5.22 Process for manufacture of transparent silica flakes.

Titania is deposited as hydrated titanium oxide on the surface of the SiO_2 flakes. The thickness of the layer is monitored and precisely controlled. After drying and calcining, anatase is formed and a specific color is produced corresponding to the film thickness. The anatase modification is used in the cosmetic industry. In principle, the manufacturing process is similar to the "anatase" procedure. However, a thin intermediate SnO_2 layer is applied to the surface of the SiO_2 flakes before the TiO_2 deposition. The SnO_2 layer has a rutile structure which seeds epitaxy of the TiO_2 rutile modification with its higher refractive index, brilliant color intensity and superior light stability. Consequently, the rutile pigments are preferred when these properties are advantageous.

SiO_2 can be coated not only with TiO_2 but also with other metal oxides that are deposited from hydrolysable salts. Iron(III) oxide is deposited as hydrated iron oxide on the transparent silica flakes. Subsequent drying and calcining produces α-Fe_2O_3

(hematite) layers on the flakes. The high refractive index of iron oxide generates strong interference effects and, in conjunction with the mass tone, brilliant red pigments.

Two extraordinary optical effects are achieved by the combination of transparent silica flakes selected for precise uniform thickness and controlled depositions of metal oxide coating layers. The color of these pigments exhibits extreme angle dependence, and objects painted with them will change appearance with the direction of lighting and the location of the observer. Color changes from gold–silver to green, to green–blue, to dark blue are seen. The strong color travel is seen even under subdued lighting conditions. Figure 5.23 demonstrates how color travel is generated as a function of viewing angle with uniform silica substrates and metal oxide layer thickness. The angle-dependent color travel of three pigments through the "CIELAB" system is shown in Figure 5.24 for constant Fe_2O_3 deposition on SiO_2 substrates of different thickness.

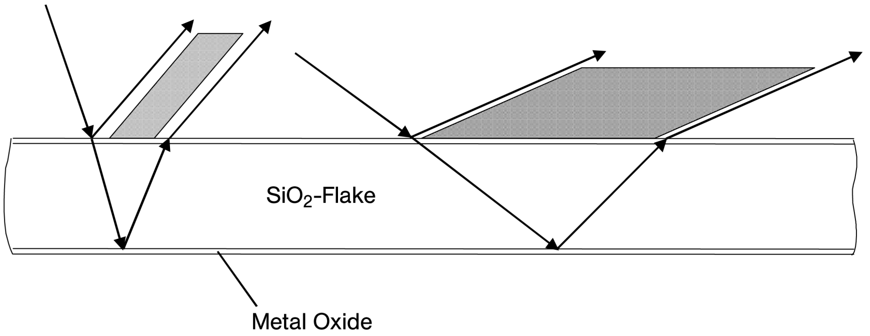


Fig. 5.23 Color variation vs. viewing angle of a SiO_2 flake pigment with a very thin metal oxide layer.

Improved color strength and very high luster are produced by the combination of precise thickness silica flake substrate materials, selected for their interference chromaticity, and by deposition of titania or iron oxide coating layers of the precise thickness required to generate the same interference color. These pearl luster pigments show stronger chromaticity L*a*b*-values than can be produced with mica-based designs.

The SEM micrograph in Figure 5.25 shows a cross section through a TiO_2 silica flake pigment. It shows clearly that both the SiO_2 flake and the TiO_2 layer thickness are precisely controlled.

Alumina Flake Pigments

Thin hexagonal monocrystalline Al_2O_3 flakes can be produced by hydrothermal processes [5.150–5.152]. The thickness of the resulting flakes is not uniform. Therefore, the resulting coated pigments merely assume a dull pearlescence.

Al_2O_3 flakes of a higher quality are produced by the following steps (Figure 5.26). An aqueous solution of an aluminum salt is mixed with small quantities of a titanium salt and phosphate. After neutralization, a sol or suspension is obtained, which is

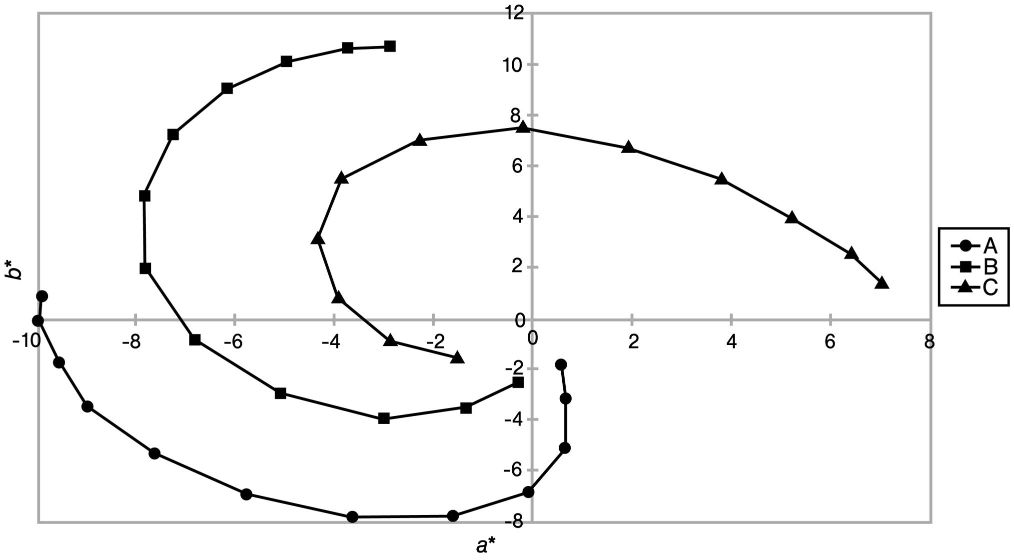


Fig. 5.24 Angle-dependent color travel of Fe_2O_3-coated silica flakes of different thickness.

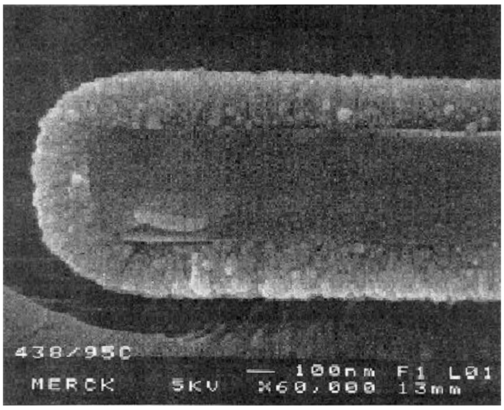


Fig. 5.25 Cross-section through a silica flake coated with TiO_2.

then dried and heated to 900–1400 °C. After washing, very thin flakes are found which consist of corundum and show a high aspect ratio, a very narrow thickness distribution, and very smooth surfaces (Figure 5.27). The thickness can be controlled by the doping and reaction conditions. The resulting flakes are used as substrates in the aqueous-phase processes described above to prepare pearl luster pigments of very high luster. The advantage over a mica substrate lies mainly in the fact that all Al_2O_3 flakes have about the same thickness, which leads to true optical three-layer systems as for the SiO_2 flakes. A very interesting crystal-like effect can be achieved by using alumina flake pigments in applications such as car paints.

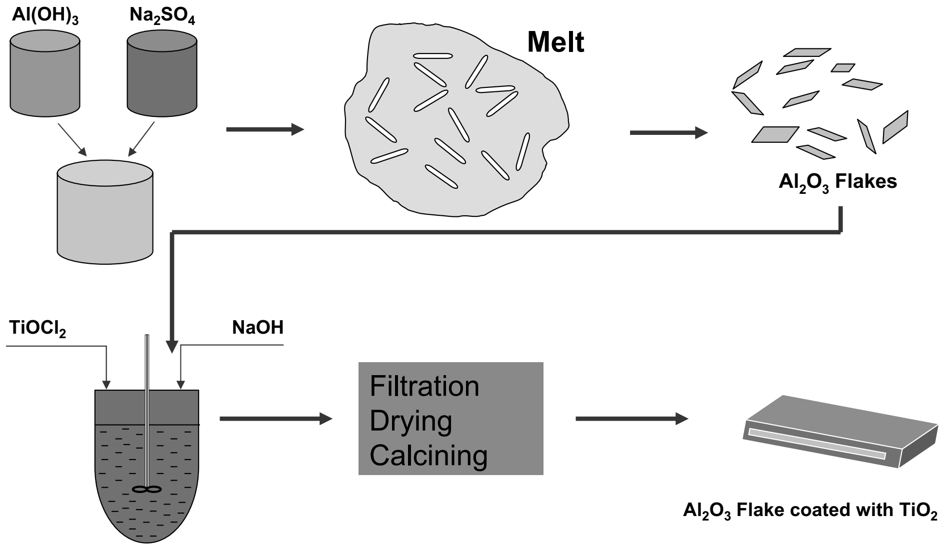


Fig. 5.26 Process scheme for alumina pigments.

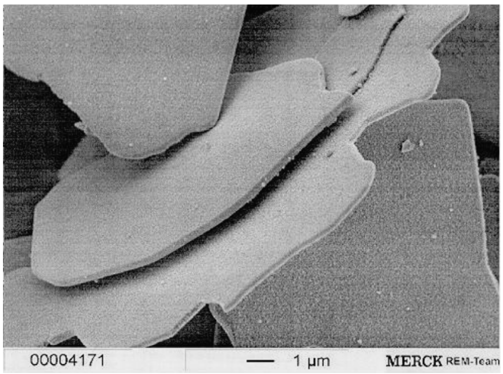


Fig. 5.27 Electron micrograph of Al_2O_3 flakes.

Borosilicate-Based Pigments

Special effect pigments with neutral body color, high luster and improved sparkling properties can be achieved from borosilicate flake substrates (glass flakes) [5.153, 5.154]. These pigments consist mostly of calcium–aluminum borosilicate platelets coated with metal oxide layers such as SiO_2, TiO_2 or Fe_2O_3. The synthetically manufactured flakes can be absolutely planar and show a smooth surface. They have a relatively uniform thickness of each single particle and therefore in most cases a homogeneous color of each platelet. The substrate particles as a whole show a thickness deviation from platelet to platelet caused by the production process. The manufacture of glass flakes that show a thickness in the range from several hundred nanometers to more than 10 µm is carried out starting from molten glass of the desired composition. The flakes are formed from the melt, for example by cooling a free-falling curtain of the molten glass that is uniform in thickness and temperature [5.155]. Borosilicate flakes can also be formed from molten material by feeding the stream in a downward direction into a rotating cup [5.156].

Effect Pigments Formed by Coating of Metal Flakes

Metal effect pigments consisting of flakes or lamellae of aluminum (aluminum bronzes), copper and copper–zinc alloys ("gold bronzes"), zinc, and other metals have been well known for a long time [5.157]. Some of these metal flakes, especially aluminum platelets, can be coated with iron oxide in a CVD process [5.126, 5.133, 5.140]. These are commercially the most important pigments based on CVD. The metal flakes are fluidized in nitrogen gas at temperatures around 450 °C. Then the reagents $Fe(CO)_5$ and O_2 are injected into the fluidized bed. For a proper coating these must be highly diluted in an inert gas. Sometimes water vapor is added to reduce electrostatic charging. The thickness of the coating is controlled by the reaction time. The only side product is carbon monoxide, which is catalytically oxidized to CO_2. The resulting pigments show golden, orange and reddish metal-like effects.

The aluminum flakes can be coated with aluminum oxide and/or silicon dioxide in the liquid phase before the CVD process to reduce the reactivity of the metal and to create multilayer color effects. These pigments show strong angle-dependent coloristic effects (color travel) [5.158]. Metal halogenides are difficult to use as gas-phase precursors for metal oxide coating because of the reactivity of the metal flakes and the corrosion of steel in chloride atmospheres. The use of $TiCl_4$ and water vapor was described about ten years ago. However, no commercial products have, as yet, been introduced.

Mica flakes can also be coated in CVD processes using the same technique as discussed for metal flakes. In addition, one can also use metal chlorides as precursors for oxide coating on mica. However, essentially the same products can be obtained more easily by precipitating the oxides from the liquid phase.

Pigments Formed by Grinding a Film

Optical coatings that shift color with viewing angle have been adapted into optically variable films, pigments, and inks during recent years [5.125, 5.130, 5.159]. These coatings are based frequently on metal–dielectric multilayer thin structures having large color shifts with angle, high chroma, a large color gamut, and light fastness. Different colors are produced by precisely controlling the thickness of the multilayers in the coatings structure. To maintain tight color tolerance, the layer thickness must be controlled to within a few atoms.

The metal layers frequently consist of chromium (semitransparent absorber metal) or aluminum (opaque reflector metal). Silicon dioxide or magnesium fluoride are the materials mostly used for the dielectric layers. In the case of pigment particles, there is a symmetrical arrangement of the layers, as shown in Figure 5.28, whereas optical coatings can also consist of a system of unsymmetrical layers. All these arrangements are the basis for an optical phenomenon called the Fabry–Perot effect.

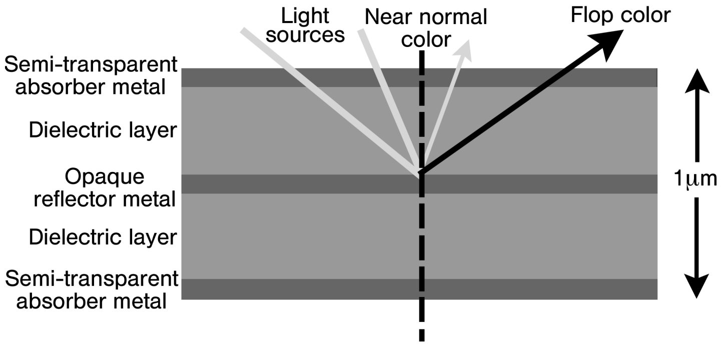


Fig. 5.28 Scheme of design of optically variable pigments (OVP).

Such multilayer interference configurations filter the spectrum into a sequence of high-reflectance regions surrounded by low-reflectance regions and thus lend themselves, in principle, to high-purity color production. The detailed spectral characteristics can be widely controlled by controlling the specific design parameters.

It has been found that for flaky pigment particles suitable for strong color-shifting effects, a symmetrical arrangement of the layers is necessary. A minimum of five layers and, for some optical purposes, even more may be required. The need for many layers tends to make such a design relatively impractical in any high-volume coating production. Therefore, for practical purposes, only the five-layer arrangement plays a role.

The pigment flakes can typically be manufactured sequentially in a series of specialized roll-coating machines. In the first machine a carrier film, the so-called release layer, is deposited on a moving polymer web (transfer foil). This release layer is soluble in organic solvents so that the later formed multilayer film can be removed from the web at the end of the process. After depositing this release layer, the transfer foil is placed in a vacuum deposition roll coater and the first metal layer (e.g., chromium) as the semitransparent absorber metal is deposited, followed by the first dielectric layer (e.g., magnesium fluoride) and the opaque metal layer (e.g., chromium). The second dielectric layer and the second semitransparent absorber metal layer follow by the same deposition process. After this symmetrical multilayer interference coating has been deposited, the coated foil is removed from the vacuum chamber. In a subsequent step, the formed thin multilayer film is removed from the supporting transfer foil by dissolving the release layer. Transformation into pigment particles is done by grinding the removed part of the film into small platelets, which now show pigment dimensions (thickness 0.2–2 μm, diameter 1–100 μm).

Such types of effect pigments can be used for several applications and are on the market as so-called optically variable pigments (OVP). They have found broad application, especially in preventing counterfeiting of important documents such as banknotes, stock certificates, visas, passports, or car licenses. When incorporated into security inks and printed on bank notes and other documents of value, the pigments are effective against color copying by printers, copiers, or cameras and unauthorized lithographic reproduction [5.160].

Uses

Special effect pigments are used as colorants or part of color formulations for all systems where traditional pigments are applied, but where additional color depth, brilliance, iridescence, color travel, and other spectacular effects are required [5.122, 5.123]. Mica-based pigments dominate; their combination of pearl and interference effects, brilliance, stability and behavior in different application systems is as yet unsurpassed. Pearl luster pigments require transparent or at least translucent binders. Formulations with absorption pigments have to take their transparency and color mixing rules into account.

Special care has to be taken to ensure parallel alignment of the platelet-shaped pigment particles during their application. In most cases the pigments can be dispersed homogeneously by simply and carefully stirring them into a suitable liquid system.

Today, special effect pigments are a standard component of solvent and water-based automotive and industrial coatings. The main reasons are both the decorative effect and the technical quality. The automotive designer has a wide range of color and composition possibilities at his disposal. Attractive and individual paint is provided not only by the various colors of special effect pigments, but also by using different particle sizes in combination with other absorption pigments [5.122, 5.137, 5.161].

Industrial paint applications for special effect pigments are e.g. furniture, bicycles, airplanes, rail wagons, cans and containers, building exteriors, interior decoration, artificial pearls and jewelry. The main reasons for their use are the achievable special effects, the attractiveness of the colors and the good application behavior [5.122].

Special applications of bright electro-conductive pigments based on metal-oxide-coated mica are conductive plastic surfaces and antistatic coatings [5.122, 5.148].

Plastics are one of the best-known applications for special effect pigments. The pigments are used with all thermoplastic methods such as injection molding and extrusion. They can also be applied in duromers. Fascinating marble effects can be obtained using plunger-type injection machines, injection molding with so-called marble units and with intermittent injection molding machines [5.122].

Attractive products can also be created using film blowing, blow molding and co-extrusion. Usually 0.5 to 2% of a pearl luster pigment is added to color plastics. A special application of some effect pigments is the laser marking of plastics. The pigment that is incorporated in the polymer is responsible for a dark or white coloring of the plastic material by interaction with a laser beam. Other mica-based effect pigments are designed with structures to achieve special solar reflective properties. Applications of mica pigments with high IR reflection are for example agricultural films (selective reflection of a part of the NIR, climate control in greenhouses) and IR-reflective plastic parts for domed and continuous roof lights [5.122, 5.148].

Printing with special effect pigments fulfills the highest esthetic requirements. Many products are printed with them especially when the articles should reflect a touch of luxury and artistic style. The pigments can be used with all important printing techniques, such as offset, screen, gravure and flexographic printing methods and also in coating techniques such as overprint-varnishing (OPV) and paper coating. They can be used in solvent and water-based printing inks as well as in UV-based systems. New application forms of special effect pigments for printing applications are preparations for liquid inks (e.g. pearlets) and special preparations for offset printing [5.122, 5.162, 5.163].

Cosmetic applications require specific effect pigments that are approved for use according to cosmetic regulations. The applications of these pigments include color cosmetics (lipsticks, eyeshadows, blushers, eye pencils, make-up, mascaras, nail lacquers), personal care products (shampoos, body washes, lotions, creams, oral care products, hair gels), and special effect items (theatrical and costume make-up, temporary hair color sprays) [5.164].

For ceramic and glaze applications, the effect pigments based on substrates like mica are coated with an additional SnO_2 layer to give stabilization against the aggressiveness of the frits at high temperatures [5.165].

5.3.2
Metal Effect Pigments

5.3.2.1
Definition

Metal effect pigments are flake-shaped metallic particles supplied in the form of powders, pastes, pellets, suspensions or color concentrates [5.166–5.168]. Typical metal effect pigments include aluminum (“silver bronze”) and copper- and copper/zinc-alloys (“gold bronze”).

Besides the metal effect pigments there are also metallic pigments and powders for functional coatings like anticorrosion, reflective, heat resistant and conductive coatings. These include zinc, stainless steel and silver pigments.

Aluminum pigments themselves are colorless pigments (pigment metal 1, CI 77000) but may be combined with transparent color pigments or dyes or other effect pigments. The color of gold bronze pigments (pigment metal 2, CI 77400) depends on the copper/zinc-alloy and range from copper (0% Zn) over pale gold (ca. 10% Zn), rich pale gold (ca. 20% Zn) to rich gold (ca. 30% Zn).

Additionally there are oxidized gold bronze pigments available, which obtain deeper color shades by a controlled oxidizing process during manufacturing.

5.3.2.2
History and Technology

The technology of manufacturing metal pigments goes back to the gold-beaters craft. Upon industrialization, this handcraft was followed by stamping technology, which in some countries and for some special applications is still in use. The stamping technology was followed by ball milling processes, including dry milling (Hametag-process) [5.169] and wet milling (Hall-process) [5.170].

The dry milling process is still the most commonly used method for making gold bronze, whereas the wet milling process is the state-of-the-art technology for manufacturing aluminum pigments.

Atomized aluminum powder is milled in ball mills in the presence of mineral spirit and a lubricant. After the disintegration process, the pigment slurry is sieved and classified and pressed on a filter press to remove the excess solvent. The press cake (typical solvent content ca. 75 to 80%) is then blended with organic solvents to form an aluminum paste typically containing 65% solids and 35% solvent.

In applications, where aluminum powder is requested (e.g. in powder coatings) or where the rest of the remaining mineral spirit would not be compatible with the application medium (e.g. in printing inks, waterborne coatings and inks, masterbatches etc.), the mineral spirit of the press cake is removed in vacuum driers and substituted by any kind of solvent, water, plasticizer, mineral oil or other liquids.

Another very common supplied form of metal effect pigments are the so-called “pellets” or “granulates” [5.171, 5.172]. Here the pigments are supplied in dust-free and easy to handle preparations of metal pigments with a few percent of resin. These pellets are solvent-free and offer the end user a wide variety in formulation besides the other advantages. Both, aluminum and gold bronze pigments are available in pelletized form and are mainly used in printing inks and masterbatches.

A rather new technology is the process for making the so-called “vacuum metallized pigments (VMPs)”, where extremely thin and smooth metallized films are dissolved from the carrier, then disintegrated and processed as a pigment suspension in a variety of solvents [5.173].

Besides the “bare” metal effect pigments there is a whole variety of specially treated or encapsulated metal pigments, to create new effects or to modify the pigment properties according to the needs of special applications:

A CVD-process is known to produce iron-oxide-coated aluminum flakes which form high brilliance colored aluminum pigments with highly interesting interference effects [5.174]. Some of the very new optically variable pigments consist of multilayer flake pigments with a metallic core to obtain metallic reflection and coverage [5.175].

Other metallic pigments are coated with inorganic (mostly silica) or organic (polymer) materials to improve their chemical and thermal stability in waterborne coatings, powder coatings, masterbatches, non-conductive coatings etc.

5.3.2.3
Characterization

Leafing/Non-Leafing

One of the most typical properties of metallic pigments is their wetting behavior in different solvents (including water) or binder solutions. Metal effect pigments are basically divided into leafing and non-leafing types (Figure 5.29).

Leafing pigments float on the surface of the wet film, orienting themselves parallel to the surface and thereby forming a dense metallic layer on top of the coating. This layer has a high reflectivity and provides excellent barrier protection of the film (resin).

This property is not only used for creating a high metallic “chrome effect” in decorative coatings and printing inks, but also for manifold applications in functional coatings like roof coatings, tank coatings, anticorrosion coatings etc.

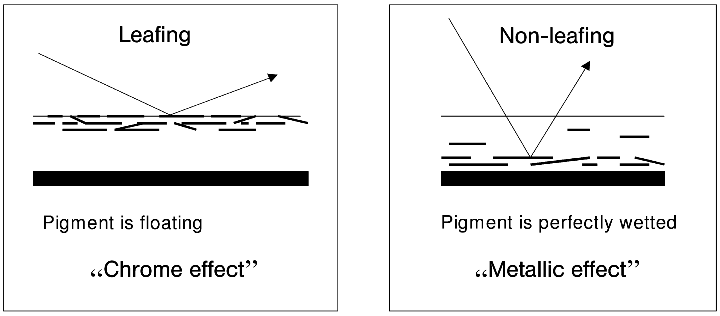


Fig. 5.29 Wetting behavior of metal effect pigments: leafing and non-leafing.

Non-leafing pigments on the other hand are perfectly wetted in the binder and therefore oriented more or less parallel to the substrate on the bottom of the wet film. The cured films are rub-resistant with an excellent adhesion to following clear coats. The pigmented film can easily be tinted with transparent color pigments or dyestuffs, thereby creating the typical polychromatic "metallic effect".

Particle Shape

The shape of the pigment particle depends very much on the manufacturing conditions. Basically we distinguish between the traditional "cornflake-type" (irregular shaped) and the so-called "silver dollar-type" (lenticular, round-shaped, smooth surface). The thickness of these pigments varies from 0.1 to 1 μm (Figure 5.30).

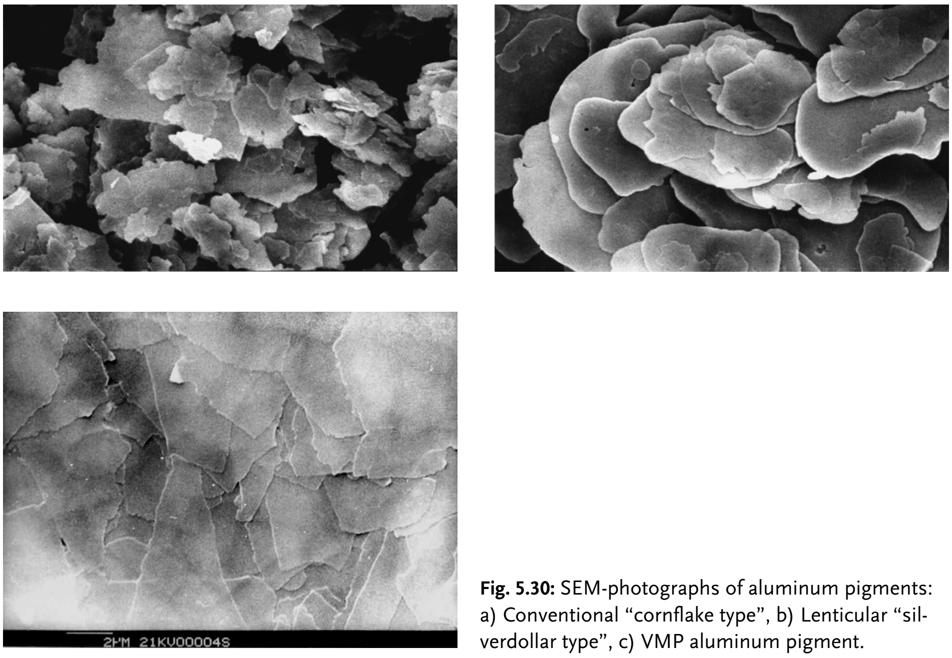


Fig. 5.30: SEM-photographs of aluminum pigments: a) Conventional "cornflake type", b) Lenticular "silverdollar type", c) VMP aluminum pigment.

The VMPs (vacuum metallized pigments) differ very much from these traditional pigment flakes. Due to the original PVD-process, they are extremely thin (ca. 0.03 μm) and provide a very smooth, highly reflective surface. The particle shape has a tremendous influence on the metallic effect (see below).

The anisotropic shape of the metallic flakes should be considered during dispersion and application of these pigments: high shear forces may damage the pigments and the effect and should therefore be avoided.

Particle Size/Particle Size Distribution

The size of the particles depends also, like the particle shape, on the manufacturing conditions and varies from a few μm up to 100 μm, depending on the optical effect required and the application conditions.

The fineness of the pigment is characterized by the maximum particle size (mentioned in the catalogues as sieve residue according to standardized DIN or ASTM testing methods) and the average particle size D_{50} measured preferably by laser beam diffraction methods. These methods are not yet standardized and the readings depend very much on the equipment and the testing conditions. Furthermore the particle size distribution can be characterized by the "span", i.e. the width of the distribution curve.

5.3.2.4
Optical Principles

The Metallic Effect

The metallic effect is caused by the reflection of light at the plane surfaces of the metallic flakes, which is overlaid by the scattering of light at the edges (Figure 5.31). The metal flakes act like tiny mirrors, following the physical principle that the reflection angle is the same as the angle of illumination.

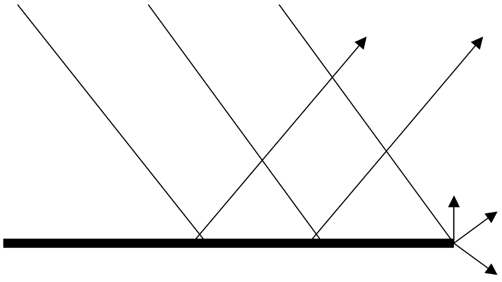


Fig. 5.31 Light reflection and light scattering at metal effect pigment surfaces.

Whereas, from an ideal mirror, 100% of the light is reflected, leading to 100% gloss, the reflection at a metallic effect surface is overlaid by a certain amount of scattered light, resulting in a typical light distribution with a significant maximum in the gloss angle, but visible light around it (Figure 5.32).

This behavior also leads to another typical optical property of the metallic effect: the flop- or two-tone-effect. This effect describes the fact that, at metallic effect coatings,

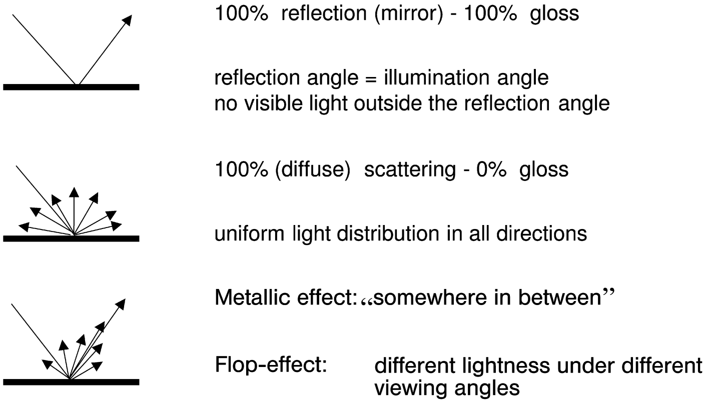


Fig. 5.32 Physical mechanism of the metallic effect.

the physically experienced lightness depends very much on the viewing angle and varies from extremely light at or close to the gloss angle to rather dark at inclined angles.

Parameters

The physical parameters for the metallic effect, which influence the ratio between reflection and scattering and thereby the flop effect, the lightness and brightness, the brilliance and sparkle, the gloss and the distinctiveness of image (DOI) etc. etc. can simply be described in terms of particle size, particle shape (morphology), particle size distribution and particle orientation in the film

Particle Size

The influence of particle size is rather clear: the coarser the particles, the more reflection, and the finer the particles, the more scattering. Coarse particles cause the so-called "high sparkle effect".

Particle Shape (Morphology)

Like the particle size, the particle shape also has a significant influence on the optical effect: the smoother the surface, the better (and more parallel) is the reflection and the rounder and more regular the particle, the lower the amount of scattering. This means, comparing "cornflake-types" and "silverdollar-types" of aluminum pigments with similar particle size distribution in the same formulation, the round "silver dollars" show much more lightness and brightness and a much smoother effect ("silky").

Even more extremely, one can realize the influence of the smoothness of the pigment surface, if one looks at applications with vacuum metallized aluminum pigments manufactured from vacuum metallized films. These pigments have a foil- or mirror-like surface, achieving extra brilliant and high gloss effects. They are therefore preferred for use in reflective coatings, high brilliant decorative coatings and printing inks (as a substitute for hotstamping foils).

Particle Size Distribution

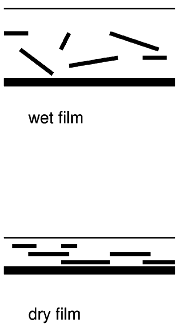
As the particle size of the individual flakes plays a significant role in generating the metallic effect, the particle size distribution is even more important to describe the total effect: the smaller the share of fine and ultra-fine particles, the higher will be the brightness, brilliance and flop, as well as the chroma in tinted systems.

On the other hand, fine particles increase the tinting strength, hiding power, gloss and distinctiveness of the image. In many applications pigments with a controlled particle size distribution are required to get optimal metallic effects.

Particle Orientation in the Film

Last but not least, the role of the particle orientation within the dry film has to be considered. Preferably, all the flakes are oriented parallel to the substrate, because the resulting parallel light reflection yields a maximum of lightness, brilliance and flop.

On the other hand, a poor orientation results in an irregular reflection, causing "salt and pepper effects", "cloudiness" and a poor metallic effect and flop (Figure 5.33). A disorientation of the flakes can be created if either too wet films (or too slow-drying solvents) or too dry films (or too fast-drying solvents) are applied.



droplets arrive statistically at the substrate
pigments are mobile at spray viscosity

film too wet/solvents too „slow“:
    metal pigments de-leaf
    disorientation by Brownian movement
    formation of clouds („wet clouds“)

film too dry/solvents too „fast“:
    reduced mobility/orientation of the flakes
    formation of clouds („dry clouds“)

„shrinkage“ during solvent evaporation is pressing the flakes into a parallel situation

high solids: less shrinkage - poorer orientation - poorer effect
    extremely with powder coatings!

the pigment orientation is supported by:
    fast drying (formulation)
    additives (e.g. wax dispersions, microgels)

Fig. 5.33 The influence of particle orientation on the metallic effect.

Furthermore, the shrinkage during solvent evaporation presses the flakes into a parallel situation. This fact also explains, why in high solid content coatings and, even more extremely, in powder coatings (Figure 5.34) (less or no shrinkage) the pigment orientation is poorer than in low solid or medium high solid content coatings. The pigment orientation can be supported by a fast solvent release of the resin (e.g. in CAB-systems) and/or by using special additives (e.g. wax dispersions, microgels etc.).

powder coatings are dry during application

the pigment flakes are statistically oriented

→no pigment orientation during application

only a short liquid phase during bake
(at rather high viscosity)

no shrinking through solvent evaporation

→hindered pigment orientation/poorer effect

the lower the baking viscosity (Tg) and
the longer the liquid phase (baking), the better is the metallic effect

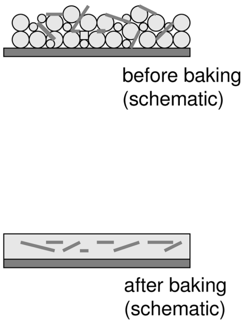


Fig. 5.34 Pigment orientation (metallic effect) in powder coatings.

5.3.2.5

Measurements

All the optical measurements for characterizing the metallic effect should be carried out with goniophotometers and/or goniospectrophotometers to take the flop effect into account [5.176–5.181].

5.3.2.6

Applications

The main applications of metallic effect pigments are paints and coatings, printing inks and graphic arts as well as plastics and colorants (masterbatches).

Coatings

The applications in the coatings industry include automotive coatings (OEM, refinish and interior as well as exterior parts), general industrial coatings, can coatings, coil coatings, powder coatings, decorative coatings, aerosols, anticorrosion coatings, roof coatings, marine paints, conductive coatings and other special applications.

The right selection of the best performing pigment depends very much on the final application. Besides the conventional leafing and non-leafing pigments there is available commercially a whole variety of special ranges for automotive coatings, waterborne coatings, powder coatings etc.

Printing Inks

In the field of printing inks and graphic arts, metal pigments are used in offset, gravure, flexographic, silk-screen and textile printing processes as well as in dusting works and different coating applications (paper, textile, leather, plastic).

The metal pigments, gold bronze as well as aluminum, are supplied in the form of powders, pastes (including solvents), granules (including resins), suspensions (VMPs), color concentrates or even press-ready printing inks.

The recommended particle size depends on the printing process:

- dusting 20–40 μm
- textile printing 12–40 μm
- screen printing 10–25 μm
- rotogravure printing 10–14 μm
- flexographic printing 6–14 μm
- offset printing 2–6 μm

Also, the choice of solvents in pigment pastes and suspensions depends very much on the printing technology and ink formulation. Preferred solvents are

- Offset inks: mineral oils
- Rotogravure and flexographic inks: alcohols, esters, and aromatic hydrocarbons
- Waterborne inks: water, alcohols, and glycols
- UV inks: reactive thinners

The main end uses are in cigarette-, food- and non-food-packaging, illustration, labels, gift wrap paper, wallpaper, tissues etc.

Masterbatches

The most typical application of metal pigments (aluminum as well as gold bronze) in plastics is the tinting of masterbatches, which can be used for injection molding, blow molding, extrusion, calendering and other processing technologies for thermoplastics. However, they are also used in thermosetting materials like polyester putties, polyester and epoxy floorings, art objects and others.

Preferred supplied forms are powders (gold bronze), pastes (aluminum) in plasticizers (like white oil, DINP etc.) and pellets in polyethylene. Due to the chemical nature of gold bronze, there are special coated pigments for use in high temperature processes (tarnish- or heat-resistant gold bronze). Also for use in PVC, special chemically resistant aluminum and gold bronze pigments are available.

Special Applications in Non-Polluting Coatings

For many years, the coatings and printing ink industry has been working hard, forced by legislation or national recommendations, to reduce the amount of organic solvents (VOCs) used. This can be achieved by increasing the solid content from low solids via high solids and "extra high solids" finally to solvent-free powder coatings.

An alternative would be to substitute organic solvents by water in waterborne coatings and printing inks. A third way, which is currently becoming increasingly important for printing inks, is to apply radiation-curing systems, where reactive thinners are used instead of organic solvents and these thinners are incorporated in the dry film without solvent emission.

Waterborne Coatings

Due to its chemical properties, aluminum reacts in aqueous systems, especially in alkaline or acidic media, to yield hydrogen gas. In the case of aluminum pigmented waterborne coatings, this would not only be a safety risk, but would also destroy the metallic effect [5.182].

This problem can easily be solved by using stabilized aluminum pigments. Pigments inhibited with phosphoorganic compounds, chrome treatments or by organic or inorganic encapsulation are commercially available. Further possibilities are published in Ref. [5.183].

The formulations should be kept as close as possible to the neutral point pH 7, and the neutralizing bases for the solvation of the resins should be as weak as possible (DMEA, NMP etc. are much more highly recommended than amines or even ammonium).

Today, a large and increasing proportion of the automotive OEM metallic basecoats in Europe and North America are already waterborne and refinish basecoats are also available in waterborne versions. Other paint applications have followed and the significant growth of waterborne systems can easily be seen in the statistics of the paint associations. Also in printing inks, the use of waterborne inks is steadily growing.

Powder Coatings

Powder coatings are absolutely free of organic solvents and should therefore be considered as the most environmentally beneficial coating systems. In additional to the absence of solvents, the overspray can be recycled and reused, supporting the ecological targets even more.

For the processing of metallic effect pigments in powder coatings, there are basically three possible technologies: coextrusion, dry blending and bonding.

The “classic” method for making powder coatings, coextrusion, is not recommended for the application of metallic pigments. The high shear forces during extrusion would mechanically destroy the pigment flakes and thereby spoil the metallic effect.

“Dry blending”, i.e. the addition of metallic pigments to the ready-made powder coating in a final blending step, was for a long time the only recommended method to make metallic powder coatings. The advantage of this method is the gentle handling of the flakes giving the best metallic appearance. The disadvantage, however, is that the metallic particles seem to be differently charged compared with the resin particles, and therefore tend to separate in the overspray. A reuse of the overspray without color matching could be problematic.

In the so-called “bonding-process”, the metallic flakes are thermally and mechanically bonded to the surface of the resin powder, avoiding separation in the overspray and thereby giving problem-free reuse of the material. Furthermore there are optical advantages in bonded metallic powder coatings due to the very homogeneous distribution of the metallic flakes.

Today, there are many applications for metallic effect powder coatings, such as steel furniture, tools, transportation, household equipment, architectural coatings etc.

Besides regular aluminum and gold bronze pigments in powdered form there are specially treated (coated) metal pigments available for powder coatings, achieving chemical resistance, good chargeability, compatibility and pigment distribution.

5.4
Transparent Pigments

Transparent inorganic pigments are conveniently divided into two groups: colored and colorless. The colorless pigments, which do not absorb in the visible light range, are functional nano-materials with specific properties that are described in the sections below. The colored pigments may also possess these functional properties.

The transparency and hiding power resulting from the light scattering of the applied pigment depend on the size of the pigment particles in the application medium and, in the case of pigments that do not absorb in the visible light range, on the difference between the refractive indices of the pigment and the binder. With increasing particle size, the scattering of a pigment per unit weight increases to a maximum, while the absorption per unit weight decreases as the total surface area decreases. To achieve maximum transparency with a given pigment, dispersion of the pigment must be as close to optimum as possible. Aggregates and agglomerates (DIN 53206 [5.184]) must be destroyed as the pigment is incorporated into the binder or plastic.

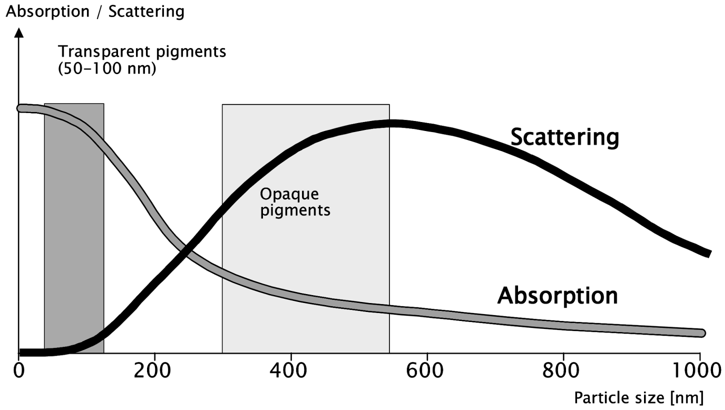


Fig. 5.35 Absorption and scattering by pigments as a function of particle size.

The pigment must be present in the application medium largely as primary particles. The transparency of a colored pigment with a given chemical composition depends entirely on obtaining primary particles of a particular size during manufacture (Figure 5.35).

Colored pigments are transparent in clear binders if their particle size lies in the 2 to 15 nm range. If the particles are needle-shaped, the diameter in the direction of the light is the determining factor. In practice, the transparency of a pigmented system is expressed as in DIN 55988 [5.185] by the transparency value T, which is determined from the quotient of the path length or concentration h and the color difference ΔE^{*}_{ab} measured according to DIN 6174 [5.184] against an ideal black background.

5.4.1
Transparent Iron Oxide Pigments

Figure 5.36 gives an overview of how the pigment properties of hematites are related to their particle sizes. Transparent iron oxides consist of nanoparticles with a primary particle size of 0.001 to 0.05 μm and are supplied in the yellow to red color range. Their applications include effect coatings (mixed with effect pigments), pure yellow and red shades (mixed with titanium dioxide), and wood protection coatings. Suitable binders are baking finishes (transparent yellow iron oxide <180 °C), water-based binders, acrylic-isocyanate systems, acid-curing systems, amine-curing systems, and air-drying binders. Only transparent red iron oxide can be used to color transparent plastics because of the high heat stability required. Since this pigment is extremely difficult to disperse, it is best applied in the form of a preparation. The pigment particles of transparent iron oxides are two to three powers of ten smaller than those of opaque iron oxides. Depending on the manufacturing process, the primary particles

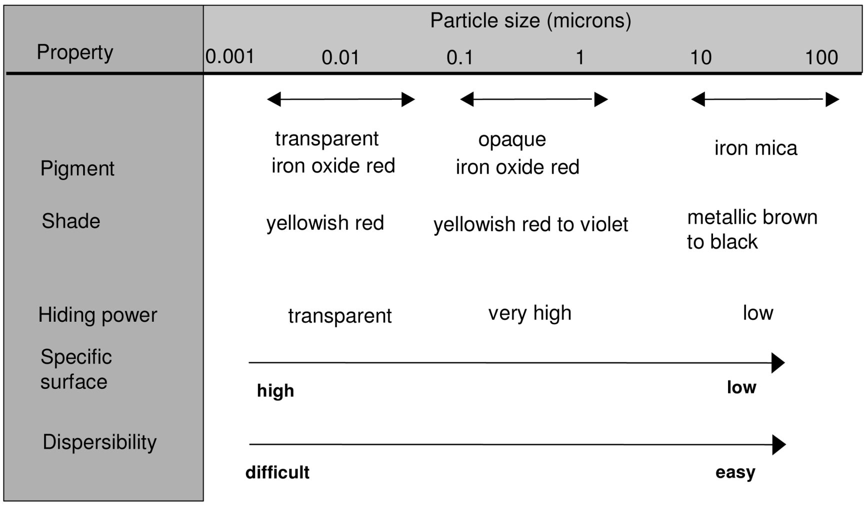


Fig. 5.36 Properties of Fe_2O_3 (hematite) pigments.

are needle-shaped (precipitation process) or spheroidal (iron pentacarbonyl process). The particle sizes of opaque and transparent iron oxides are compared in Figures 5.37 and 5.38.

Fig. 5.37 Red iron oxide, transparent (precipitation process) [5.186].

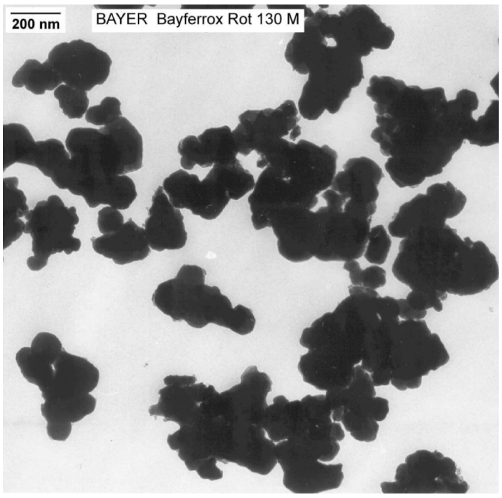


Fig. 5.38 Red iron oxide, opaque [5.187].

5.4.1.1

Manufacture

Transparent yellow iron oxide is manufactured by precipitation of iron(II) hydroxide or carbonate from a very dilute iron(II) salt solution and subsequent oxidation, e.g. with air, to FeOOH. The quality is determined by parameters such as the concentration of the iron(II) salt during precipitation, precipitation temperature, oxidation time, pH and maturing time of the precipitated pigment particles in the suspension. The pigment is washed by decanting, filtered, dried and ground. The particles are needle-shaped with a length of 50 to 150 nm, width of 10 to 20 nm and thickness of 2 to 5 nm, depending on the product (Figure 5.39) [5.188].

Fig. 5.39 Yellow iron oxide, transparent (precipitation process) [5.186].

Transparent red iron oxide is manufactured by thermal decomposition of yellow iron oxide and elimination of water at temperatures of 300 to 500 °C. It is best to start from the dried, crushed filter cake. The pigment is subsequently ground. Pigments with particularly low conductivity values are obtained by additional treatment [5.186].

It is also possible to obtain transparent red iron oxide with a hematite content of 85% directly by precipitation of iron(II) hydroxide or carbonate from iron(II) salt solution and oxidation with air at ca. 30 C in the presence of one of the chlorides of magnesium, calcium or aluminum [5.189].

Semitransparent iron oxide pigments of extreme chemical purity are obtained by direct combustion of iron pentacarbonyl in an excess of air at 580–800 °C to form iron oxide and carbon dioxide (Figure 5.40). The resulting pigments range from orange to red in color. The pigment particles are 10 to 20 nm in size, X-ray amorphous and isometric in shape [5.190, 5.191]. Compared with transparent red iron oxides from the precipitation process, pigments produced by the carbonyl process are relatively easy to disperse, but the larger particle size also means they are not so highly transparent.

A comparison of transparent iron oxide pigments formed by the precipitation and the combustion process is shown in Figure 5.41.

5.4.1.2
Properties and Application

Transparent iron oxides have the same fastness properties as opaque iron oxide pigments, but much higher color strength and significantly higher color purity. Table 5.19 summarizes the properties of selected transparent iron oxide pigments [5.192].

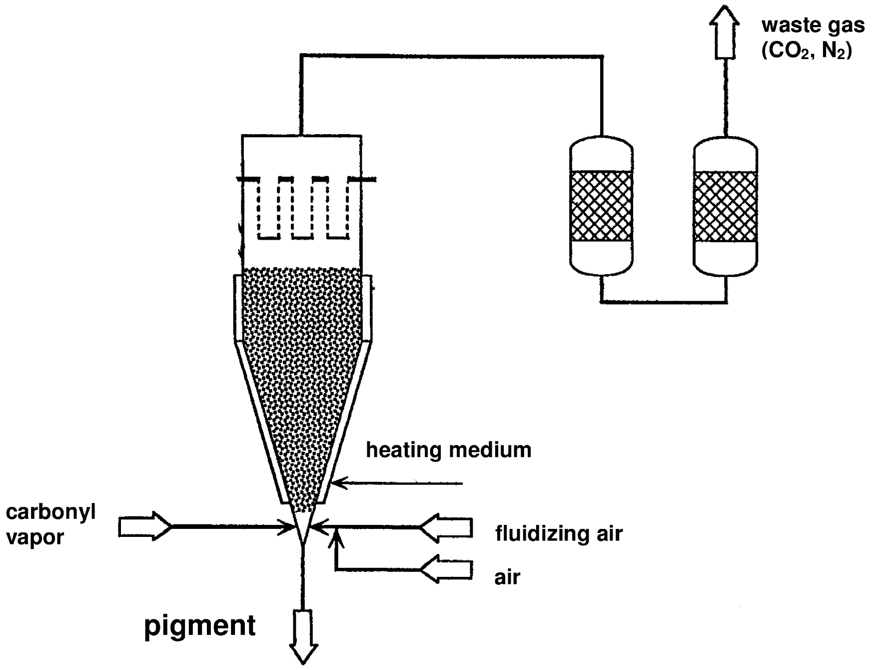
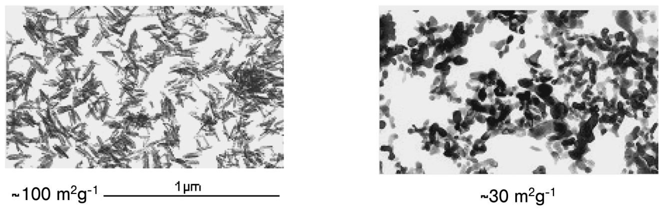


Fig. 5.40 Schematic diagram of the manufacture of iron oxides by combustion of iron pentacarbonyl.



Fe_2O_3 by precipitation
Sicotrans® Red L 2817

Fe_2O_3 by combustion
Sicotrans® Red K 2915

Precipitation process

$$2\,FeSO_4 + 4\,NaOH + 0.5\,O_2 \longrightarrow 2\,FeOOH + 2\,Na_2SO_4 + H_2O$$
$$2\,FeOOH \xrightarrow[\Delta T]{} Fe_2O_3 + H_2O$$

Combustion process

$$2\,Fe(CO)_5 + 6.5\,O_2 \longrightarrow Fe_2O_3 + 10\,CO_2$$

Fig. 5.41 Transparent iron oxide pigments.

Transparent iron oxide pigments are characterized by high UV absorption making them particularly suitable for the coloration of plastic bottles and films for food packaging and the manufacture of wood protection coatings. The precipitated, needle-

Tab. 5.19: Properties of transparent iron oxides.

Transparent iron oxide	Yellow, needles	Red, needles	Red, isometric
Chemical composition	α-FeO(OH)	α-Fe_2O_3	Fe_2O_3
Structure	goethite	hematite	X-ray amorphous
Color Index, part 1	Pigment Yellow 42	Pigment Red 101	Pigment Red 101
Color Index, part 2	77492	77491	77491
Manufacturing process	precipitation	precipitation	iron pentacarbonyl
Density, $g\ cm^{-3}$	3.9	4.5	4.9
Bulk volume, $l\ kg^{-1}$	1.4–1.7	1.4–1.8	3.6
Specific surface (BET), $m^2\ g^{-1}$	80–90	90–100	30
pH	3–9	3–9	5–7
Conductance, $\mu S\ cm^{-1}$	<600	200–900	<200
Fastness to solvents	5	5	5
Stability to acids (2% HCl)	4–5	4–5	4–5
Stability to alkalis (2% NaOH)	5	5	5
Stability to heat, °C	<180	300	300

Assessment scale: 1 = poor, 5 = very good.

shaped pigment particles are much more transparent than those produced by the combustion of iron pentacarbonyl, but are also much harder to disperse. The use of fully dispersed pigment preparations can be a good alternative.

5.4.2
Transparent Cobalt Blue

Transparent cobalt blue (Color Index: Pigment Blue 28:77346) consists of minute, very thin, more or less hexagonal flakes. It is an ideal spinel with the composition $Me^{II}Me^{III}{}_2O_4$. The spinel structure is shown in Section 3.1.3.

The primary particles have a diameter of ca. 20 to 100 nm and a thickness of ca. 5 nm. The specific surface area as determined by the BET method is ca. 100 $m^2\ g^{-1}$. Transparent cobalt blue has excellent light and weather fastness and very good chemical resistance. With regard to these fastness properties it easily outperforms organic blue pigments of comparably transparency. However, the pigment's low color strength means it has never achieved any real market success. Transparent cobalt blue is manufactured by precipitating the hydroxides from very dilute solutions of cobalt and aluminum salts according to the following reaction:

$$2\ Al(OH)_3 + Co(OH)_2 \rightarrow CoAl_2O_4 + 4\ H_2O$$

The hydroxides are filtered, washed, dried, calcined at ca. 1000 °C and finally dry-ground [5.193].

5.4.3
Transparent Functional Pigments

Transparent functional pigments do not have any "color properties" in the visible light range. Their main field of application is based on their ability to absorb UV radiation. They can be used to protect organic materials such as plastics and coating resins as well as human skin (in the form of sun-creams). However, care must be taken when using these pigments, because the large surface area of the particles increases their reactivity. Figure 5.42 shows the dependence of the light scattering of anatase pigments on particle size. Primary particles <ca. 25 nm do not scatter light [5.194].

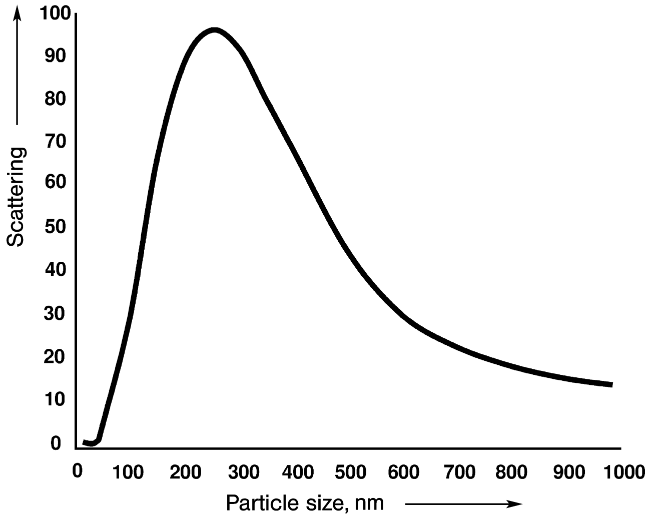


Fig. 5.42 Scattering of anatase pigments as a function of particle size (daylight).

5.4.3.1
Transparent Titanium Dioxide

Transparent titanium dioxide exists in both rutile and anatase forms. The average primary particle size (uncoated) ranges from 8 to 25 nm. The specific surface area has values between 80 and 200 $m^2\ g^{-1}$.

Typical applications are:

- UV absorbers
- Catalysts (DENOX)
- Effect pigments in coatings
- Gas purification by absorption

- Heat stabilizers for silicone rubber
- Prevention of oxidative degradation of polymers by UV light
- Raw material for ceramic materials

Transparent titanium dioxide can be manufactured by various wet-chemical and gas-phase processes. The properties of the reaction products can vary greatly, depending on the reaction conditions and starting materials. To reduce the high photochemical activity of untreated transparent titanium dioxides, the pigments are coated with a variety of inorganic oxide combinations (e.g. of silicon, aluminum and zirconium oxides) [5.195].

The following reactions are used to manufacture transparent titanium dioxides:

- Anatase: hydrolysis

  $TiOSO_4 + H_2O \rightarrow TiO_2 + H_2SO_4$
- Rutile: hydrolysis

  $TiOCl_2 + H_2O \rightarrow TiO_2 + 2\ HCl$
- Rutile/anatase: combustion in an oxyhydrogen flame

  $TiCl_4 + 2\ H_2 + O_2 \rightarrow TiO_2 + 4\ HCl$
- Amorphous: hydrolysis of organic titanates

  $Ti(OC_3H_7)_4 + 2\ H_2O \rightarrow TiO_2 + 4\ C_3H_7OH$

5.4.3.2
Transparent Zinc Oxide

The most significant property of transparent zinc oxide is again the absorption of UV radiation. The main application of zinc oxide is in sunscreens. The usual industrial manufacturing process is either direct combustion of high-purity zinc metal in a plasma with oxygen [5.196] according to the reaction:

$$2\ Zn + O_2 \rightarrow 2\ ZnO$$

resulting in zinc oxide powder with a primary particle size distribution of ca. 20 to 30 nm, or hydrolysis of very dilute organozinc compounds [5.197] according to the reaction:

$$Zn(OR)_2 + H_2O \rightarrow ZnO + 2\ ROH$$

This process produces primary particles of ca. 15 nm, but it is time-consuming and expensive.

5.5
Luminescent pigments

5.5.1
Introduction

Luminescent materials (or phosphors) are generally characterized by the emission of light with energy beyond thermal equilibrium, therefore the nature of luminescence is different from black body radiation. As a consequence, external energy has to be applied to luminescent materials to enable them to generate light. Luminescence can occur as a result of very different kinds of excitation, like photo- or electroluminescence. In practice, the luminescence generally is due to excitation with X-rays, cathode rays or excitation with UV or even visible light.

Luminescence originates from electronically excited states in atoms and molecules and the emission process is governed by quantum mechanical selection rules. Forbidden transitions generally are slower than allowed optical transitions. Emission originating from allowed optical transitions, with decay times of the order of μs or faster is called fluorescence; the term for emission with longer decay times is phosphorescence. The time in which the emission intensity decreases to 1/e or 1/10 (for exponential decay and hyperbolic decay, respectively) is called the decay time.

Luminescent materials have changed the world. Energy saving lamps, many kinds of displays and modern medical equipment all rely on luminescent materials and it is hardly imaginable that large scale application of luminescent materials started only slightly more than 100 years ago (for an overview see e.g. Ref. [5.198]).

In this section, historic aspects of luminescent materials will be discussed first, followed by a short treatment of luminescence mechanisms and luminescence excitation schemes. Thereafter, devices based on luminescent materials and the way in which luminescent materials determine their operational performance will be discussed. Preparational aspects of luminescent materials will be described and then this section will end with an outlook.

5.5.2
Historical Overview [5.198, 5.199]

Contrary to common belief, luminescent materials have been known and used for about 2000 years. Already in ancient times, the Romans used luminescent materials for hair decoration [5.199]; the material used is thought to be CaS [5.200]. Also other luminescent materials were found in nature (e.g. naturally doped willemite, scheelite or calcite crystals). Around 1600, the Stone of Bologna attracted Galilei's interest. This barite mineral ($BaSO_4$) emits yellow to orange light with long persistence when subjected to sunlight. Although Galilei did not know the physical origin, he definitely excluded mystery as the origin of the phenomenon. In 1671, by heating the mineral with carbon black, Kirchner was able to intensify the luminescence, indicating that not $BaSO_4$, but an impurity-type luminescence of BaS is the origin of the light emission [5.201, 5.202]. One of the first reports on the synthesis of a luminescent material originates from 1603: luminescent BaS was obtained by Casciavolis by reducing minerals in an attempt to obtain gold [5.199]. As in ancient times, luminescent materials in the 1600s were only used for decorative purposes.

At the end of the 19th century, a first major milestone concerning luminescent materials and devices was the realization of gas-discharges and electron beams in evacuated glass tubes by Geissler and Braun as well as the discovery of X-rays by Röntgen [5.203, 5.204]. The visualization of gas-discharges, cathode rays or X-rays represents a first practical use of luminescent materials beyond decoration. Based on these fundamental results, the first luminescent devices were developed only a few years later, including cathode-ray tubes, fluorescent lamps and X-ray intensifying screens (see Section 5.5.5.1) [5.205–5.207]. Thereafter, research on cathode-ray tubes and the relevant phosphors for use in radar screens was very intense during the 2nd World War. In addition, the rapid and successful application of fluorescent lamps for illumination purposes and the use of X-rays for medical imaging stimulated research on novel luminescent materials in the first half of the 20th century.

The first luminescent devices contained only a single phosphor material. The emitted light was normally not white, but colored. For instance, blue emitting $CaWO_4$, which is a highly efficient phosphor, was used in X-ray intensifying screens, in Braun's early cathode-ray tubes as well as in the first fluorescent lamps by Edison [5.208]. Lighting became more colorful with so-called Zeon or Neon tubes. Based on Ne/Ar/Hg discharges and in combination with different phosphors and colored glass, differently colored lamps were realized. These lamps were presented by Claude at the World Exhibition 1937 in Paris and used for advertising [5.209]. For illumination purposes, however, emission of white light is required. Based on a single phosphor, generation of white light is possible if emission is more or less continuous over the whole visible spectral range. In line with this, Meyer invented a lamp in 1926 [5.210]. However, technical application did not start until 1938 [5.211, 5.212]. Such single-phosphor lamps containing halophosphates like $Ca_5(PO_4)_3(Cl,F)$:Sb^{3+}, Mn^{2+} are still in use. Although the physically determined efficiency of such broadband emitting phosphors is high, the lumen equivalent of their emission, taking the sensitivity of the human eye into account, is low. This is especially due to red emission beyond 610 nm, where the eye sensitivity rapidly falls off with increasing wavelength. As suggested in 1971 by Koedam and Opstelten , the use of rare-earth-element-based luminescent materials marked a second major milestone [5.213, 5.214]. Based on line-type f–f transitions, phosphor emission can be narrowed to the visible, resulting in both high efficiency and high lumen equivalent. However, due to line-type emission color rendering (the ability to reproduce all colors in a natural way) is now low. Consequently, at least three phosphors with emission in the blue, green and red spectral range have to be combined. Nowadays, such tri-color phosphor mixtures are used in fluorescent lamps worldwide. Similar considerations regarding lumen equivalent were also of importance in increasing the lumen efficiency of color TV tubes (see Section 5.5.5.1).

Although inherently incomplete, it is of interest to review briefly some of the most important theoretical aspects of luminescence. In general it can be stated, that most of the processes, leading to luminescence, are understood well nowadays. A very fundamental observation is known as the Stokes shift [5.215]. According to this, the emitted photons generally have lower energy than the radiation used in exciting the luminescence. Seitz and Mott rationalized the occurrence of the Stokes Shift in 1938 and 1939, after they developed the configuration co-ordinate diagram [5.216, 5.217]. Already before the 2nd World War, it was also recognized that luminescence is often due to rather low concentrations (sometimes impurities) of certain metal ions [5.218]. The relevant optical transitions leading to absorption and emission can be understood within the concept of orbital theory. Here, luminescence of transition metal ions can be explained based on ligand field theory and Tanabe–Sugano diagrams [5.219]. Luminescence of rare earth ions can be understood, based on transitions between (almost) atomic eigenstates of the system [5.220, 5.221]. Förster and Dexter first described energy transfer between localized centers in luminescent material [5.222–5.224]. Besides orbital theory, semiconductor theory has also contributed to the understanding of radiative transitions: Both band-to-band transitions and transitions involving localized donor and/or acceptor states fit within this framework. Nevertheless, there are also still open questions concerning the theoretical aspects. For instance, the efficiency of luminescent materials is not determined well. Only in the case of excitation with high-energy radiation (e.g. cathode rays), can the maximum energy efficiency be calculated rather accurately, using a surprisingly simple treatment [5.225]. In contrast, loss processes (which do not result in luminescence) cannot yet be predicted well quantitatively.

Today the most important producers of luminescent pigments are Honeywell and Nemoto.

5.5.3
Luminescence Mechanisms

Luminescent materials, also called phosphors, are mostly solid inorganic materials consisting of a host lattice, usually intentionally doped with impurities (Figure 5.43). The impurity concentrations generally are low, in view of the fact that at higher concentrations the efficiency of the luminescence process generally decreases (concentration quenching). Recently organic luminescent materials have gained considerable interest, in view of their application in organic light emitting diodes. In this section, however, only inorganic phosphors are discussed.

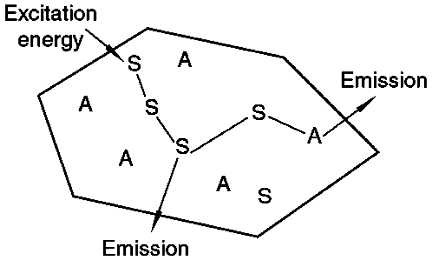


Fig. 5.43 Luminescent material, containing activator ions A (ions showing the desired emission) and sensitizing ions S (on which e.g. UV excitation can take place).

The absorption of energy, which is used to excite the luminescence, takes place by either the host lattice or by intentionally doped impurities. Moreover, the excitation energy can be transferred through the lattice by a process called energy transfer. In most cases, the emission takes place on the impurity ions. Quite frequently, the emission color can be adjusted by choosing the proper impurity ion, without changing the host lattice in which the impurity ions are incorporated.

5.5.3.1

Center Luminescence

In the case of center luminescence, the emission is generated on an optical center, in contrast to e.g. emission which results from optical transitions between host lattice band states. Such a center can be an ion or a molecular ion complex.

One speaks of characteristic luminescence when, in principle, the emission could also occur on the ion in vacuum, i.e. when the optical transition involves electronic states of the ion only. Characteristic luminescence can consist of relatively sharp emission bands (spectral width typically a few nm), but also of broad bands, which can have widths exceeding 50 nm. Broad emission bands are observed when the character of the chemical bonding in the ground and excited states differs considerably. This goes hand in hand with a change in equilibrium distance between the emitting ion and its immediate chemical environment and is commonly explained with the configuration coordinate diagram (Figure 5.44). Broad bands are observed for many optical transitions in the partly filled d-shell of transition metal ions (d → d transitions), and also for transitions between the 5d shell and the 4f shell of rare-earth ions (d → f transitions) and for emission on s^2 ions (these ions possess a 'lone pair' of s electrons), like Tl^+, Pb^{2+} or Sb^{3+}. Sharp emission bands are characteristic of optical transitions between electronic states with chemical bonding character (almost)

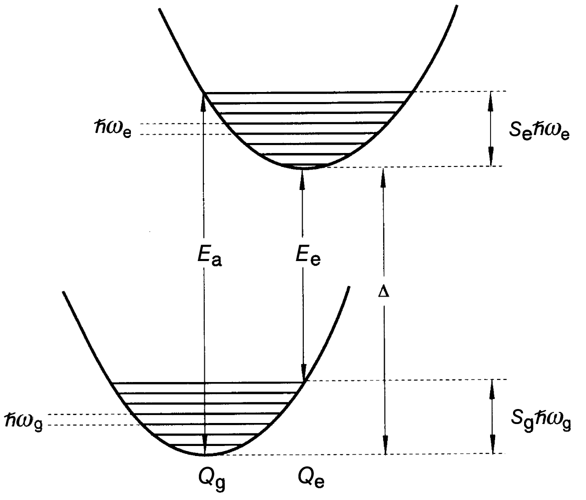


Fig. 5.44 Configurational coordinate diagram.

the same for the ground and excited states, and for the same reason also for optical transitions between electronic states that hardly participate in the chemical bonding (e.g. f → f transitions on rare-earth ions).

In the case of optical processes involving electronic states which participate in the chemical bonding, the nature of the bonding (covalent, ionic) and the symmetry of the site at which the emitting ion is incorporated play a very important role. This is generally described by ligand field theory, which is not treated here. However, the term symbols for the description of the electronic transitions will be used.

An example of a broad d → d emission band (in the green part of the spectrum) is the emission of Mn^{2+} in $BaMgAl_{10}O_{17}$:Eu,Mn (Figure 5.45). The weak blue emission band originates from a d → f optical transition on Eu^{2+}.

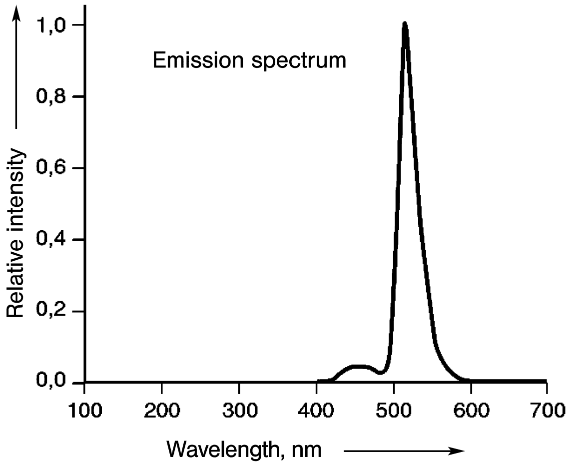


Fig. 5.45 Mn^{2+} emission in $BaMgAl_{10}O_{17}$:Eu,Mn.

The green emission is generated by a d → d optical transition on the Mn^{2+}-ion with high spin d^5 electronic configuration (all electrons have their spin oriented in the same direction). The optical transition leading to emission is $^4T_{1g} \rightarrow {}^6A_{1g}$. The electronic configurations in the ground and excited state are $(t_{2g})^3$ $(e_g)^2$ and $(t_{2g})^4$ $(e_g)^1$, respectively. The emission generated reflects how the optical properties of the ion depend on its chemical environment. This luminescent material can be applied as green phosphor in very high quality fluorescent lamps and also in plasma display panels.

An example of d → d emission, consisting of a few relatively sharp bands is the emission of Mn^{4+} in $Mg_4GeO_{5.5}F$:Mn (Figure 5.46). Please note that the emitting ion is the same, only its charge (and therefore its electronic configuration) is different. In this case, the optical transition consists of a spin-flip transition within the $(t_{2g})^3$ manifold ($^2E \rightarrow {}^4A_2$ transition), i.e. hardly changing the character of the bonding. This manifests itself in relatively narrow emission bands. This phosphor can be used as red primary in fluorescent lamps. It enables the reproduction of deep red colors.

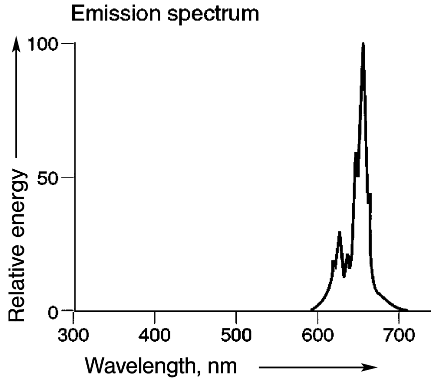


Fig. 5.46 Mn^{4+} emission in $Mg_4GeO_{5.5}F$.

The optical transitions, discussed above, are spin forbidden and consequently rather slow (decay time of the order of ms).

Most rare earth ions show sharp emission bands, due to optical transitions within the f-manifold, e.g. Tb^{3+} ($4f^8$-configuration) and Eu^{3+} ($4f^6$-configuration), in which the emission spectra of $(Ce,Tb)MgAl_{11}O_{19}$ and Y_2O_3:Eu are reproduced (Figures 5.47 and 5.48). Both these phosphors are applied in high quality fluorescent lamps and Y_2O_3:Eu is also used in projection television, based on cathode-ray tubes. In such projection televisions, small cathode-ray tubes are used, the images of which are projected onto a large screen.

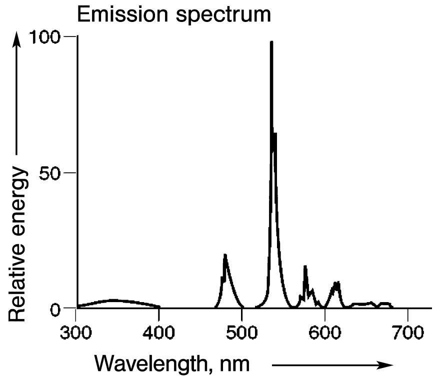


Fig. 5.47 Emission spectrum of $(Ce,Tb)MgAl_{11}O_{19}$.

There are a few green Tb^{3+}-based phosphors, suitable for application in fluorescent lamps. Despite intensive research, no substitute for Y_2O_3:Eu with the same spectral properties has been found, leaving it the only red primary with line emission at about 611 nm. The width and position of the emission bands originating from optical transitions within the f-electronic shell are almost independent of the chemical environment. The relative intensity of the separate bands, however, depends on the crystal lattice. The transitions on many rare-earth ions are spin- and parity-forbidden and therefore rather slow (in the ms range). However, for a number of rare-earth ions, broad emission bands are also known, due to d → f emission, e.g.

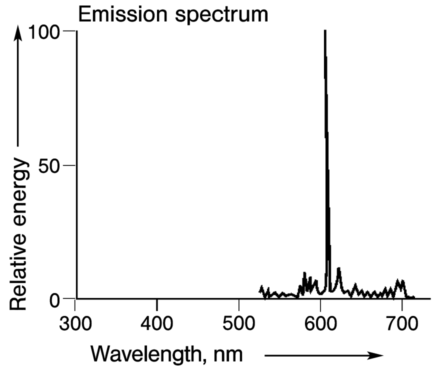


Fig. 5.48 Emission spectrum of Y_2O_3:Eu.

Eu^{2+} ($4f^7$-configuration) or Ce^{3+} ($4f^1$-configuration). These transitions are allowed and consequently very fast (in the µs range or even faster). Quite a few very important commercial phosphors are based on rare-earth ions. Rare-earth based phosphors are very frequently applied in very demanding applications.

5.5.3.2
Charge Transfer Luminescence

In the case of charge transfer, the optical transition takes place between different kinds of orbitals or between electronic states of different ions. In these cases, too, the width and position of the emission bands depend on the chemical environment.

A very well known example is $CaWO_4$, used for decades for the detection of X-rays, which shows luminescence originating from the $(WO_4)^{2-}$ group (Figure 5.49). The transition involves charge transfer from oxygen ions to empty d-levels of the tungsten ion. Here, the chemical bonding character changes very strongly, reflected in a very broad emission spectrum. As in this material no intentional dopant is introduced, it is also called self-activated.

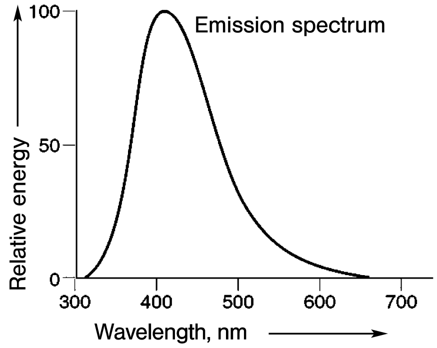


Fig. 5.49 Emission spectrum of $CaWO_4$.

5.5.3.3
Donor–Acceptor Pair Luminescence

This luminescence mechanism is found in some semi-conducting materials that are doped with both donors and acceptors. The mechanism is depicted in Figure 5.50, in which step IV results in luminescence. Ionized donors, the resulting holes in the valence band caused by ionized acceptors, capture electrons that are excited into the conduction band. The emission involves electron transfer between neutral donors and neutral acceptors. The final state (with ionized donors and acceptors) is Coulomb stabilized. Therefore, the spectral position of the emission generated on a donor–acceptor pair depends on the distance between the donor and the acceptor in a pair: the smaller the distance, the higher the energy of the photon generated. In the phosphor crystal lattice, many different donor–acceptor distances are possible, leading to a relatively broad emission band. This mechanism is operative in the blue and green emitting phosphors, which are used in color television picture tubes (ZnS:Ag,Cl and ZnS:Cu,Au, Al, respectively).

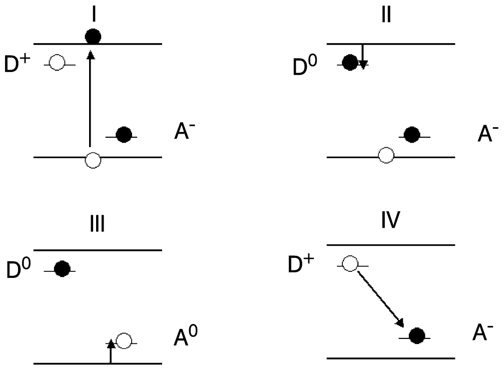


Fig. 5.50 Processes leading to donor–acceptor pair luminescence.

5.5.3.4
Long-Afterglow Phosphors

In long-afterglow phosphors, optical excitation energy is stored in the lattice by trapping photoexcited charge carriers. The most prominent example is $SrAl_2O_4$:Eu,Dy: after optical excitation of Eu^{2+}, Eu^{2+} is oxidized to Eu^{3+} and Dy^{3+} is reduced to Dy^{2+}. Thermal excitation of Dy^{2+} to Dy^{3+}, followed by capture of the electron by Eu^{3+} and subsequent Eu^{2+} emission results in time-delayed Eu^{2+} emission. The thermal excitation process of Dy^{2+} determines the time delay. This particular material still generates visible emission after several hours in the dark.

Long-afterglow phosphors can be used in watch fingers, and also in safety applications, e.g., in exit signs, which still operate in the case of a current blackout. Other long-afterglow materials are e.g. ZnS:Cu or SrS:Bi.

5.5.4
Excitation Mechanism

5.5.4.1
Optical Excitation of Luminescence and Energy Transfer

When absorption of UV or even visible light leads to emission, one speaks of optical excitation of luminescence. This process takes place in e.g. fluorescent lamps and phosphor-converted LEDs in which phosphors are used to at least partly change the wavelength of the radiation emitted by the LED. Optical absorption can take place on the already discussed impurities (optical centers), these being either the activator ions or sensitizer ions. Sensitizer ions are used when the optical absorption of the activator ions is too weak (e.g. because the optical transition is forbidden) to be useful in practical devices. In such a case, energy transfer from the sensitizer ions to the activator ions has to take place. The optical absorption leading to emission can also take place by the host lattice itself (band absorption). In this case one speaks of host lattice sensitization. Energy transfer from host lattice states to the activator ions (in some cases also involving sensitizers) has to take place.

In the blue emitting luminescent material $BaMgAl_{10}O_{17}$:Eu both the absorption and the emission process originate from optical transitions between the 4f and 5d levels of the Eu^{2+} ion. As the transition leading to optical absorption is allowed, a relatively small Eu^{2+} concentration is sufficient to adjust a sufficiently strong absorption in practical devices. The excitation spectrum of $BaMgAl_{10}O_{17}$:Eu is given in Figure 5.51.

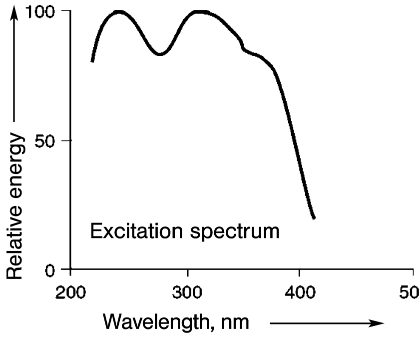


Fig. 5.51 Excitation spectrum of the Eu^{2+} emission in $BaMgAl_{10}O_{17}$.

One observes, a strong broad absorption spectrum in the UV part of the spectrum as the excited 5d state of the Eu^{2+} ion is split by ligand field interaction with the oxygen ions surrounding it.

The excitation spectrum of the Mn^{2+} spectrum in $BaMgAl_{10}O_{17}$:Eu,Mn is, in the UV, very similar to the excitation spectrum of the compound without Mn^{2+}. This is an example of Eu^{2+}-sensitized emission of Mn^{2+}, as proven by the similarity of the excitation spectrum of both the Eu^{2+} and the Mn^{2+} emission. The very localized excitation (exciton) of Eu^{2+} is transferred to the Mn^{2+} ion. The energy transfer process might involve more than one Eu^{2+} ion (excitonic energy transfer via the Eu^{2+} sublattice).

Mn^{2+} emission can also be sensitized by other ions, like Sb^{3+} in the well-known white emitting material $Ca_5(PO_4)_3(F,Cl)$:Sb,Mn. Here, orange emission is generated by Mn^{2+} and blue emission by the Sb^{3+}. This material is applied widely in fluorescent lamps. Its emission spectrum is given in Figure 5.52.

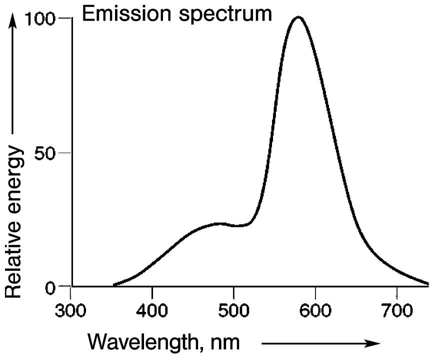


Fig. 5.52 Emission spectrum of $Ca_5(PO_4)_3(F,Cl)$:Sb,Mn.

It has to be noted that the emission spectrum depends on the Sb^{3+} and Mn^{2+} concentrations. By adjusting these concentrations, the color of the emission can be varied.

Another well-known sensitizer–activator pair is the Ce^{3+}–Tb^{3+} couple (see Figure 5.47). All green emitting phosphors applied in high quality fluorescent lamps are based on this combination.

5.5.4.2
Electroluminescence

High Voltage Electroluminescence

High voltage electroluminescence relies on an electrical breakthrough in a semiconducting material, which rationalizes the necessity to use rather high voltages. The voltage applied is typically of the order of 100 V. Charge carriers are generated and accelerated in the host lattice. In a next step, they can excite an activator ion. Generally speaking, the lifetime of such electroluminescent devices can be long but the efficiencies are rather low (of the order of 1%) and consequently applications are found in sectors where reliability is an issue and efficiency considerations are not very important (emergency signs, exit signs and, interestingly, ceiling illumination in the Maybach premium car). Prominent materials are ZnS:Mn, ZnS:Cu or SrS:Ce.

Low Voltage Electroluminescence

The advent of the blue light emitting diode (LED) and of organic electroluminescent structures has strongly revitalized interest in this luminescence mechanism. For the first time, efficient light-emitting structures can be realized which do not require either high or low pressure. In addition: hitherto luminescent devices always used a cascade: in fluorescent lamps, first a discharge is generated and the resulting invisible radiation is converted into visible light, resulting in a (considerable) energy loss. In cathode-ray tubes, first an electron beam consisting of electrons with rather high kinetic energy is generated; this subsequently impinges on the luminescent material. In the phosphors, electron bombardment finally leads to excitations where electrons in the conduction band are coupled to holes in the valence band (excitons). These excitons are transferred to activator ions. Although operating at physical limits, the phosphors' energy efficiency is limited to about 20% [5.225]. As result, there are no white light emitting devices with energy efficiency greater than 50%. Low voltage electroluminescent devices may be a way around this problem. In such devices, the step leading to emission is the recombination of electrons in conduction band states with holes in valence band states and, in principle, only the band gap energy is required to excite the luminescence. Within limits, the color of the emission can be selected by choosing the appropriate semiconductor. The generation of luminescence can be very energy efficient; the main issue is getting the light out of the emitting device. Blue emitting LEDs are available with wall plug efficiency approaching 30%; red emitting LEDs are even approaching 60% efficiency.

Apart from efficiency, the power of LEDs is also an important driving force. LEDs with input power of 30 W, with external energy efficiency of about 10%, have been demonstrated in 2003 by the Japanese company Nichia.

In this section, only luminescent materials that can be used in inorganic low voltage electroluminescent devices will be discussed in some detail. Phosphors are used for two reasons:

- Inorganic LEDs generally generate narrow line emission. Combination of LEDs emitting in different spectral regions to generate white results in white light of low quality: it cannot reproduce all colors in a natural way.
- Efficient LEDs are not yet available in all colors required. Green is a special concern.

Phosphors for LEDs have to fulfill rather harsh conditions. The Stokes Shift must be small, the absorption must be high and, in addition, as the excitation densities are of the order of 20 W cm^{-2} (the area which emits light is much smaller than e.g. in fluorescent lamps), the luminescent materials must remain efficient up to high temperatures, should not show saturation (meaning a less than linear increase in output power with input power at high excitation densities) and must be radiation stable.

5.5.4.3
Excitation with High Energy Particles

After absorption of electrons or high-energy photons (e.g. X-ray quanta) impinging on the phosphor material, secondary charge carriers, i.e. electron–hole pairs, are generated in the lattice. The electron–hole pairs thermalize, eventually leading to band gap excitations. After thermalization, the excitation is transferred to an activator (or sensitizer), resulting in emission. For each absorbed electron or high-energy photon, a large number of electron–hole pairs will be generated. Each electron–hole pair can give rise to emission of one photon on the activator ion.

Robbins has treated these processes more quantitatively [5.225]. A comparison of predicted and experimentally obtained efficiencies is given in Table 5.20. Quite good agreement is observed.

Tab. 5.20: Energy efficiencies of luminescent materials obtained on excitation with high-energy particles. n_{the} is the maximum calculated efficiency, n_{exp} is the energy efficiency observed experimentally.

Phosphor	n_{the}	n_{exp}
CsI:Tl	0.14	0.14
ZnS:Ag	0.25	0.20
ZnS:Cu	0.21	0.17
CaS:Ce	0.16	0.22
CaS:Mn	0.15	0.16
La_2O_2S:Eu	0.12	0.11
Y_2O_3:Eu	0.07	0.08
YVO_4:Eu	0.07	0.07

5.5.5
Application of Luminescent Materials

5.5.5.1
Application Areas and Phosphors Used

An overview of phosphors used in the most important application areas is given in Table 5.21. In many applications, the blue- and the red-emitting CRT phosphors are coated with a daylight absorbing pigment, to enhance contrast in daylight viewing conditions. The blue-emitting phosphor is coated with a particle coating of (blue) $CoAl_2O_4$, the red-emitting phosphor with a particle coating of (red) α-Fe_2O_3. Coating the green-emitting phosphor with a green-absorbing pigment is less useful in view of the high sensitivity of the human eye to green light. Work on CRT phosphors has almost stopped in view of the strong advances in liquid crystal displays (LCDs) and plasma display panels. However, even LCDs also require luminescent materials, as they need a backlight: either thin or flat fluorescent lamps or LEDs.

In plasma display panels, the most severe energy loss is encountered in the discharge. This is a consequence of the small dimensions of the picture elements (pixels). The phosphors used have been known for a long time. The operational lifetime of the blue emitting phosphor still poses a problem.

In fluorescent lamps, the tricolor mix results in white light generating lamps with higher brightness than lamps based on the halophosphate, because of a better matching of the emission spectrum of the tricolor phosphor mixture to the eye sensitivity, while the ability of the lamps to reproduce all colors in a natural way (color rendering) is still very good. Fluorescent lamps contain mercury, which is an environmental disadvantage. One possibility is to reduce Hg consumption by fluorescent lamp constituents. Present fluorescent lamps contain much more Hg than necessary for proper lamp operation. Alternatively, Hg-free fluorescent lamps, based on a Xe-discharge might be a solution. However, as the Xe-discharge generates radiation in the VUV, the energy efficiency of the phosphors will be lower, reducing the energy efficiency of the lighting device. However, on excitation with VUV radiation, more than one visible photon can be generated per absorbed VUV photon, principally enabling Hg-free fluorescent lamps to be as efficient as current fluorescent lamps. This will be dealt with in the Outlook.

Research on phosphors for X-ray detection mainly deals with applications in Computed Tomography (CT) and Position Emission Tomography (PET). The X-rays (CT) or γ-rays (PET) are converted into visible light by these phosphors. The visible light detection is by photomultipliers or photodiodes. Apart from energy efficiency (energy efficient X-ray phosphors reduce the amount of harmful radiation to which a patient is exposed), the temporal behavior is also important. The emission decay time should be short (ns for PET, which is a consequence of the measuring principle: the two photons, which are generated in the positron annihilation process have to be detected in coincidence; μs for CT to enhance the scan speed). In addition, obtaining translucent or even transparent ceramic materials (scintillators) is an issue here. The thickness of these crystals is of the order of millimeters for CT and centimeters for PET scintillators. In general, the scintillators are made by single crystal growth or by hot pressing techniques.

X-ray phosphors are also used in X-ray intensifying screens. The X-rays are first converted into visible photons, which subsequently irradiate the film. In most cases, the photographic film is sandwiched between two phosphor sheets. Light moving into the direction away from the photographic film can nevertheless be used by application of TiO_2 reflecting layers. The typical thickness of such a phosphor layer is of the order of a few hundred micrometers.

In LED lamps based on a blue-emitting LED, addition of a red-emitting phosphor (the emission of which is due to Eu^{2+}) to the yellow-emitting $(Y,Gd)_3Al_5O_{12}$:Ce enables the production of white-emitting LED lamps which generate light with a low color temperature. Phosphor converted LEDs, based on $(Y,Gd)_3Al_5O_{12}$:Ce only emit a rather bluish white, i.e. the light has a rather high color temperature. Red-emitting materials, which can be excited effectively with blue or near-UV light require rather covalent hosts. Interestingly, a class of materials, which has been unknown to phosphor applications till now, looks very promising for this application: multinary nitrido silicates. Phosphors such as $LaSi_3N_5:Eu^{2+},O^{2-}$ or $Ba_2Si_5N_8:Eu^{2+}$ are likely the first representatives of a potentially large group [5.226, 5.227]. LED lamps can also be based on near-UV emitting LEDs. At least two phosphors are needed to generate white light in such a case (blue and yellow). Alternatively, three phosphors are used, emitting in the blue, green and red part of the visible spectrum. At present, there are no proven concepts here. In addition, there might be an issue with the UV stability of the LED encapsulation and finally UV-emitting LEDs might have an intrinsically lower efficiency. Charge-transporting layers, transporting electrons and holes to the emitting (In)GaN layer, generally consist of doped InGaN layers. For optimal light output, the charge-transporting layer should have a larger band gap than

Tab. 5.21: Prominent phosphors and their applications

Emission color	Application				
	Cathode-ray tubes and projection television tubes (PTV)	Plasma display panels	Fluorescent lamps	X-ray detection	LEDs
UV			$Ba_2SiO_5:Pb^{2+}$ (sun tanning) $CeMgAl_{11}O_{19}$(sun tanning) $LaPO_4:Ce^{3+}$ (sun tanning) $SrB_4O_7:Eu^{2+}$ (sun tanning, photo copiers)		
Blue	$ZnS:Ag^+,Cl^-$ $ZnS:Ag^+,Al^{3+}$	$BaMgAl_{10}O_{17}:Eu^{2+}$	$BaMgAl_{10}O_{17}:Eu^{2+}$ $Sr_4Al_{14}O_{25}:Eu^{2+}$ $Sr_5(PO_4)_3Cl:Eu^{2+}$	$NaI:Tl^+$ $Ba(F,Br):Eu^{2+}$ (storage phosphor) $LaBr_3:Ce^{3+}$ $Bi_4Ge_3O_{12}$ $Gd_2SiO_5:Ce^{3+}$ $Lu_2SiO_5:Ce^{3+}$ $LuAlO_3:Ce^{3+}$ $YTaO_4:Nb^{5+}$	

Tab. 5.21: Continued.

Emission color	**Application**				
	Cathode-ray tubes and projection television tubes (PTV)	Plasma display panels	Fluorescent lamps	X-ray detection	LEDs
Green	ZnS:Cu^{+},Au^{+},Al^{3+} ZnS:Cu^{+},Al^{3+} Zn$_2$SiO$_4$:Mn^{2+} (PTV) Y$_2$SiO$_5$:Tb^{3+} (PTV) InBO$_3$:Tb^{3+} (PTV) LaOCl:Tb^{3+} (PTV)	(Y,Gd)BO$_3$:Tb BaAl$_{12}$O$_{19}$:Mn^{2+} Zn$_2$SiO$_4$:Mn^{2+} BaMgAl$_{10}$O$_{17}$:Eu^{2+},Mn^{2+}	GdMgB$_5$O$_{10}$:Ce^{3+},Tb^{3+} LaPO$_4$:Ce^{3+},Tb^{3+} CeMgAl$_{11}$O$_{19}$:Tb^{3+} Zn$_2$SiO$_4$:Mn^{2+}	CsI:Tl^{+} Gd$_2$O$_2$S:Tb^{3+} Gd$_2$O$_2$S:Pr^{3+}	
Yellow			Y$_3$Al$_5$O$_{12}$:Ce^{3+}		(Y,Gd)$_3$Al$_5$O$_{12}$:Ce^{3+}
Red	Y$_2$O$_2$S:Eu^{3+} Y$_2$O$_3$:Eu (PTV)	Y$_2$O$_3$:Eu^{3} (Y,Gd)(P,V)O$_4$:Eu^{3+}	Y$_2$O$_3$:Eu^{3+}	(Y,Gd)$_2$O$_3$:Eu^{3+}, Pr^{3+}	
White	ZnS:Ag^{+} + (Zn,Cd)S:Ag^{+}		Ca$_5$(PO$_4$)$_3$(F,Cl):Sb^{3+},Mn^{2+}		

the emissive layer. This implies that the active layer should have a higher In content than the charge-transporting layers. This condition cannot be realized for (almost) pure GaN emissive layers unless efficient charge-transport layers with larger band gaps (implying a different chemical composition) are found.

5.5.5.2
Energy Efficiency Considerations of Important Luminescent Devices

In general, the luminescent materials applied operate at physical limits, in terms of absorption of the exciting radiation and the quantum efficiency (number of visible photons generated divided by the number of photons absorbed) with which luminescence is generated. In cathode-ray tubes, the energy efficiency of the phosphors used is of the order of 20% [5.225]. In plasma display panels, fluorescent lamps and LEDs, the quantum efficiency amounts to about 100% and the absorption coefficient is also very high. Nevertheless, the energy efficiency of luminescent devices is rather low, when the energy loss is taken into account (Table 5.22). The phosphor energy loss factor in Table 5.22 is mainly determined by the Stokes Shift (the difference in photon energy of radiation absorbed and radiation emitted). This results in energy loss, which can be significant, even when the quantum efficiency is 100%.

Tab. 5.22: Energy efficiencies of important luminescent devices and a breakdown into the most important energy loss factors.

Device	Cathode-ray tube	Plasma display panel	Fluorescent lamp	Phosphor-converted LED lamp
Energy efficiency (%)	1–2	2	Straight fluorescent: 25 Compact: 15	20
Major energy loss factors	Shadow mask: 70–90 Phosphors: 80 Deflection yoke: 50	Discharge: 90 Phosphors: 70	Phosphors: 55 Discharge: 30 (straight) Discharge: 20 (compact)	LED: 70 Phosphors: 25

It is observed that, although the phosphors operate at physical limits, nevertheless the energy efficiency of the devices is rather low, especially in display applications.

5.5.6
Preparation of Luminescent Materials

Traditionally, luminescent materials are prepared by mix and fire techniques: small grains of reactants (generally with diameters in the μm range or smaller) are thoroughly mixed (either dry or in a suspension) and heated. The heating temperatures typically exceed 1000 °C. To facilitate the reaction and to obtain luminescent materials of sufficient crystallinity (which generally improves the efficiency of the luminescence process significantly), a flux agent or a melting salt can be added. This generally results in lower reaction temperatures and improved crystallinity. Such agents can also be used to optimize the grain size of the luminophores, whereby the optimum size of the particles depends on the specific application.

A suitable flux promotes crystallinity of the luminescent material being manufactured and also the reactivity, by dissolving at least one of the reactants. Fluxes can be divided into two types: a pure non-volatile liquid, e.g., a molten salt or a molten oxide (melting salt), and a volatile liquid or gas (volatile flux).

A melting salt generally shows no reaction with the starting materials, it is always a melt. One can use large amounts (up to e.g. 30% by weight of the phosphor) and the material does not decompose or evaporate during phosphor synthesis. Examples are Na_2MoO_4, $Na_2B_4O_7$, Na_2SiO_3 or $Na_4P_2O_7$.

A flux often reacts with the starting material, sometimes a melt, when used in small amounts (e.g. less than 10% by weight of the phosphor) and always shows decomposition or evaporation during phosphor synthesis. Frequently used fluxes are NH_4Cl, NH_4Br and AlF_3.

Reactivity can be improved by using starting materials which decompose during heating, like carbonates or hydroxides. After decomposition (in the examples given CO_2 or H_2O leave the reaction mixture), one ends up with a much more reactive mixture, as a result of the larger specific surface area.

Moreover, co-precipitation can be used. Using co-precipitation, a reaction mixture where the starting materials are mixed on an atomic scale can be obtained. By dissolving the reactants and co-precipitating them one obtains an intimately mixed starting mixture. Just to mention an example: $Y(NO_3)_3$ and $Tb(NO_3)_3$ are dissolved in H_2O and co-precipitated by adding to excess oxalic acid (2 to 1 on a molar basis), dissolved in hot water. Alternatively, the oxides can be dissolved in hot dilute nitric acid (4 M). The oxalates obtained are converted into the oxides by heating at 800 °C. This method can be used if an insoluble salt can be identified for each of the reaction constituents. Other possible co-precipitation routes involve sulfates or hydroxides.

Spray drying methods can also be used. Here, one first dissolves the reactants in a medium, preferably H_2O. Small droplets are transported in a gas stream and heated, resulting in a very fast evaporation of H_2O. As a result, an intimate reaction mixture is obtained.

An interesting combination of methods is the polysulfide flux method, which can be used for the preparation of Ln_2O_2S (Ln: trivalent rare-earth ion)-based luminescent materials (e.g. Y_2O_2S:Eu or Gd_2O_2S:Pr) [5.228]. In this method, the mixed oxides of the metals are mixed with excess sulfur and an alkali metal carbonate. On heating, the alkaline carbonate decomposes and reacts with sulfur to form a liquid polysulfide flux. The oxides react with the polysulfide flux to form the oxysulfide. Flux residues can be removed by washing the reaction product in water.

Different routes have to be chosen in cases where the concentration of dopants is very low, e.g. in the ZnS phosphors for CRT application. Here, the dopant concentrations are of the order of 100 ppm (by mole). Minute amounts of these activator ions can be precipitated onto ZnS grains, e.g. by preparing a suspension of ZnS in water and adding soluble activator salts. The activator is precipitated onto the ZnS by adding e.g. $(NH_4)_2S$.

Some reactions require a reducing atmosphere to incorporate activator ions in an oxidation state which is lower than the maximum oxidation state, e.g. Eu^{2+}, or to prevent oxidation of the host lattice, e.g. in the case of the preparation of ZnS phosphors. This can be achieved by executing the reaction in diluted H_2 or in CO. A CO atmosphere is easily obtained by heating graphite grains in a closed vessel, in which a second, smaller, vessel containing the reaction mixture is placed.

5.5.7
Outlook

About 100 years of research on luminescent materials has resulted in phosphors with impressive maturity. In almost all applications, phosphors perform at their physical limits. We will close this section by considering two research areas, which may lead to important new application fields: cascade phosphors and quantum dots.

5.5.7.1
Cascade Phosphors

This class of luminescent materials with more than one absorbed or emitted photon is gaining interest. Fundamentally, a well-selected combination of energy levels,

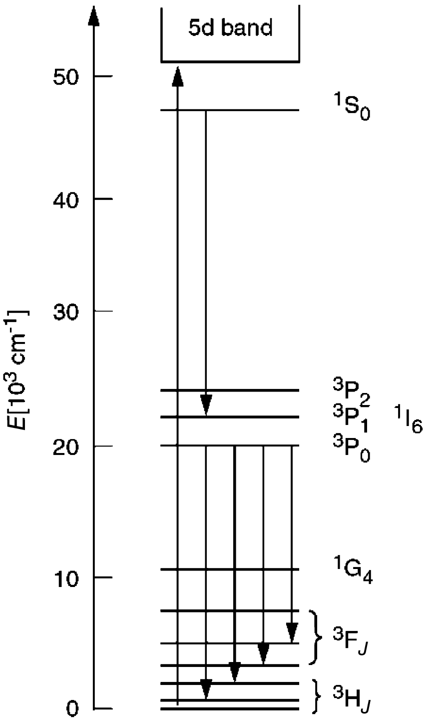


Fig. 5.53 Energy level scheme of Pr^{3+} and the cascade transitions.

normally f-levels of lanthanide ions, is required to establish a cascade transition. With $CaWO_4:Yb^{3+},Er^{3+}$ as a first example, absorption of two photons with lower energy (e.g. deep red or IR), followed by emission of one photon with higher energy (visible) was proven by Auzel in 1966 [5.229]. Such so-called up-conversion processes are known for the summation of up to five photons. However, due to the comparatively low efficiency (< 1%) of the cascade process itself, as well as the low absorption cross-section of f–f-transitions, application is limited to areas where energy efficiency is not important.

The opposite effect, the so-called down-conversion was reported in 1974, independently, for $YF_3:Pr^{3+}$ [5.230, 5.231]. Here, two photons with lower energy (visible) are emitted per photon absorbed at energy above about 5.7 eV (Figure 5.52). Absorption preferably takes place in the 5d band of Pr^{3+}, as the underlying 4f–5d optical transition is parity allowed (Figure 5.53).

The emitted photons are located in the blue and red spectral region of the spectrum, respectively. In 1999, a first example of a quantum cutting material with two visible photons at similar wavelength (in the red spectral region), was presented: $LiGdF_4:Eu^{3+}$ (Figure 5.54) [5.232].

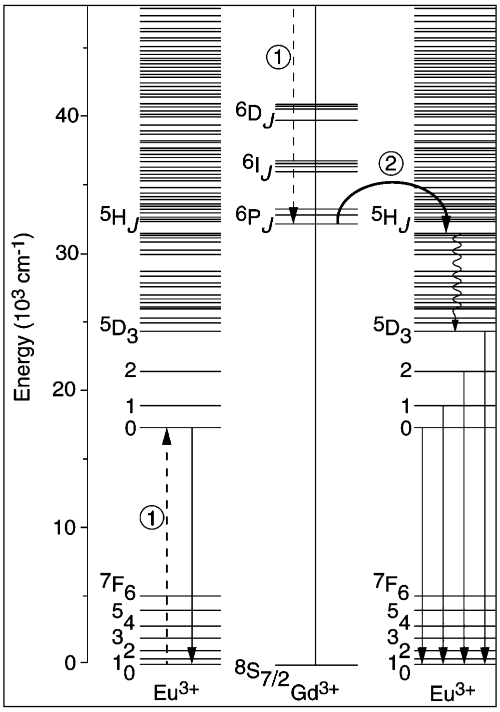


Fig. 5.54 Energy transfer and down-conversion in $LiGdF_4:Eu^{3+}$.

Such down-conversion phosphors are needed for energy efficient Hg-free lamps, which are driven by a Xe/Ne discharge. In order to establish f–f transitions with VUV-excitation and to avoid band-to-band absorption by the host lattice, large band-gap materials such as fluorides have to be applied. Once again, new scientific input drives luminescence research.

5.5.7.2
Quantum Dots

Phosphor research is not only triggered by new application areas, the reverse situation can also occur. Quantum dots are a very good example of this [5.233–5.235]. Due to size quantization effects, which occur in semi-conductors with radii typically less than 10 nm, the spectral position of the emission can be shifted over a large spectral range (e.g. over the complete visible spectral range), just by varying the particle size. This enables tunable narrow band emission. Furthermore with diameters of 2 to 10 nm, quantum dots are small enough to realize transparent non-scattering luminescent layers. This latter property is extremely interesting for applications such as electroluminescent displays and flexible light sources. Moreover, quantum dots are promising luminescent markers for optical imaging in medicine [5.234, 5.236, 5.237].

Taking these few examples from amongst many others, it can be seen that research on luminescent materials is still extremely challenging. Driven by both new materials and new application areas, the search for new and improved luminescent materials is an important research topic both in industry and academia.

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