



The world of inorganic pigments

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Abstract

Inorganic pigments have been very important substances for human life for thousands of years. They have contributed and continue to contribute to the beautification of our daily life and habitat and to the accentuation and differentiation of objects, and influence thoughts, moods, and feelings. The industrial manufacture of inorganic pigments based on growing chemical and physical knowledge started around 1800. Before that, pigments based on natural materials or manufactured by mostly empirical processes were used. Most of the technically relevant inorganic pigments were developed and first produced on an industrial scale in the nineteenth and twentieth centuries. Ongoing developments are aiming to improve existing conventional pigments as well as synthesize new, innovative colorants, especially in the classes of effect pigments and functional pigments. The objective of this text is to present comprehensive knowledge about inorganic pigments, including definitions, types of pigments and their properties, historical pigments, modern inorganic pigments, synthesis methods, and applications. It is also intended to show the current status of new pigment developments.

Graphical abstract

Collection of samples of inorganic pigments



Extended author information available on the last page of the article

Keywords Effect pigments · Functional pigments · Inorganic pigments · Iron oxide pigments · Titanium dioxide pigments

Definitions

Nowadays, pigments are defined as substances consisting of small particles that are practically insoluble in their application system and applied as colorants or because of their special corrosion-inhibiting or magnetic properties [1]. They differ from dyes, which also belong to the class of colorants, in that the latter are almost completely soluble in their application medium. The most important application systems for pigments are automotive and industrial coatings, paints, plastics, printing inks, cosmetic formulations, and construction materials. Other applications for pigments are found in paper, rubber, glass, porcelain, glazes, and stains.

The term “pigment” is derived from the Latin word “*pigmentum*,” which was originally used in the sense of a coloring material. In the Middle Ages, the term “pigment” was also used for colored plant extracts. In the terminology of biology, the term is still used today to describe plant and animal colorants that are present in “dissolved” form as extremely small particles in cells or cell membranes, as deposits in tissue, or suspended in body fluids. In all these cases, the use of the term “pigment” is misleading. In the interest of uniform terminology, it should be replaced here by the more appropriate term “dye” [2].

The term “colorant” covers all colored compounds regardless of their origin or use. Some pigments and dyes exist in natural and synthetic variations. Pigments are applied to surfaces (substrates), requiring binders in which the particles are embedded (paints, coatings, printing inks, and cosmetic formulations). When coloring plastics, the entire polymer material is often pigmented. Dyes are applied to different surfaces during use. Examples include textiles, leather, paper, and hair, to which the dyes are applied in dissolved form. Unlike pigments, dyes must have an affinity for the substrate to which they are to be fixed.

Classification of pigments

Pigments can be classified according to either their chemical composition or their optical and technical properties. The distinction between inorganic and organic pigments is fundamental. Figure 1 shows a classification of pigments and colorants within the category of “colorants” (coloring materials). This figure illustrates that dyes are, by nature, organic compounds, and that white dyes do not exist.

Fillers, as substances closely related to pigments, are also included in Fig. 1. Like pigments, these are solid materials that are added to application media to improve the properties of the system or reduce the consumption of more expensive

binder components. Fillers that are used mainly for cost reduction are also called extenders. Like pigments, fillers are insoluble in the medium used. They have the ability to improve coatings and other application systems in terms of their density, porosity, and permeability to gases and water. There is no clear differentiation between fillers and pigments in terms of their refractive index, but it is generally accepted that this index is below 1.7 for fillers and above this value for pigments [2].

Figure 2 contains a detailed classification of inorganic pigments. White, colored, and black pigments exist, as well as pigments with special properties. In addition, the most important representatives of the various pigment categories are listed. White pigments are represented by titanium dioxide (rutile and anatase), zinc sulfide (including the lithopones), and zinc oxide. Colored pigments show the widest variation, ranging from blue (complex metal oxides, ultramarine, Prussian blue) through green (chromium(III) oxide, complex metal oxides), and yellow (iron(III) oxide hydroxide, complex metal oxides, lead chromate, bismuth vanadate, cadmium sulfide) to red (iron(III) oxide, cadmium selenide, lead molybdate, cerium(III) sulfide, calcium lanthanum oxonitride, lanthanum tantalum oxonitride). The most important representative black pigment is carbon black. On the basis of this variety of colored, white, and black pigments, it is possible to obtain almost all conceivable colored and achromatic (white, black, and gray) shades. Both single pigments and mixtures of two or more pigments can be used to achieve a specific shade.

Special pigments are divided into the classes: effect pigments (luster pigments) with two subclasses of special effect pigments (pearlescent pigments, interference pigments) and metal effect pigments, transparent pigments, luminescent

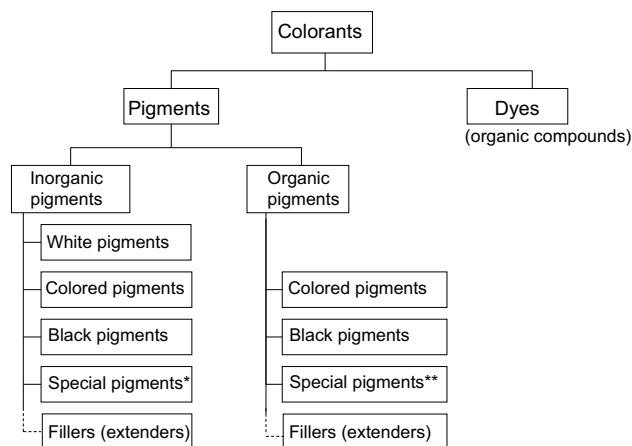


Fig. 1 Classification of colorants (*effect pigments, transparent pigments, luminescent pigments, functional pigments, **effect pigments, luminescent pigments)

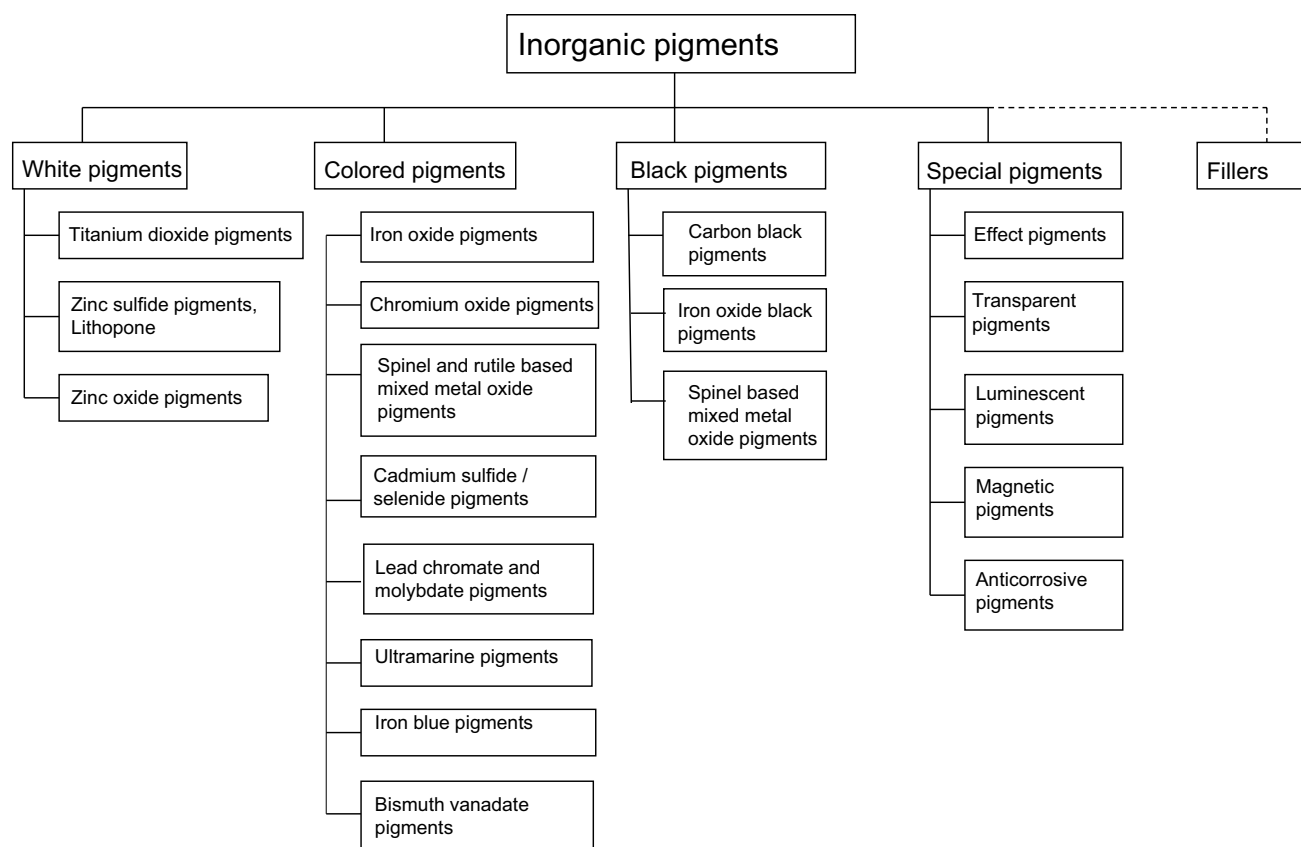


Fig. 2 Classification of industrially important inorganic pigments

pigments (with two subclasses of fluorescent pigments and phosphorescent pigments), and functional pigments [2].

The optical behavior of effect pigments is based on the directional reflection of visible light from predominantly two-dimensional and aligned metallic (metal effect pigments) or highly refractive transparent pigment particles (pearlescent pigments), or on the phenomenon of interference (interference pigments).

Transparent pigments are characterized by very small particles with size in the range below 100 nm and high specific surface area. Most of the technically relevant pigments consist of particles that are even smaller than 30 nm. These are classified as nanomaterials. Pigmentation with these pigments leads to a transparent appearance of the application systems.

Luminescent pigments (luminescent materials, lumino-phores, and phosphors) show optical effects based on their ability to absorb radiation and emit it as light of longer wavelength with a time delay (phosphorescence) or without a time delay (fluorescence). Light emission often occurs in the visible spectral range. External energy is necessary to enable luminescent materials to generate light.

The importance of functional pigments lies not in their color but in various physical properties, which cannot be

derived from the original term “*pigmentum*.” Such materials, which exhibit magnetic, anticorrosive, electrically conductive, infrared (IR)-reflective, ultraviolet (UV)-absorbing, and other physical properties, can be appropriately described by the term “functional pigments.” Some of the transparent pigments and the luminescent pigments can also be classified as functional pigments. The reason why functional pigments are classified as pigments is because of their similar morphological and application–technical properties.

Another classification of inorganic pigments is based on their chemical composition (Table 1).

General properties of pigments

In general, inorganic pigments are more stable against the influence of light, temperature, chemicals, and atmospheres than organic pigments. Inorganic pigments also offer the advantage of lower production costs. Organic pigments usually require multistage syntheses and expensive starting materials for their production. Both factors lead to comparatively high market prices for organic pigments. However, compared with inorganic colored pigments, organic pigments are often more color-intense and thus more attractive

Table 1 Classification of inorganic pigments based on chemical composition

Chemical composition	Pigment examples
Oxide, oxide hydroxide	TiO ₂ , ZnO, α-Fe ₂ O ₃ , α-FeOOH, γ-Fe ₂ O ₃ , Fe ₃ O ₄ , Cr ₂ O ₃ , CrOOH, PbO, Pb ₃ O ₄ , Mn ₃ O ₄ , -MnOOH, Sb ₂ O ₃
Complex oxide	CoAl ₂ O ₄ , CuCr ₂ O ₄ , Co ₂ TiO ₄ , (Ti,Ni,Sb)O ₂ , (Ti,Cr,Sb)O ₂
Carbonate hydroxide	2PbCO ₃ ·Pb(OH) ₂ , 2CuCO ₃ ·Cu(OH) ₂ , CuCO ₃ ·Cu(OH) ₂
Sulfide, selenide	ZnS, CdS, Cd(S,Se), CdSe, γ-Ce ₂ S ₃ , HgS, As ₂ S ₃
Chromate, molybdate	PbCrO ₄ , Pb(Cr,S)O ₄ , Pb(Cr,S,Mo)O ₄ , ZnCrO ₄ , BaCrO ₄ , SrCrO ₄
Vanadate	BiVO ₄ , 4BiVO ₄ ·3Bi ₂ MoO ₆
Stannate	Pb ₂ SnO ₄ , PbSn ₂ SiO ₇ , Co ₂ SnO ₄ , CoSnO ₃
Phosphate	Co ₃ (PO ₄) ₂
Antimonate	Pb(SbO ₃) ₂
Arsenate	Cu(AsO ₃) ₂
Ultramarine	Na ₆ Al ₆ Si ₆ O ₂₄ (NaS _n)
Hexacyanidoferrate (hexacyanoferrate)	K[Fe ^{III} Fe ^{II} (CN) ₆]·xH ₂ O (x = 14–16)
Oxonitride	CaTaO ₂ N, LaTaON ₂
Element	C, Al, Cu, Cu/Zn, Au

for various applications. As also occurs with dyes, the aforementioned lower stability of organic pigments often leads to their degradation over time when interacting with UV radiation or atmospheric influences. The use of UV absorbers when applying organic colorants is an effective way of extending their lifetime in application media.

The choice of a pigment for a specific application can be based on several criteria (Table 2).

A pigmented system is described as a dispersion of pigment particles in a translucent binding medium, which is initially liquid and after hardening of the binder preferably solid. In most cases, a thin film is formed, e.g., a paint layer, with thickness of a few to hundreds of micrometers. In some cases, such as in cosmetic formulations, the application takes the form of a liquid dispersion. Incident light undergoes reflection, refraction, and absorption when interacting with the dispersion, resulting in the visual appearance of the pigmented medium. The optical properties of a pigmented system are mainly determined by the following factors:

- Pigment properties such as particle size, particle size distribution, particle shape, refractive index, scattering coefficient, and absorption coefficient
- Properties of the application medium (binder) such as refractive index and absorption
- The pigment volume concentration in the pigmented system

Geometric parameters such as particle size (diameter), size distribution, and shape are among the particularly important properties of pigments. Particles are defined as the smallest individual units of a pigment or powder in general. The structure, size, and shape of particles can vary to a great extent. Typical units of particles occurring in pigments are primary particles, agglomerates, and aggregates (Fig. 3):

- Primary particles (individual particles): particles that are recognizable as individual units when using suitable imaging methods (optical microscopy, electron microscopy); primary particles are the optimum units for a pigment from the point of view of the application.

Table 2 Criteria for choice of a pigment and specific pigment properties important for the application

Criteria for the application of pigments	Specific pigment properties
Color criteria	Color, color strength (measure of the ability of a pigment to impart color to other materials), lightening capacity (measure of the ability of a white pigment to brighten other materials), hiding power (measure of the ability to hide the surface of an object)
Chemical and physical criteria	Chemical composition, particle size, particle size distribution, density, moisture and salt content, content of water- and acid-soluble components, hardness
Stability criteria	Stability to (especially UV) light, heat, moisture, chemicals
Behavior in binders and other application media	Dispersion behavior, interaction with the components of the binder

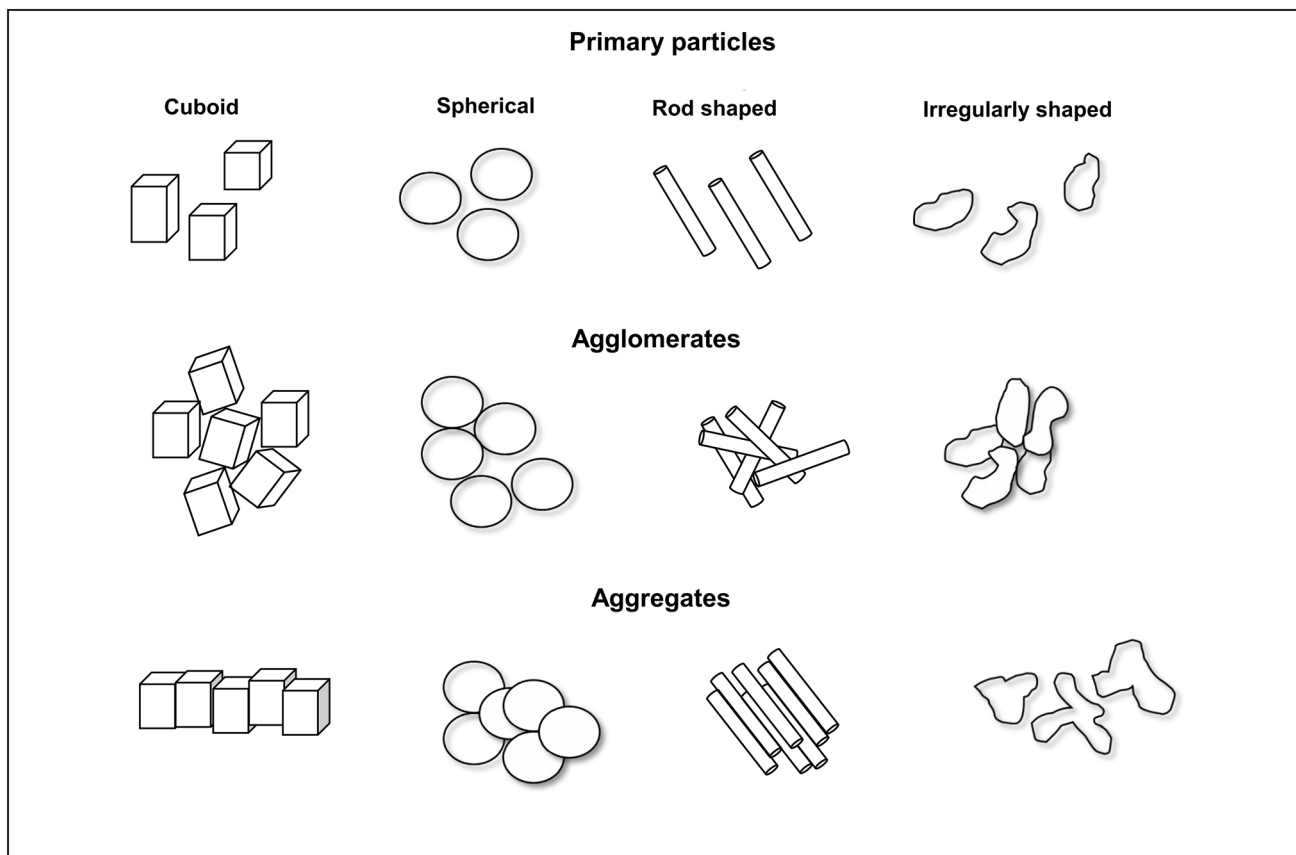


Fig. 3 Primary particles, agglomerates, and aggregates

- **Agglomerates:** assemblages of primary particles and/or aggregates, where contact between the particles typically occurs via corners and edges; agglomerates can usually be easily destroyed by mechanical action and converted into primary particles or smaller units.
- **Aggregates:** aggregations of primary particles, where contact between the particles typically occurs via surfaces; this results in particles that adhere firmly to one another and are difficult or impossible to separate from each other; they often pose a problem in terms of application technology.

Interaction of pigments with light

The decisive factor regarding the optical appearance of a pigment is its interaction with light in the spectral range visible to the human eye (about 400–750 nm). The following interactions are to be considered for the most important pigment classes (Table 3).

Figure 4 provides a comparative illustration of this interaction using pigment particles embedded in an application medium. The color that occurs in colored pigments due to

the absorption of light originates from the interaction of visible light with the valence electrons of the pigments, which are to be regarded as solids. The elements involved (cations and anions), their oxidation state or electron configuration, and the respective crystal structure are decisive for a specific absorption. The special electronic structure of the pigments derived from this is the basis for electronic transitions between different energy states and thus for the absorption of certain wavelengths of light and the formation of color [3, 4].

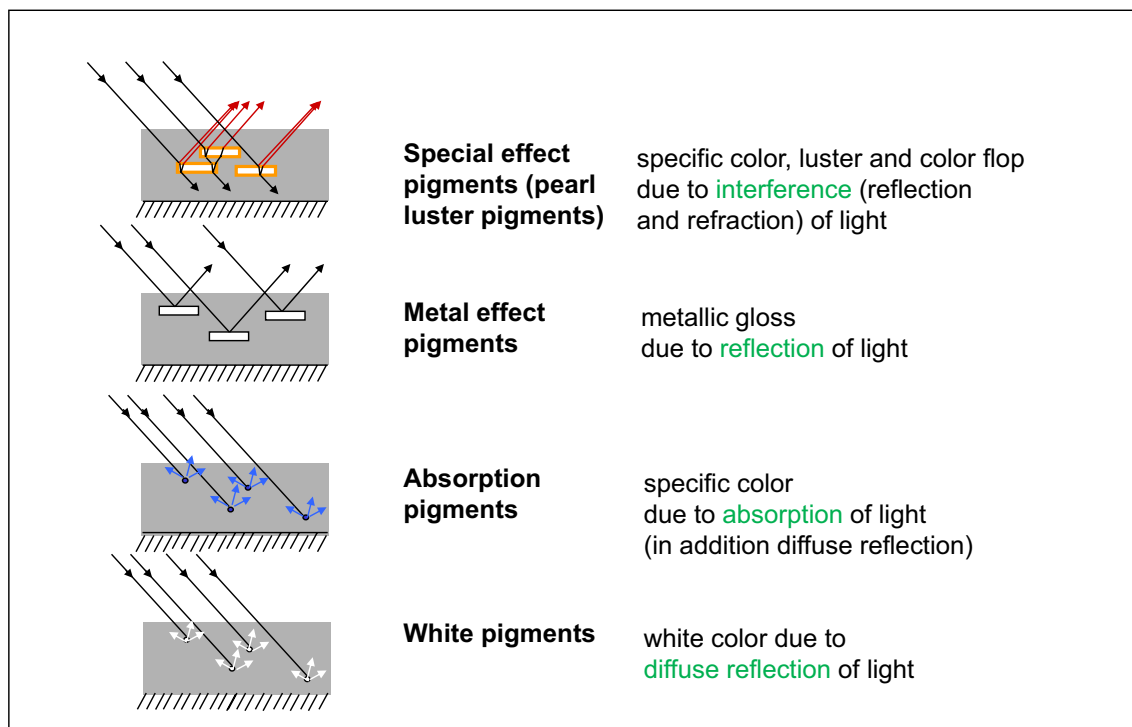
The fundamental relationships among the optical characteristics of pigments can be comprehensively discussed on the basis of four theoretical considerations [2]:

- Lorenz–Mie theory
- The theory of multiple scattering
- Kubelka–Munk theory
- Colorimetry

Mie or Lorenz–Mie scattering refers to the elastic scattering of electromagnetic waves at spherical objects, for example, pigment particles in an application medium, whose diameter corresponds approximately to the wavelength of

Table 3 Pigment classes and optical effects on which they are based

Pigment class	Optical effect
White pigments	Nonselective scattering of visible light by the pigment particles
Colored pigments	Selective absorption of visible light combined with light scattering by the pigment particles
Black pigments	Nonselective absorption of visible light by the pigment particles
Effect pigments	Directional reflection of visible light from predominantly two-dimensional and aligned metallic (metal effect pigments) or highly refractive transparent pigment particles (pearl-effect pigments), or the phenomenon of interference (interference pigments)
Luminescent pigments	The ability of these pigments to absorb radiation and emit it as light of longer wavelength with a time delay (phosphorescence) or without a time delay (fluorescence)

**Fig. 4** Optical interaction of visible light with particles of different pigment types in an application system, e.g., in a coating

the radiation. This scattering can be described physically with Lorenz–Mie theory. Mie scattering produces the Tyndall effect [5, 6].

The theory of multiple scattering is the mathematical formalism that is used to describe the propagation of a wave through a collection of scatterers, for example, a variety of pigment particles in an application system [7–10].

Kubelka–Munk theory describes the light absorption and scattering properties of pigmented systems, such as paint films or coatings [11–13].

Colorimetry is concerned with the quantification and physical description of human color perception. It is similar to spectrophotometry, but has specifically aims to reduce spectra to the physical correlates of color perception, mostly

to the tristimulus values of the CIE 1931 XYZ color space and related parameters [14, 15].

Figure 5 shows the relationship between the optical properties of pigments and pigmented systems and their theoretical principles. Reflection spectra and spectral reflection factor curves can be almost entirely derived from physical parameters and relations by using these four fundamental approaches [2].

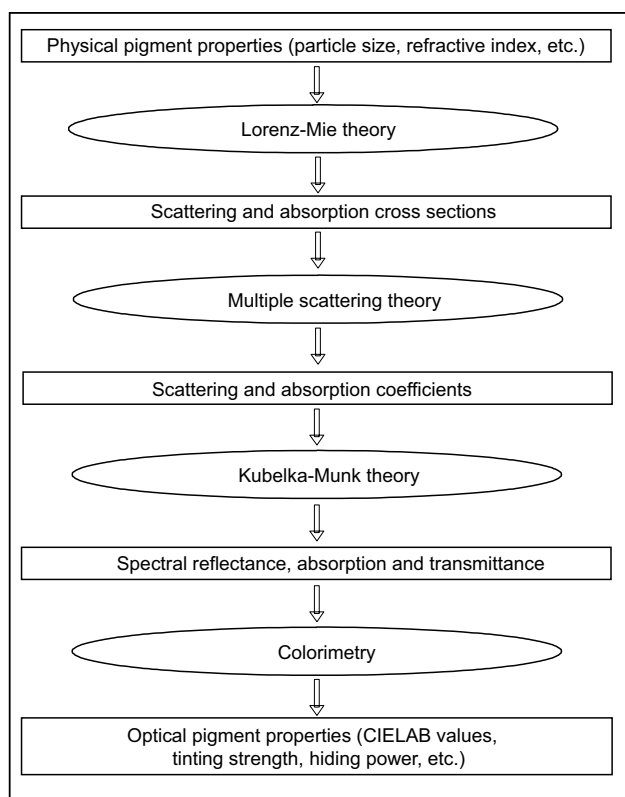


Fig. 5 Relationship between optical properties of pigments and pigmented systems and their theoretical principles [2]

Historical pigments: from the beginning of pigment use to the eighteenth century

The history of pigments is closely linked to the cultural history of mankind. The beginning of the use of inorganic pigments goes back to the early history of human society. Thousands of years ago, our ancestors were already able to color textiles, skins, and utensils in a simple way using naturally occurring substances. These were mostly of plant origin, but could also come from animals [2, 16–18].

Cave paintings such as those at Altamira and Lascaux date back to the Ice Age. They were almost certainly made between 15,000 and 30,000 years ago. Natural manganese oxides and charcoal were used for black tones, while yellow, orange, and red tones were produced with the help of naturally occurring iron oxides. Calcium carbonate was the basis for white and light shades. The earth colors used were sometimes oxidized by fire and mixed with fats or resins. Yellow ochre and red ochre (earths) were prepared from rocks by crushing, slurring, and grinding. Red ochre could be obtained by heating yellow ochre. It can be assumed that, already in this period, natural materials in powdered form were also used as pigments for body painting. Thus, the use of pigments for the purpose of coloring surfaces can be

considered one of the oldest cultural activities of mankind. The artists of the Ice Age used pigments mostly without a binder. The rock paintings survived the millennia only because seepage water, which contained colorless minerals, covered the pigments with protective transparent mineral layers [19–21].

Methods for producing inorganic materials suitable for use as pigments were further developed several millennia later, especially in the ancient centers of Egypt and Babylon. The walls of temples, burial chambers, and stone buildings, as well as wood and ceramic surfaces, were used for color design. The pigments used were iron oxide black, manganese oxide black, and lead sulfide (galena) for black tones, iron oxide red and copper in colloidal form for red tones, and calcium carbonate and kaolinite for white tones. Arsenic sulfide and Naples yellow were the first yellow pigments, while ultramarine in the form of crushed lapis lazuli, Egyptian blue, cobalt aluminate, and ground glass containing cobalt (smalt) were used for blue tones. The first green pigments were green earth and malachite. Some of these pigments were not of natural origin. They were synthesized by empirical chemical methods. The use of toxic substances such as arsenic and antimony compounds in cosmetic formulations was widespread. Metals such as gold, silver, and copper were also already used as colorants in the design of surfaces. Egyptian blue was the most important pigment in Egypt, as blue was considered a divine color. It was made from lime powder, quartz sand, copper oxide, and soda (flux) [22, 23].

A thousand years later, another red pigment was available in Ancient Greece in the form of cinnabar. This naturally obtained pigment was also used in many ways during the Roman Empire. The main source for this was the deposit in Almadén in Spain. With white lead and red lead oxide, further pigments came into use in Ancient Rome and were to play an important role in color design in the following centuries. New trade routes to the Far East enabled the import of organic and inorganic colorants, among which indigo and various colored minerals were particularly important. Both Greeks and Romans decisively developed the existing techniques in the application of pigments [24–27].

In the Middle Ages, book painting was initially of paramount importance. Panel painting on an independent surface (initially a wooden panel but subsequently canvas) developed only over the course of time. In the twelfth century, Venice became the main hub for colorants in the world. Various noble families from Venice and Florence began to promote art. Painters and other artists came to the most important metropolises in Italy at that time and took on commissions for their patrons. The church was traditionally also an important client for painters and sculptors. Fresco painting experienced its heyday in the early Renaissance with the painter Giotto di Bondone (ca. 1270–1337). The

Florentine painter Cennino Cennini (ca. 1370–1440) was the first to publish a handbook on painting with the title “*Il libro dell’arte o trattato di pittura*” [28]. This book, written around the year 1400, was the most influential textbook on painting of the Late Middle Ages. It has remained of special cultural-historical and art-historical importance until today because the author was the first to disclose the secrets of painting including all the relevant materials used [2, 18].

The compatibility of the pigments used with the chalky substrate was a specific problem in the frescoes to be created. Blue hues were typically applied *a secco* because the available blue pigments were attacked and thus altered by the lime. The color palette ranged from earth colors (yellow ocher, Terra di Siena) to mineral colors and synthetically produced pigment colors (lead tin yellow and smalt). The colors were produced on the basis of recipes, some of which were kept secret. Existing knowledge was passed on and used again and again, but the basic colorants and binders were always further developed and sensitively adapted to the differentiated fields of application [18, 28–31]. From the very beginning, artists’ colors were among the most desirable colorants and thus contributed greatly to the development of new pigments, dyes, and binders over the centuries [18, 32–35].

Painting underwent a significant development in the Renaissance, with techniques of oil painting reaching a completely new quality. The range of pigments already used earlier was extended to include green earth (natural earth pigment as a weathering product of ferrous silicates, purified). Color-intense varieties of this green pigment came from the Verona area (Veronese green earth) and from Bohemia (Bohemian green earth). Other important paint pigments were Naples yellow, auric pigment, lead tin yellow, cinnabar, realgar, carmine (calcium and aluminum salts of carminic acid), malachite, white lead, and painter’s charcoal [18, 36–38].

In the eighteenth century, on the basis of the level of knowledge of chemistry achieved at that time, which had increasingly developed from alchemy into a science, the targeted synthesis of various inorganic pigments was achieved for the first time. Thus, in the course of this century, pigments such as Prussian blue, Schweinfurt green, or cobalt blue became available. In particular, the discovery of Prussian blue as a new blue pigment is well known. The color maker Johann Jacob von Diesbach (who lived around 1700) and the alchemist Johann Conrad Dippel (1673–1734) were the first to succeed in synthesizing this pigment, in 1706 in Berlin. It took some time until the preparation route was fully developed. The synthesis was finally made public by the chemist and pharmacist Caspar Neumann (1683–1737) from Berlin, who provided the recipe for Prussian blue to the Royal Society for anonymous publication [39, 40]. Today, Prussian blue is one of the technically important blue

pigments, mainly being used in paints and printing inks. In technical applications, the pigment is usually referred to as iron blue [2]. The pigment has even been used in the design of blue postage stamps [41]. The production of Prussian blue and other newly developed pigments initially took place in workshops and small companies. These were to become the nuclei of the rapid upswing in color chemistry that took place in the nineteenth century.

A specialty among the historical pigments is Maya blue. This pigment was rediscovered in 1931 at the archaeological site of Chichén Itzá [42]. This intensely colored blue pigment was widely used in wall painting, pottery, sculptures, and luxury art in Mesoamerica and even as a therapeutic agent in pre-Columbian times. It can be described as a hybrid organic–inorganic material resulting from the attachment of indigo, a blue dye extracted from leaves of anil (*Indigofera suffruticosa* and other plant species), to the clay matrix of palygorskite, a fibrous phyllosilicate with an ideal composition of $(\text{Mg,Al})_4\text{Si}_8(\text{O,OH,H}_2\text{O})_{24}\cdot n\text{H}_2\text{O}$ [43, 44]. In this context, it is interesting to refer to the preparation of indigo from *Indigofera suffruticosa* by electrochemical monitoring using the voltammetry-of-microparticles approach [45].

The chemical and physical–chemical analysis of inorganic pigments used in art and on archeological objects is of great interest to obtain knowledge about historical pigments. Today, a large number of modern methods for the identification of pigments are available for such analyses. The instrumental techniques most frequently used for such analysis of cultural artifacts to obtain data on the chemical composition of pigments contained are classical chemical analysis, activation methods, faradaic electrochemical methods, spectroscopic methods, and thermoanalytical methods. The instrumental techniques that can provide data on the crystal and molecular structure of pigments include diffraction and spectroscopic methods as well as mass spectroscopy. Information on the texture and strata structure can be obtained using light microscopy, electron microscopy, and atomic force microscopy [46].

Table 4 presents the most important representative historical pigments (in the period from early human history until the eighteenth century), including both inorganic and organic pigments.

Modern inorganic pigments: current status and new developments

In the nineteenth century, the development of the synthesis of new inorganic pigments, which had begun in the previous century, continued steadily. Many of the chemical factories that were now being established began to specialize in the industrial production of inorganic and organic pigments and

Table 4 Representative historical pigments

Color	Representatives
White	Lead white ($2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$), kaolin
Black	Coal (charcoal), groutite ($\alpha\text{-MnOOH}$), manganite ($\gamma\text{-MnOOH}$), hausmannite (Mn_3O_4)
Yellow	Yellow ochre ($\alpha\text{-FeOOH}$), auric pigment (As_2S_3), lead ochre (PbO), lead tin yellow (Pb_2SnO_4 , $\text{PbSn}_2\text{SiO}_7$), Naples yellow ($\text{Pb}(\text{SbO}_3)_2$), zinc yellow (Zn_2CrO_4), Indian yellow ($\text{C}_{19}\text{H}_{16}\text{O}_{10}$)
Red	Red ochre ($\alpha\text{-Fe}_2\text{O}_3$), Terra di Siena ($\alpha\text{-Fe}_2\text{O}_3$), vermilion (HgS), lead red (Pb_3O_4), alizarin madder varnish, alizarin red ($\text{C}_{14}\text{H}_8\text{O}_4$)
Green	Green earth (Fe silicates), Schweinfurt green ($\text{C}_4\text{H}_6\text{As}_6\text{Cu}_4\text{O}_{16}$)
Blue	Lazurite (lapis lazuli), Egyptian blue ($\text{CaCuSi}_4\text{O}_{10}$), azurite ($2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$), malachite ($\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$), cobalt blue (CoAl_2O_4)
Brown	Burnt umber ($\text{Fe}_2\text{O}_3 \cdot x\text{MnO}_2$), brown ochre ($\alpha\text{-Fe}_2\text{O}_3 + \text{Mn}$ oxides), limonite (mixture of different Fe oxides)

in the technical synthesis of dyes. In addition to expanding the range of colors, chemical processes provided easy and cost-effective access to improved colorants with reproducible quality.

In this way, numerous new inorganic pigments expanded the range of technically useful colorants in the nineteenth century, including chrome oxide green, cadmium yellow, zinc white, ultramarine blue, iron oxide red, and metal bronzes (Cu/Zn). Other synthetic inorganic pigments appeared on the market in the twentieth century: titanium dioxide, cadmium red, iron oxide yellow, iron oxide black, bismuth vanadate, and effect pigments based on mica. After the first synthetic organic pigments became available in the nineteenth century, their range also expanded greatly in the twentieth century.

The application systems for pigments also changed and expanded greatly. Automotive and industrial coatings, plastics, modern printing inks and cosmetics, as well as building materials became the drivers for the development of new color-imparting products. Today, a wide variety of modern inorganic pigments are available for different applications (Table 5).

Figure 6 shows color charts of selected, technically significant inorganic pigments. It should be borne in mind that

the color impression shown here can only be a color orientation. The color impression achieved in a given application depends on various factors, above all on the quality of the pigment (composition, impurities, and particle size distribution), the application system, the concentration of the pigment in the application system, and the type of application.

Modern pigments are produced on an industrial scale in batch processes on a ton scale. For the production of inorganic pigments, precipitation and solid-state reactions at high temperatures are the main options. For special pigments, crystallization processes from molten salts, hydrothermal reactions, and gas-phase processes are used. Technical pigment syntheses are based on mature chemical processes that lead to reproducible pigment quality. Users can thus be supplied with pigments offering the same quality in terms of color and other properties time and time again. Suppliers and users, e.g., in the fields of coatings, paints, printing inks, plastics, and cosmetics, are in close contact with each other to constantly harmonize the requirements for pigments. Quality control is a crucial part of the production process. Natural pigments now only play a role in iron oxide pigments (for building materials).

The global pigment market reached a volume of around 12 million tons in 2020. It is dominated by the white pigment

Table 5 Representative modern inorganic pigments

Color, effect	Representatives
White	Titanium dioxide (TiO_2 /rutile and anatase), zinc oxide (ZnO), zinc sulfide (ZnS), lithopone ($\text{ZnS} + \text{BaSO}_4$)
Black	Carbon black, iron oxide black (Fe_3O_4), spinel black (CuCr_2O_4)
Yellow	Iron oxide yellow ($\alpha\text{-FeOOH}$), chromium titanium yellow ($(\text{Ti,Cr,Sb})\text{O}_2$), nickel titanium yellow ($(\text{Ti,Ni,Sb})\text{O}_2$), lead yellow (PbCrO_4), cadmium yellow (CdS), bismuth yellow (BiVO_4)
Red	Iron oxide red ($\alpha\text{-Fe}_2\text{O}_3$), molybdate red ($\text{Pb}(\text{Cr,S,Mo})\text{O}_4$), cadmium red ($\text{Cd}(\text{S,Se})$)
Green	Chromium oxide green (Cr_2O_3), chromium oxide hydrate green (CrOOH), cobalt green (Co_2TiO_4)
Blue	Cobalt blue (CoAl_2O_4), ultramarine blue: ($\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NaS}_n)$), iron blue ^a ($[\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6] \cdot x\text{H}_2\text{O}$)
Brown	Mixtures of different iron oxides
Special color effects	Pearlescent pigments, interference pigments, metal effect pigments

^aTechnical quality of Prussian blue

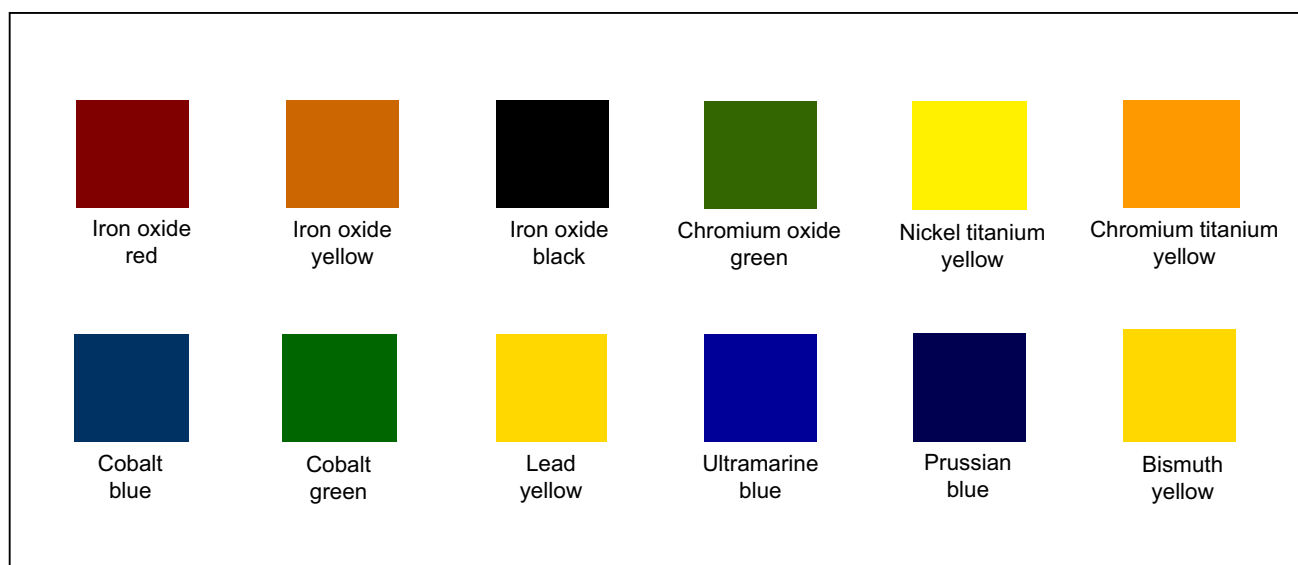


Fig. 6 Color charts of selected, technically important inorganic colored and black pigments

titanium dioxide (rutile and anatase). Indeed, TiO_2 pigments account for around 60% of global pigment production. In terms of the quantities produced, iron oxide and carbon black pigments lie in second and third place, respectively. Well over 90% of all colorants used today are inorganic pigments. Nevertheless, with an annual production of less than 1 million tons, organic pigments are also an attractive class of colorants with a wide range of applications [47]. The complexity of the industrial production of inorganic pigments is briefly outlined below using three examples.

Technical synthesis of titanium dioxide and iron oxide pigments

The following condensed descriptions of the production of titanium dioxide and iron oxide pigments are a selection intended to demonstrate important processes used in the production of inorganic pigments, such as precipitation and solid-state reactions, in general. An additional reason for choosing titanium dioxide and iron oxide pigments is the great economic importance of these products.

Titanium dioxide pigments

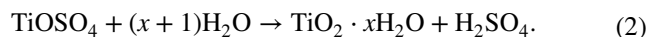
Two processes are available for the industrial production of high-quality titanium dioxide white pigments: the sulfate process, first used in 1916, and the chloride process, which reached production maturity in 1960 [2, 48–50]. The task in both processes is to produce pure white TiO_2 pigment starting from mostly black or gray titanium-containing raw

materials (ilmenite or titanium slag in the sulfate process; natural or synthetic rutile in the chloride process). Specified parameters such as average particle size, particle size distribution, particle shape, and crystal structure (rutile, anatase) must be achieved, dependent on the intended application.

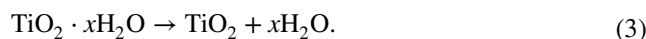
In the sulfate process, ilmenite or titanium slag is dissolved in hot concentrated sulfuric acid:



During subsequent cooling, iron(II) sulfate (green salt) crystallizes out and can be separated from the resulting sulfuric acid solution. After separation of various transition-metal ions, the colorless titanyl sulfate solution now present is subjected to hydrolysis by addition of water:



A titanium dioxide hydrate precipitate is formed, which, after filtration, washing, and drying, is fed to calcination at 800–1000 °C:



After this step, the granulometric properties of the obtained coarse titanium dioxide particles are adjusted by a grinding process. TiO_2 pigments synthesized in this way are often stabilized against UV radiation using a specific surface treatment (aftertreatment). Rutile is the more stable TiO_2 modification compared with anatase, but is also UV active to a lesser extent. An additional aspect of such a treatment is the improvement of the application properties of the pigments, especially with regard to their compatibility with the binder system. The surface treatment is carried

out mostly using a thin colorless layer (often consisting of SiO_2 , Al_2O_3 , and/or ZrO_2 , but also organic components), which is applied to the TiO_2 particles by wet chemical means to completely coat them on the surface. Furthermore, it is possible to perform intrinsic stabilization by incorporating suitable ions into the crystal lattice of the TiO_2 already during its synthesis. TiO_2 pigments produced by the sulfate process often consist of rutile/anatase mixtures. Pure rutile or anatase pigments can be obtained by a suitable choice of reaction parameters (calcination temperature and dopants).

In the chloride process, natural or synthetic heavily contaminated rutile reacts at 800–1200 °C with chlorine gas and coke (summary equation without partial reactions):



The resulting titanium tetrachloride is separated from solid chlorides by distillation. Subsequently, the very pure TiCl_4 thus obtained reacts with oxygen at more than 1000 °C, producing TiO_2 in the form of a pigmentary powder:



TiO_2 pigments produced by the chloride process are also partially stabilized intrinsically or by means of surface treatment. Similarly to the sulfate process, the ratio of rutile to anatase can be influenced by the choice of suitable reaction parameters.

For exterior applications of TiO_2 pigments, which are of great practical importance especially in the field of automotive coatings, stabilized rutile pigments are almost exclusively used. The additional use of UV-absorbing substances in the pigmented paint helps to ensure that TiO_2 -containing coatings easily achieve the required long lifetimes.

Titanium dioxide pigments are the best-known white pigments in terms of optical properties, because of the high refractive indices of 2.7 for rutile and 2.5 for anatase. The refractive index as is optical material property that is defined as the ratio of the speed of light in vacuum and the phase velocity of light in a medium into which the light enters. High values, as in the case of titanium dioxide, indicate high reflection and strong hiding power and explain the exceptional properties of titanium dioxide as a white pigment. The wide use of TiO_2 pigments is also due to the fact that they are very suitable for brightening any other color shade.

The chemical classification of titanium dioxide, which for many years was considered unproblematic from a regulatory point of view, has been the subject of intense discussion in the last few years. In 2021, the responsible EU authority changed the classification in such a way that several titanium dioxide powder qualities (depending on the particle size) are to be classified as carcinogenic. Mixtures containing titanium dioxide in powder form with 1% or more of

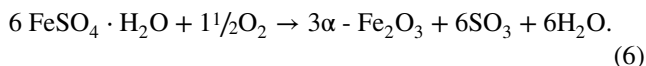
the particles with aerodynamic diameter $\leq 10 \mu\text{m}$ are consequently also classified as dangerous [51].

Iron oxide pigments

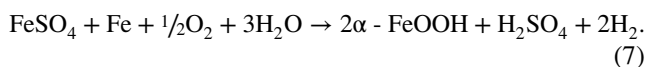
Several processes are used today for the production of high-quality iron oxide color and black pigments [2, 52, 53]:

- Solid state reactions (roasting process) for red, black, and brown pigments
- Precipitation reactions (Penniman–Zoph process, scrap process) for yellow, red, orange, and black pigments
- Aniline process (Laux process) for yellow, red, and black pigments

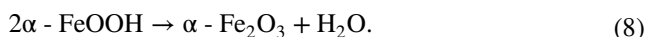
In all cases, iron(II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, green salt) is used as the starting material. In the roasting process, oxidative calcination produces $\alpha\text{-Fe}_2\text{O}_3$ (summary equation without partial reactions):



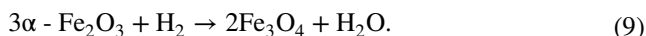
The so-produced iron(III) oxide is used as a red pigment or can be converted into black Fe_3O_4 by additional thermal treatment under reducing conditions. The Penniman–Zoph process starts with an FeSO_4 solution that, in the presence of an $\alpha\text{-FeOOH}$ seed suspension, reacts with iron scrap to form pigmentary $\alpha\text{-FeOOH}$ (summary equation without partial reactions):



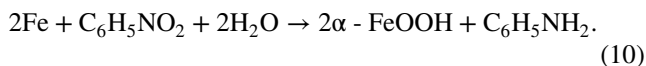
The iron oxide yellow obtained in this way can be converted into iron oxide red by calcination in air at temperatures above 500 °C:



Thermal treatment of $\alpha\text{-Fe}_2\text{O}_3$ in reducing atmosphere, e.g., under hydrogen or hydrogen-containing gases, can be used for the production of black Fe_3O_4 pigments:



In the Laux process, aromatic nitro compounds react with iron filings in the presence of AlCl_3 to form $\alpha\text{-FeOOH}$ and aniline:



The synthesis of $\alpha\text{-FeOOH}$ can also in this case be followed by a further reaction to obtain $\alpha\text{-Fe}_2\text{O}_3$ and Fe_3O_4 . The latter is the most important black pigment besides carbon black, but is also used as a magnetic pigment. The use

of iron(II) chloride instead of aluminum chloride in the Laux process leads directly to Fe_3O_4 pigments with very high tinting strength.

Attempts to develop new inorganic pigments

In the field of inorganic pigments, great efforts have been made in recent decades to develop new products and introduce them to the market. These efforts have been successful above all in the area of effect pigments, and to some extent also in functional pigments. In the case of white, colored, and black pigments, however, no new representatives have been added since the market launch of the yellow pigment bismuth vanadate in the mid-1970s [2]. At least, since the beginning of the use of bismuth vanadate, it has been possible to reduce the use of cadmium sulfide and chromate pigments, which are classified as toxic or carcinogenic [54].

In the 1990s, a new red pigment, $\gamma\text{-Ce}_2\text{S}_3$, was developed and launched on the market [55, 56]. One of several processes for producing this pigment involves the reaction of $\text{Ce}(\text{OH})_3$ with H_2S at temperatures ranging from 700 to 1000 °C. Attempts to use $\gamma\text{-Ce}_2\text{S}_3$ to displace red pigments containing cadmium, lead, and chromate failed because it is not sufficiently stable in the presence of moisture and changes with the release of hydrogen sulfide.

Another attempt to develop and market new color-intense yellow, orange, and red pigments was made around the year 2000 on the basis of oxonitrides (LaTaON_2 , CaTaO_2N , SrTaO_2N) [57]. The production of such pigments involves a complicated solid-state reaction, the transfer of which from laboratory to production scale has failed so far. In addition, the high manufacturing costs prevented the further pursuit of this development that is interesting from a coloristic point of view. Oxonitride pigments are therefore not important from an industrial point of view for future developments.

A few years later, yttrium-indium-manganese oxides with composition $\text{YIn}_{1-x}\text{Mn}_x\text{O}_3$ were reported to be suitable as high-color blue pigments [58]. The production of such pigments proceeds via the solid-state reaction route. The probability of technical applications of such pigments can be considered low, since both the availability of the raw materials and the production costs are problematic.

Basically, three challenges have to be overcome in all new pigment developments:

Effectiveness = technical performance (higher color strength, better dispersibility in the application medium, and increased hiding power)

Economy = customer benefits (improved utility value through lower pigment consumption and lower price per kg of pigment)

Ecology = environmental and toxicological safety (low content or complete absence of critical heavy metals and low CO_2 footprint in pigment production).

Only if these three criteria can be evaluated positively can it be assumed that a pigment idea will be pursued to market maturity [59].

Effect pigments

The challenges regarding the development of new pigments have been fulfilled for many modern effect pigments, which have been the front-runners in the field of inorganic pigments since the 1980s. This applies in particular to special effect pigments (transparent effect pigments, pearlescent pigments, and interference pigments), but also to a lesser extent to metallic effect pigments. Especially with special effect pigments, unique gloss and color effects, e.g., iridescent, glittering, and iridescent colors, can be achieved in the application. It is important that the platelet-shaped pigment particles are oriented parallel to the substrate or surface and parallel to each other in their application system. This is the only way to achieve the desired optical effects in coatings, printing inks, plastics, or cosmetic formulations.

Typical metal effect pigments consist of thin metal platelets with diameter of up to 100 μm and thickness of less than 1 μm . Suitable metals for such pigments are aluminum and copper, but also zinc/copper alloys [60]. The starting materials for metal effect pigments are the corresponding metals in the form of ingots. These are usually melted and then sprayed in liquid form. The resulting metal grit is then mechanically formed into thin platelets in ball mills in the presence of mineral oils, oleic and stearic acids. Dry grinding is out of the question for safety reasons, as the fresh metal surfaces produced during the grinding process are extremely reactive. In the case of aluminum pigments, which are of greatest technical importance, a differentiation is made today between the following three types in the order of their time of origin: “cornflake type,” “silver dollar type,” and “VMP type” (vacuum metallized pigment). While the cornflake and silver dollar type are produced by the process described above, the VMP type, developed only in recent years, is produced by vacuum evaporation of metallic aluminum and deposition of the vapor onto a polymer foil. The thin aluminum layer formed on the foil after cooling is detached and ground into pigment particles. The pigment particles obtained in this way are very thin. Their thickness is usually well below 50 nm. Figure 7 shows electron micrographs of the three types of aluminum pigment. The metallic gloss effects to be achieved are stronger when the pigment surfaces are smoother and fewer scattering centers are present at the edges and surfaces. Thus, from an optical point of view, the silver dollar type and above all the VMP type

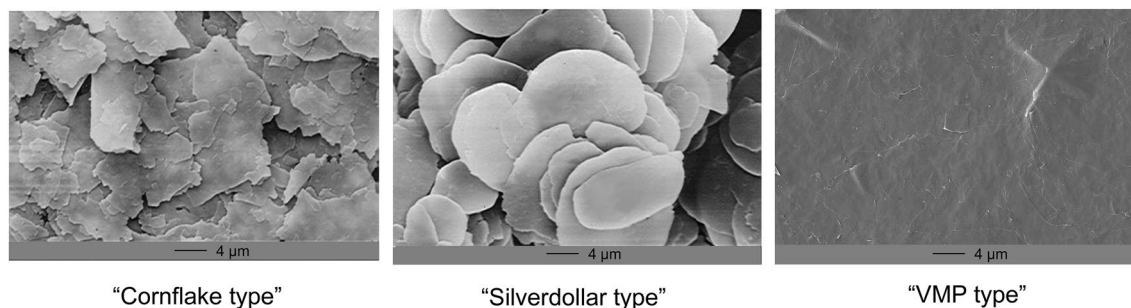


Fig. 7 Scanning electron micrographs of the three aluminum types used for effect pigments (Source: Carl Schlenk AG)

represent further developments of the traditional cornflake type [61].

Typical special effect pigments are based on the layer–substrate principle. Thin platelets consisting of natural or synthetic mica, silicon dioxide, aluminum oxide, or glass take over the function of a substrate. All these substrate materials are optically low-refractive. The dimensions are on the order of magnitude mentioned for metal effect pigments. Titanium dioxide, α -iron(III) oxide, and other optically highly refractive metal oxides form thin layers on the substrate platelets. The thickness of the metal oxide layer is mostly in the range of 40–250 nm [62, 63]. In the interaction with light, reflection, refraction, and interference play the most important role for these pigments. Depending on the coating material, absorption also comes into play, e.g., in the presence of iron oxide layers. Gloss and color effects are determined by the choice of substrate and coating. Multiple layers can also be deposited on the substrate platelets. In such cases, an alternating arrangement of high- and low-refractive-index layers is usually considered. Interference colors are produced by the superposition of wavelengths of incident light reflected at the interfaces. The color effect thus produced depends on the layer thickness of one metal oxide or more than one metal oxide (if several metal oxide layers are used). Figure 8 shows the typical structure of a layer–substrate pigment. As an example of such a pigment, a cross-section through a TiO_2 –mica pigment is included (scanning electron micrograph).

The layer–substrate principle was first used for effect pigments based on platelets of natural mica. To date, mica platelets coated with TiO_2 or α - Fe_2O_3 are among the most important pigments in this class [2]. The production of such pigments starts with the grinding of natural muscovite mica. The platelets produced during the milling process are classified to produce several grain fractions. The fractions play a decisive role in determining the optical properties of the pigment particles produced in the further manufacturing process, since their size and shape are derived from the mica platelets used. In the next step, the mica particles of a fraction are suspended in water. A titanium salt solution

(TiOCl_2 , TiOSO_4) or iron salt solution (FeSO_4 , FeCl_3) is dropped into the suspension at elevated temperature and defined pH with stirring. Under these conditions, titanium dioxide hydrate or iron oxide hydrate nuclei are formed, which are deposited on the mica platelets if the reaction is carried out appropriately. In the course of the reaction, an oxide hydrate layer grows on the platelets, the thickness of which is determined and adjusted by the amount of titanium or iron salt solution added. After the precipitation reaction is complete, the next steps are filtration, washing, drying, and calcination (700–950 °C). Only after thermal treatment is titanium dioxide or iron(III) oxide formed from the oxide hydrate on the surface of the mica platelets. This simultaneously achieves the high refractive indices that are so important for the reflection of light at the pigment surface. In addition, the layers adhere firmly to the substrate surface after calcination. In the case of titanium dioxide, the anatase modification is always formed after thermal treatment. To obtain rutile layers, thin tin dioxide layers are first deposited on the mica platelets. The structural relationship between SnO_2 and TiO_2 (rutile) causes the titanium dioxide formed during calcination to crystallize in the rutile modification. As with the titanium dioxide white pigments, surface coatings are also used for the metal oxide mica pigments for reasons of increased stability and improved compatibility with the application medium [2, 64].

More recent developments in special effect pigments include pigments based on platelet-shaped silica (goniochromatic color effects, i.e., strongly dependent on the viewing angle), aluminum oxide (extremely sparkling color effects, especially in paints, e.g., in automotive coatings), and borosilicate glass (particularly intense and pure interference colors). For some years now, platelets made of synthetic mica have also been available as substrates. A special production process has been developed for each of these substrate materials. The technology ranges from web coating (silicon dioxide) to crystal growth from molten salt (aluminum oxide, synthetic mica) to spraying of liquid glass drops from a glass melt onto a smooth substrate [64].

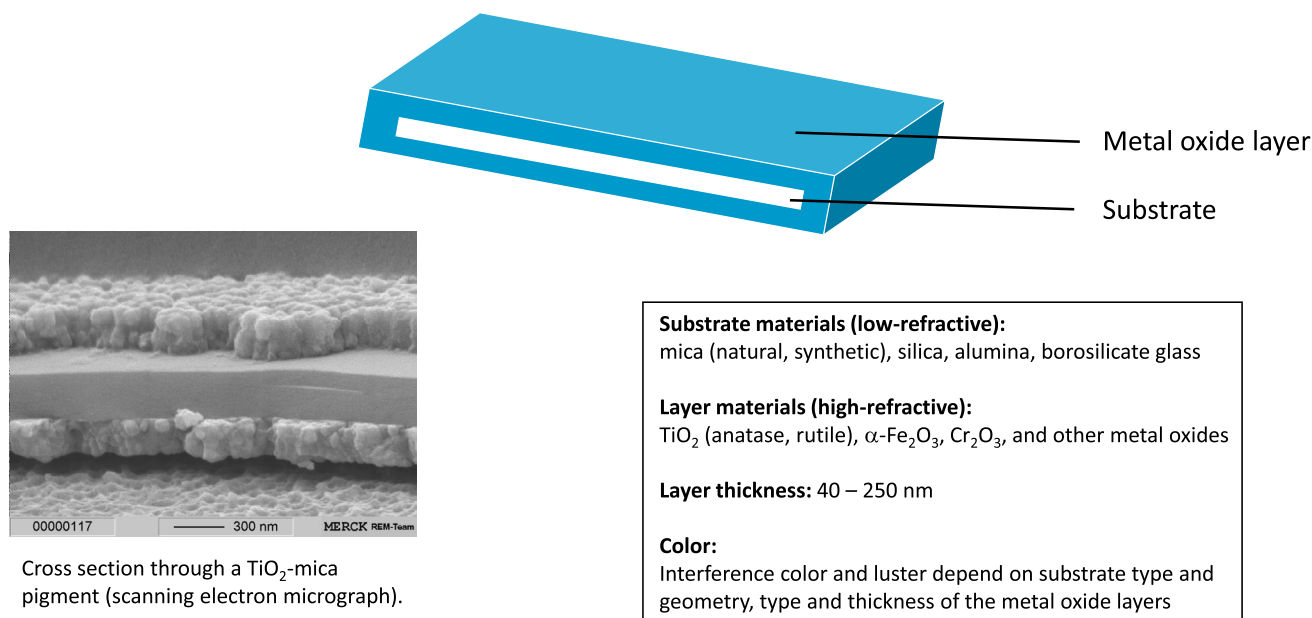


Fig. 8 Structure of layer-substrate pigments

New developments also include various effect pigments in which iron oxide layers are deposited on aluminum platelets. Such pigments combine the high hiding power of metal effect pigments with strong red, orange, and gold tones resulting from the absorption of the iron oxide in combination with interference phenomena [2].

Inorganic pigments with functional properties such as anticorrosive and magnetic pigments have been available for a long time. However, there is still a need for the development of improved but also completely new products in this segment. This involves functions such as corrosion protection, electrical conductivity, IR reflection, UV absorption, or laser markability. In all functional applications, pigment and application medium must be well matched to achieve the desired property of a surface, e.g., a paint film [65–68].

Some newer functional pigments are based on the layer-substrate principle already presented for special effect pigments. This principle can also be used in a suitable way for electrically conductive, IR-reflective, and laser-markable pigments [64, 65, 68]. Table 6 contains a list of such pigments with compositions and applications.

Electrically conductive pigments based on mica platelets coated with a conductive (Sn,Sb)O₂ layer exhibit

conductivity sufficient for antistatic flooring and electrostatic wet painting. Their advantage over conductive carbon black pigments is the light-gray color of the mica pigments, which offers the user extended coloristic possibilities.

Certain infrared-reflective pigments based on the layer-substrate principle are attracting growing interest for various applications. The main focus is on the range of solar thermal radiation (near infrared, 750–1400 nm). Mica pigments with TiO₂ layers of suitable thickness reflect a large part of solar thermal radiation from their surface while at the same time allowing through the main part of the light visible to the human eye and important for photosynthesis in plants (photosynthetic active radiation (PAR), 400–750 nm). Thus, such pigments, embedded in polymers, can be used in a favorable way for greenhouses and agricultural films, but also for transparent roof elements and exterior parts of buildings, where the aim is to avoid temperature rises under solar influence while maintaining the transmission of visible light [64, 65].

Functional pigments based on the layer-substrate principle are also suitable for laser marking of polymers. Layers consisting of TiO₂ or (Sn,Sb)O₂ deposited on mica platelets are particularly suitable for this purpose. When focused

Table 6 Functional pigments based on layer-substrate principle [2]

Pigment composition	Property	Application
(Sn,Sb)O ₂ /mica	Electrical conductivity	Antistatic flooring, electrostatic painting
Fe ₃ O ₄ /mica	Magnetism	Magnetic surfaces
TiO ₂ /mica	Solar heat reflection	Greenhouses, transparent roof lights
TiO ₂ /mica, (Sn,Sb)O ₂ /mica	Laser marking of polymers	Laser marking of plastics



Fig. 9 Examples of plastic parts with black (left) and white (right) laser marking

laser beams impinge on the pigment particles embedded in the polymer, very strong local heating occurs as a result of absorption of the laser light by the particles. This process can lead to carbonization of the polymer in the area of the absorbing particles and thus to dark-gray to black coloration. Even small amounts of 0.1% pigment in the polymer are sufficient to produce high-contrast markings. Lasers of different wavelengths are used for laser marking of polymers: CO₂ laser (10,600 nm), Nd:YAG laser (532 or 1064 nm), and excimer laser (193–351 nm). The markings created in the polymer are very durable and abrasion resistant. Typical applications for laser marking of polymers are found in the marking of electrical equipment, electronic components, medical devices, automotive components, and traceability codes and serial numbers of various products. Figure 9 shows examples of black and white marking of plastic parts containing laser-markable pigments. Light-colored laser markings are also possible. Here, pigments that lead to local foaming of the partially evaporating polymer when interacting with laser beams are used [2, 68].

Summary

The history of inorganic pigments began thousands of years ago. From the use of natural pigments in cave and wall painting to the synthetic pigments most commonly used today, it has been a long road marked both by man's search for ever new color design possibilities and by the use of empirically gained knowledge and later systematic, scientifically based chemical research. Today, a wide range of inorganic white, colored, black, and effect pigments are available, which when supplemented by organic pigments,

can comprehensively serve all relevant applications in color design. However, there is great interest in replacing pigments containing cadmium, lead, and chromate with pigments of the same color quality. Little progress has been made in this respect in recent decades (the exception being the yellow pigment bismuth vanadate, launched in 1975). Many inorganic compounds would be well suited as pigments in terms of their color but are not considered due to their toxic or carcinogenic properties. Many developments in recent decades have been directed primarily at optimizing the properties of existing pigments in terms of grain size, crystal structure, purity, stabilization (UV radiation), and good compatibility with the application medium. Innovations that have led and continue to lead to a large number of new products are to be found in effect pigments and functional pigments. Innovative new developments can also be expected in this field in the coming years.

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