Kirk-Othmer Encyclopedia of Chemical Technology.
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PIGMENTS, INORGANIC

1. Introduction

Originally derived from colored minerals, inorganic pigments are now highly engineered particles that impart color or functionality to the objects in which they are used. While inorganic pigments are still used in traditional applications, such as paints, ceramics, and cement, their resistance to the effects of radiation, temperature, and chemical attack has also led to use in high technology applications, such as fibers, engineering plastics, and highly durable coatings applied to roofing panels and even space equipment.

Inorganic pigment particles maintain their physical form, unlike dyes that dissolve in the substrate that they color. These particles are typically larger, easier to disperse, and more color stable in different applications than organic pigments. However, organic pigments tend to have higher strength, and often provide more vibrant colors.

The basic technology for making inorganic pigments is in many cases hundreds or thousands of years old. If one were to consider grinding red ochre across a cave wall as creating pigment particles, pigment production may be considered to be tens of thousands of years old, with the proof being the magnificent cave paintings found in France and Spain. Pigment technology has evolved, and within each pigment chemistry, the most cost efficient pigment in terms of particle size, crystal structure, or composition is used to provide the desired color. These pigments can also provide properties other than color, the most common are corrosion protection, interaction with ultraviolet (uv) or infrared (ir) light, and modifying physical properties.

Pigments are designed to interact with light, and synthetic pigments are optimized to the size that optimizes opacity, or provides the strongest absorption as to minimize the amount of pigment needed. For a pigment to be highly effective at either of these tasks, it must be of a size similar to that of the wavelength of light. The wavelength of visible light ranges between 0.4 and 0.7 μ, and pigment particles generally range in particle size between 0.1 and 10 μ.

Inorganic pigments are typically oxides, sulfides, chromates, silicates, phosphates, and carbonates of metallic elements. Most commonly, they contain some transition metal, due to their ability to interact with light. Since this interaction is also affected by crystal structure, the preparation of these pigments must be done under conditions that yield the desired structure.

Some new pigments have been developed due to improved understanding of crystal chemistry, but often the development of these new pigments is driven by environmental regulation of older pigments, or because new applications require a different set of properties than previously existed.

Today's inorganic pigment producers offer a wide range of pigments, from simple oxides, to complex oxide crystals, and even heterogeneous pigments with nano-sized phases incorporated into an inorganic matrix. Although development of inorganic pigment no longer lies in the forefront of chemistry, as it did in late nineteenth century Germany, extensive technology is still required to be a competitive manufacturer.

Historical classification of inorganic pigments into the classification of naturally occurring and synthetically produced is no longer useful, as most are now manufactured synthetically.

2. Properties

Pigments are produced, marketed, and utilized as either fine powders or dispersions of pigment particles in a carrier. The value of the supplied pigment form comes from its ability to color to an object with a minimum of additional processing. This color is controlled by the pigments' physical characteristics (crystal structure, particle size and distribution, particle shape, agglomeration, etc) and by their chemical properties (chemical composition, purity, stability, etc). The commercial value of pigments can also be enhanced by various surface treatments. The function of these treatments is to improve pigments coloristic values and durability or to simplify their physical handling.

In order for the color of an object to be controlled by the pigment, the pigment must provide opacity. Opacity is the ability to obscure the subject on which it is applied by preventing the transmission of light through the medium.

Pigments provide opacity to a transparent or translucent surface. The amount of opacity that is provided is a function of the refractive index difference between the pigment and the media in which pigment particles are dispersed. The multiple light reflections, or dispersion in the pigment–medium interface results in light only interacting with the top surface of an object, which therefore controls its color. This property is especially important in thin films, such as paints, where goal is to hide the original color of the object. A pigment with the particle size between 0.16 and 0.28 μm gives the maximum dispersion of visible light.

Any agglomeration of pigment particles can affect their opacity. Much effort has been spent by both pigment manufacturers and users to create the optimum particle size, and to maintain this size by keeping them well dispersed in the medium in which they are used.

The pigment color is determined by absorptions in the crystalline compound. As light photons are absorbed, the energy is transferred into electronic transitions in the crystal. These transitions are typically reversible, and generate heat. By changing the neighboring elements and their relative location in an inorganic crystal, the energy or these electronic transitions changes, and alters the color. Color is very dependent on composition and crystal structure, and can vary with impurities, physical stresses, and even temperature.

The performance characteristics of a pigment also depend on the medium in which it is used. In the case of ceramic applications, the pigment must be stable to high temperatures. These pigments must also be resistant to attack by alkali silicate melts since this is the basis for most glazes used to decorate ceramic objects. Once formed, the glaze protects the pigment from the environment, and weathering or chemical stability of the pigment is not an issue.

In the case of coloring of cement, the medium is relatively porous and the pigment is not totally protected from the environment. Color changes due to oxidation, hydration, and acidic and basic environments are often a concern.

In paints, the pigment must be compatible with the resin curing system. This means that it must have an affinity for the resin to stay dispersed, and it must be inert or facilitate the chemical processes that cause the resin to cure. For outdoor applications, the pigment–resin system must also be weather resistant. This refers to the coating's ability to resist color change or degradation from environmental stresses, such as uv light, moisture, temperature, and acidic environments.

In plastics, pigments must meet many of the same concerns as in paints, but also must be stable in a polymeric organic melt at higher temperatures. Failure may occur either by reduction of the pigment by this melt, or by partial dissolution of the inorganic pigment. The resultant inorganic impurities in the melt may degrade the polymer's performance.

Because of this interaction between the pigment and the medium in which it is dispersed, there are various resources to assist the formulator in choosing the correct pigments to use (1,2,3). Measuring properties other than color can assist the pigment manufacturer and user to determine the pigment's suitability.

2.1. Chemical Properties

2.1.1. Composition

Elemental analysis, impurity content, stoichiometry, and solubility are determined by a chemical or instrumental analysis. The use of instrumental analytical methods is increasing because they are usually faster and more accurate than wet chemical techniques. Atomic absorption spectroscopy (AA) and X-ray fluorescence (XRF) methods are the most useful instrumental techniques in determining chemical compositions of inorganic pigments. Chemical analysis of major components is carried out to determine pigment stoichiometry. Analysis of trace elements, especially toxic metals or compounds, is important to insure the pigment complies with regulatory requirements.

2.1.2. Crystal Structure

Crystal structure is measured by X-ray diffraction (XRD). Diffracted X-rays of a powder sample yield an angle dependent "powder diffraction pattern" that is related to the atomic spacings in a crystal. Powder diffraction patterns have three main features that can be measured: d spacings, peak intensities, and peak shapes. Through the use of existing powder diffraction files, or by using Rietveld ab initio structure determination, it is possible to determine the crystalline phases in the powder. Evaluation of these crystalline phases present can show if the pigment is fully reacted, if undesirable phases are present, and help to determine the oxidation state of the elements in the crystal. The width of the diffraction peaks also describes the degree of the crystallinity.

Typically, only one phase is preferred, such as single oxides (Fe_2O_3, Cr_2O_3, TiO_2, etc), and most CICP pigments. In these pigments, a secondary compound or crystal structure dilutes the properties of the desired pigment. In most cases, analyzed pigments are not completely unknown and comparing the powder diffraction pattern to known materials is sufficient in finding present phases or unreacted starting materials in the pigment. The most common structures of inorganic pigments are rutile, corundum, anatase, and spinel. Inclusion pigments, encapsulated pigments, and lithophones are typical examples of multicompound pigments.

Crystal structure determination is widely used to track phase development during the preparation of inorganic pigments synthesized by both wet chemical and solid solution routes. This information is used to refine formulation and processing conditions to yield the desired crystalline phase. Expertise in the preparation and evaluation of powder diffraction patterns is important, since the results can be dependent on particle orientation, particle size, and the scattering cross-section of the elements in the phase. X-ray analysis has become an indispensable tool of the inorganic pigments' development and production.

2.2. Physical Properties

2.2.1. Particle Size

Particle size and distribution are the most fundamental measured properties of powders. They impact a number of pigment characteristics. Those affected the most are the color (4,5), color strength, hiding power, and rheological properties. Particle size and distribution data can be easily misinterpreted. Only the data for spherical powders would be easy to measure and to interpret. The actual powders, however, consist of a population of particles of many different shapes. To complicate the matter further, powders are usually not formed from a mixture of single, free flowing particles. The particles can be interconnected together by weak forces (ie, electrostatic forces, liquid bridges) forming agglomerates, or by solid bridges (ie, chemical bonds, sintered necks) resulting in hard aggregates. To prevent powder dusting and make handling easier, some pigments are intentionally agglomerated to granules by the addition of granulating agents.

To permit a good description of powder population, a representative sample of the powder has to be collected, measured, and the results interpreted using statistical methods. To simplify the mathematical evaluation it is usually assumed that particles are spherical and the particle size is calculated as an average size. Particle size distribution (PSD) can either be presented in a graphical form as a distribution function, a histogram, or in a tabular form.

For inorganic pigments to be useful in most applications, they must have an average particle size between 0.1 to 10 μ. There are a growing number of applications for transparent pigments with particle sizes $< 0.1\ \mu$ for applications where transparency is desired. The most common of these "nano" pigments are transparent iron oxide and transparent titanium dioxide, which provide durability, absorb specific wavelengths, but provide little hiding.

The direct observation methods, optical microscopy and electron microscopy, describe the particle shape, which may have a large effect on the pigment suitability. However, a large number of particles must be evaluated to get a statistically significant measurement of particles size. Optical microscopy can estimate particle sizes down to $\sim 1\ \mu$, observation of smaller particles requires either scanning or transmission electron microscopy that can resolve to < 5 nm.

Sedimentation, light scattering, and electrical zone sensing techniques provide no information regarding the shape of the individual particles, but provide quick statistical information regarding the total particle size distribution. These indirect techniques are often used for quality control of the pigment powder. Of these techniques, laser scattering is the most utilized, due to its robust operation. It is important to note that the measured particle size of a material only correlates to its optical properties if they are equally dispersed. While this is difficult to achieve, particle size measurement with a strong ultrasonic dispersion often correlates well with optical properties of well-dispersed pigment systems.

One of the critical properties of a powder is the maximum particle size of the pigment particle. In many applications, the pigment must pass through a narrow tolerance aperture. In this case a small number of coarse particles may make the pigment unusable. Evaluation for suitability is often performed by a sieve test. In the typical sieve test measurement, a sample is placed on the top of one or a column of several sieves arranged in the order from the largest to the smallest sieve aperture. In a dry sieve test, the screens are vibrated mechanically or ultrasonically, and in a wet test the liquid carries the dispersed pigment through the screens. The samples collected on the individual sieves are weighed. When standard woven wire sieves are used, powders in ranging from 850 to 20 μm can be measured.

The coarse particles may also be detected in the end use application. One such test is the Hegman test for paints and dispersions, where coarse particles are detected as streaks or surface roughness in a gauge with a gradually decreasing opening.

2.2.2. Surface Area

Surface area measurement is typically performed by the Braunauer, Emmett, and Teller method (BET) that measures absorption onto a surface. This technique gives one number, typically reported in square meters per grams (m^2/g), and does not describe the shape or distribution of particle sizes in the sample. This technique is less dependent on particle dispersion than other indirect measurement methods. It may also give a good correlation to opacity or strength since the scattering and absorption of light often occurs at the surface of a particle. In the case where a dispersant is needed to keep the pigment deagglomerated, surface area can be used to calculate the approximate amount of dispersants to use.

2.3. Optical Properties

2.3.1. Color

The color provided by a pigment is affected by the difference in index of refraction between the pigment and the medium in which it is dispersed, and the pigment's size and shape. However, the ability to color an object at all is based on the intrinsic light absorptions of the pigment (6,7).

Light absorption in a material is due to chromaphores in the pigment. These chromaphores are atomic, molecular or ionic species that have electronic transitions that correspond to the same energy as visible light.

As light passes through the material, the electron is promoted to an excited state and light is selectively absorbed by these transitions. The unabsorbed light passes out of the pigment, and eventually reaches the eye. Because the light reaching the eye is missing the absorbed light wavelengths, color is perceived.

The wavelength for this absorption is related to the electronic transition by the formula:

$$\lambda = hc/E$$

Where E is the energy of the electronic transition, h is Planck's constant, and c is the velocity of light.

Important absorptions in inorganic pigments are *d–d* transitions, where electrons remain on the same atom but are promoted from one localized orbital to another, charge-transfer transitions where the electron is transferred to an adjacent atom, and band gap absorption where electrons are excited to a delocalized energy band.

Many transition metal compounds, such as Cr_2O_3 and NiO, are the result of *d–d* transitions. Chromates and mixed-valence transition metal compounds owe their color to charge-transfer transitions. Semiconductor type materials such as CdS yellow and Cd(S,Se) reds owe their color to the relatively low energy needed to promote electrons to a delocalized energy band.

The location of the atoms in the crystalline lattice modifies the energy levels available to the electrons. Hence, a given chromaphore may have a much different color in a different crystal, or at a different lattice site in the same crystal. The spinel crystal structure is a good example of this effect, with a range of transition metals able to be arranged on tetrahedral or octahedral sites.

2.3.2. Infrared Reflection

Transitions at energy levels outside the visible region may affect the ability of pigments to absorb or reflect ir energy. The energy in solar radiation is divided into uv (5%), visible (44%), and ir (51%) regions. The amount of solar radiation absorbed in all of these regions causes the surface to heat up. Due to the large amount of energy in the ir region, pigment manufacturers are optimizing and developing new chemistries to reflect ir radiation, and keep surfaces cool (8). These pigments, often referred to as ir reflecting pigments, are utilized on exterior surfaces where both a dark color and lower heat levels are desired.

2.3.3. Pigment Opacity and Hiding Power

A character, ie, color or pattern, of a substrate becomes obscured when coated with a pigment containing film, such as a paint or ceramic glaze. The degree of the obscuration, known as opacity, depends on the amount and the type of pigment used and the thickness of the applied film. The color of the reflected light is the result of the combination of the colors of substrate, pigment, and dispersion medium. In most cases, the dispersion medium is clear and it does not contribute to the color. At a certain pigment loading and/or film thickness the substrate becomes completely hidden and the pigment determines its color.

The ability of a coating to hide the substrate is called its *hiding power*. Hiding power of a uniform coating is expressed as the area of substrate that can be hidden by a unit volume of the coating (ft^2/gal or m^2/L). When the hiding power of a paint is low, several coats must be applied in order to hide the substrate. Some paints have an excellent hiding power and only one coating is necessary to hide the surface.

For white pigments, the hiding power can be expressed through the Lorentz-Lorenz equation (9) as a function of pigment (n_p) and medium (n_m) refractive indexes. For most organic binders with an average refractive index of ~1.5, and for pigments with a refractive index between 1.5 and 2.75, the hiding power (HP) can be approximated by an equation derived from the Lorentz-Lorenz one:

$$\mathrm{HP} \approx 0.16(n_p - n_m)^2$$

The larger the difference is between the pigment and binder refractive indices, the better the hiding power of the coating. For color pigments, the relationship between the hiding power and the pigment's physical properties is considerably more complex. Hiding power is also affected by the pigment particle size.

Hiding power and tinting strength of paint depends on the pigment concentration in the organic matrix. The concentration is usually expressed as the pigment volume concentration (PVC):

$$\mathrm{PVC} = V_{\mathrm{P}}/(V_{\mathrm{P}}+V_{\mathrm{O}})$$

where V_{P} is the pigment volume and V_{O} is the volume of the organic matrix.

Hiding power of a coating increases with the increasing pigment volume concentration. A critical pigment volume concentration (CPVC) is the pigment concentration, where individual pigment particles are dispersed in the matrix without directly touching each other. This concentration can be determined from the amount of linseed oil that is necessary to form a pigment paste (10): The knowledge of the critical pigment volume concentration is particularly important for coating formulation. Coatings with a higher pigment volume concentration than CPVC are porous and do not protect substrates well. Coatings with too low pigment volume concentration will have a tendency to blister.

Hiding power can be determined visually or instrumentally. Visually, the hiding power is measured by applying successive thin layers of coating until the substrate pattern is not visible. The result of this test is quite subjective. The hiding power can be determined instrumentally from the amount of the incident light reflectance of coated white and black substrates. Relationships derived from Kubelka and Munk theory (11) are applied in actual calculations.

2.3.4. Tinting Strength

The ability of a pigment to change the color of an opaque film is known as its *tinting strength*. In pastel colors, where a colored pigment is mixed with an opacifying white pigment, such as TiO_2, the tint strength determines how much colored pigment is needed to develop the desired shade. As such, it is one of the primary factors in evaluating the value of the inorganic pigment.

In a heavily opacified system, the amount of pigment needed to reach a desired color is inversely related to the tint strength.

The tint strength of a pigment may be determined visually by adding pigment to an opacified system until the same color results. The relative tint strength is calculated by the following equation:

$$\text{Relative tint strength} = (\text{amount of original pigment}/\text{amount of tested pigment})$$

The tint strength can also be calculated instrumentally. This is typically done by measuring the minimum reflectance values of a trial containing the standard and tested pigment at the same loading in an opacified system, the reflection of an unpigmented sample at the same wavelength, and calculating using the Kubelka Munk theory (12). The tint strength calculation is commonly found on most color measurement systems. The resultant tint strength value is often used by color formulators to determine the amount of pigment to use in their formulations.

2.3.5. Color Matching

Color matching is a process in which a technician prepares a formulation (a mixture of pigments in a desired medium) that has the color desired by the customer. The medium, as well as the processing conditions should be identical to those used by the customer.

Experienced color matchers can achieve a good color match by trial-and-error without any instrumentation. With improvements in color matching software, computer assisted color matching is becomming more common. It allows the formulator to choose the most cost-effective, least metameric formulations and calculates iterative trials that lead to the desired color values in a shorter time.

As the color space is three dimensional (3D), a mixture of at least four colorants is needed for color matching. Typically, one of these colorants moves the color either lighter or darker, and the others control the hue. The use of more than six colorants is discouraged because it allows multiple formulas to have the same color, but may be metameric.

One example of a four component system is the triaxial stains for ceramic glazes. The color matching is carried out using three high chroma pigment standards, namely, iron zircon coral, vanadium zircon blue, and praseodymium zircon yellow, with white provided by ground zircon. Higher loadings of colored pigments makes the color darker, and shifting the relative ratio of these pigments controls the hue.

A number of color matching philosophies have been developed in the industry and it is safe to say that color matching still falls somewhere between an art and a science (13).

2.4. Durability

An important property of a pigment is its ability to maintain its color when exposed to light, weather, heat, and chemicals. This property is seldom measured for pigments alone; rather it is determined for its dispersion in a desired medium (eg, paints, plastics). The observed changes are the result of complex pigment and media reactions and their possible interactions. Typically, testing is run with known standards included, and the conditions well defined.

2.4.1. Lightfastness and Weathering

The ability of a pigment to maintain its color when exposed to light is typically referred to as lightfastness. The ability of the pigment and the resin system to maintain its color under typical exterior environmental conditions is described as it's resistance to weathering. While a pigment may be evaluated because it is lightfast, it will not be used outdoors unless it weathers well in its desired application.

Lightfastness is measured by exposing pigmented film to an artificial or natural light, with the assumption that the medium does not contribute to the color shift. Weathering is measured by exposing the pigmented system to a harsh environment (eg, Florida exposure) for a predetermined time. Both lightfast and weathering are relative terms for the color change between the exposed sample and its original color values.

Many pigments, when exposed to high intensity light (sun, uv lamp) can get darker, change their shade or lose the color saturation. The color and its saturation change mainly for organic pigments. Inorganic pigments, particularly those containing ions that can exist in several oxidation states (eg, Pb, Hg, Cr, Cu) usually get darker. Some color changes can be reversible, while others are permanent.

Light, particularly its uv component, can also attack the organic medium in which the pigments are dispersed. The breakage of C—H, C—C, and C—O medium bonds leads to overall coating deterioration. The use of pigments that absorb the light in the uv region can therefore improve the coating stability.

Some pigments are photoactive and can accelerate the decomposition of the organic matrix. This decomposition frees pigment particles from the matrix, resulting in a so-called *chalking* of the paints or plastics. A continuous loss of pigment occurs. Chalking caused by titanium dioxide white, particularly its anatase form, is the best known example of a pigment accelerating the decomposition of the organic matrix. The mechanism of the chalking process is quite complicated and it requires not only light, but the presence of both water and oxygen (14,15). The whole process can be accelerated by heat. To reduce chalking of white paints, titanium dioxide pigment particles are surface treated with inorganic and organic coatings.

Various accelerated weathering procedures available in color testing laboratories may give a quick assessment of the performance of the pigment-medium system. Due to the wide variety of artificial exposure techniques, comparisons should only be made for trials run under the same conditions.

Before the final judgment of the system performance is made, accelerated test results should always be confirmed by outside exposure. Because outdoor exposure varies season to season, weathering comparisons are only valid on trials run at the same time. In the United States, Florida weather was considered to be an industry standard for testing colored coatings and plastics, but in some cases "North East Industrial" climates have been shown to be more severe, and testing in this environment is gaining acceptance.

2.4.2. Heat Stability and Chemical Resistance

Heat stability is measured as a change in the hue of the colored system and a degree of yellowing of the white system after exposure to a desired high temperature for a certain time. This property is particularly important in coloring engineering plastics. It can also be expressed as the maximum temperature at which the color of the system does not change. In many cases there is a need to compare the heat stability of several pigments. This can be done by the heat–time exposure of pigmented binders and by comparing the measured color differences.

In determining the chemical resistance, color changes of pigmented binder surfaces are measured after their exposure to various chemicals, such as water–sulfur dioxide, or water–sodium chloride systems. These systems imitate the actual environment to which the colored articles could become exposed.

2.4.3. Surface Treatments

The surfaces of pigment particles may not be suitable for the application in which they are to be used. To remedy this situation, end treatments are applied to the surface of pigment particles, giving them enhanced properties for many applications.

Most inorganic pigments are hydrophilic, and therefore can be readily wetted only by polar solvents, such as water. The wettability and dispersion of inorganic pigments in an organic matrix, such as a polymer or solvent, may be improved by the physical or chemical absorption of surface active compounds containing polar groups, such as $-NH_2$, $-OH$, or longer aliphatic chains on pigment particles. The absorption of these compounds makes the pigment surface hydrophobic. Compounds that help to form a bridge between the inorganic particles and an organic polymeric matrix are called coupling agents. The most common coupling agents are based on the tetrafunctional organometalic compounds of titanium, silicon, aluminum, and zirconium (16).

In some cases, a pigment's thermal and chemical resistance can be improved by the encapsulation of the pigment particles by an insoluble, colorless layer of metal oxide or metal hydroxide on the surface of the pigment. Common coatings are silica, SiO_2, or aluminum hydrate, $Al(OH)_3$. The function of the coating is to make a shell that prevents direct contact between the pigment surface and the medium in which it is used.

2.5. Specifications, Standards, and Quality Control

Specifications are written to insure that consistent quality is obtained from the pigment manufacturer. In most cases, this quality is specified to be within a measured color tolerance to a standard pigment. Additional specifications relating to stability, purity, pH, and particle size may also be written.

As stated earlier, there are a wide range of variables that may cause a color shift in the coloration of an object. Because of this, pigment producers typically control their color by standardized tests which approximate end use applications. In the case of TiO_2, typical specifications include color values, hiding power values, and chemical properties that are known to affect performance.

Colored pigments are typically specified by their color compared to a common standard pigment in a standard test technique. This comparison is performed in a masstone trial, a tint trial, or both types depending on the specific application. The masstone trial shows the color of the pigment alone in a relatively colorless medium. A match in a masstone test demonstrates that the ratio of absorbtion to scattering at various wavelengths is the same between the standard and tested pigment. However, it does not define the absolute absorption value. The tint trial is prepared with the pigment mixed in a medium with another highly scattering pigment, typically a white. By adding in a known scatterer, and still maintaining the same color to standard, the absolute absorption is shown to be the same between the standard and trial. This method allows prediction of the performance over a range of applications with only two trials, and is common in the industry.

At this time, there are no international standards governing the production of inorganic pigments. Given the highly customer-oriented business, it might be too difficult to set up any. Pigment producers meeting at least the International Standard ISO 9002 have a quality system established that guarantees some controls over the product consistency.

3. Production Volumes of the Key Inorganic Pigments

World production of inorganic pigments in 2004 can be estimated to be ~6.5 million metric tons with sales close to $15 billion. The global production of inorganic pigments has been growing at a rate of ~2.5% for the past 10 years, with this growth rate to a large extent controlled by titania white. This output can be compared with the world production of organic pigments, which for 2000 was 270 thousand metric tons, worth $3.0 billion (17).

Production growth is occurring primarily in South East Asia, with China becoming not only a major producer of titania white and iron oxide pigments, but a major user as well. Colored pigment production on chemistries, such as chrome oxide, and iron oxides are also being relocated to China. This rapid change is due to large differences in production costs making older facilities unprofitable.

About 8 million metric tons of carbon blacks are produced worldwide, but most of them are not used for the pigmentary applications. The United States is the largest producer, followed by Western Europe and Asia. For pigmentary applications the use is estimated to be $<$ 150 thousand metric tons. As tires are getting smaller and lasting longer due to their improved quality, the consumption of carbon blacks in the United States has been steadily decreasing in the last decade. The Pacific Rim region consumes ~1.7 million, Western Europe ~1.1 million, and the former Eastern Europe ~1.5 million metric tons. Overall, between 10 and 15% of the produced carbon blacks are used for pigmentary applications excluding the manufacture of tires. The world's leading producers of carbon blacks are: Cabot Corporation, Degussa AG, Columbian Chemicals, China S.R. Corporation, Adita Birla (Birla Carbon) and Sid Richardson Carbon & Energy. These companies have production facilities in various parts of world and produce about two-thirds of the world's carbon black.

Titanium dioxide is by far the most often used pigment by the industry (18). In 2004, the estimated worldwide production was ~4.4 million metric tons. Compared to the decade spanning 1982–1992, where the average annual increase was 5.4%, in the decade from 1994 to 2004 the rate of annual increase was only 2.5%. There are ~50 world producers of titanium dioxide pigments. The world's leading suppliers are DuPont (~25% worldwide share of pigmentary grade titanium dioxide, all by the chloride process). Other producers include Huntsman Tioxide, and Millennium International Chemicals, Tiwest, Kemira Oy and Kronos.

Iron oxide is the next most used inorganic pigment with an estimated worldwide consumption in the year 2000 of 1.5 million metric tons billion (19). China is the leading producer of iron oxide pigments with an estimated 30% of the world production. Other estimates place Europe production at 25%, mostly synthetic, India at 20%, mostly natural, Japan at 15%, and North America 10%. The production of iron oxides in the United States is declining. At its peak in 1999, production was 183,000 MT, and by 2003 reported production had dropped to 90,000 MT (20).

The four major producers that produce about one-half of the world's synthetic iron oxide are Lanxess (spun off from Bayer), Cathay Pigments, Elementis, and Rockwood Pigments.

Out of that total production, the United States consumed ~300,000 MT, mainly for pigmenting construction products (34%) and for coating applications (23%). Western Europe consumed ~350,000 MT with the United Kingdom accounting for ~20% of it. The Japanese demand for iron oxide, though small, has grown from ~30,000 to 50,000 MT in the last decade.

Other pigments, while quite important, are consumed in considerably smaller amounts. Also, the market data for these pigments are not as readily available as those for carbon blacks, titanium dioxide, and iron oxides.

Lithopone, an important white pigment, is produced mainly in the former Soviet Union, the Czech Republic, and the People's Republic of China. Today's worldwide production can be estimated to be $<$ 250 thousand metric tons (21).

While the worldwide production of zinc oxide is estimated to be $\sim$500 thousand metric tons annually, only $\sim$75–100 thousand metric tons are used for pigmentary applications by the paint industry. About 250 thousand metric tons are consumed by the rubber industry, and the rest is used in the production of plastics, paper, cosmetics, pharmaceutical products, ceramics, and glass.

Due to environmental regulations, the consumption of lead-based pigments (lead chromate, in particular) has been decreasing steadily at an average annual rate of $\sim$5% in the last decade; in 1993 it was estimated to be $\sim$20 thousand metric tons. Cadmium-based pigments have been hit particularly hard by new regulations. As the result, their consumption in 1993 can be estimated to be between 1.5 and 5 thousand metric tons. The future of this pigment category is particularly questionable in North America.

The worldwide consumption of the CICP (Complex Inorganic Colored Pigments), previously referred to as mixed-metal oxide (MMO) pigments in 2004 can be estimated to be $\sim$30 thousand metric tons. The major worldwide suppliers of these pigments are Bayer AG and Dr. H. Heubach AG in Germany, Engelhard Corporation, Rockwood Pigments and Ferro Corporation in the United States. (The pigment business of DMC2, Degussa Metals Cerdec Catalysts was purchased by Ferro Corporation in 2001.) All these companies have worldwide manufacturing and/or distribution centers. Other suppliers of mixed metal oxide pigments include Shepherd Color in the United States and Ishihara in Japan.

Figure 1 illustrates graphically how the production volumes of other key pigments (usually expressed in thousand of metric tons) are dwarfed by the production volumes of titanium white, iron oxides, and carbon backs.

4. White Pigments

The most common white pigments used today are titanium dioxide, zinc oxide, leaded zinc oxide, zinc sulfide [1314-98-3], and lithopone, a mixture of zinc sulfide and barium sulfate [7727-43-7]. The use of lead whites and antimony oxides has been decreasing steadily for environmental reasons.

4.1. Titanium Dioxide

4.1.1. History

Chemically, titanium white is titanium dioxide either in an anatase or rutile form. The history of this pigment is relatively short compared to other white pigments. Commercial production of this pigment was discovered during this century in Norway and in the United States during the investigation of ways to convert ilmenite to iron or titanium–iron alloys. The first industrial productions of titanium white were reported in 1918 in Norway, the United States, and Germany. These processes were not producing pure titanium dioxide as a white pigment, but as a mixture with barium sulfate.

The first manufacturing of pure titanium white for pigment use (anatase form) was reported in 1923 in France. However, the real growth of the production and use of titanium white pigments began in the early 1930s and continued today, but the rate of growth has decreased recently. In 2004, the worldwide production is estimated at 4.4 million tons.

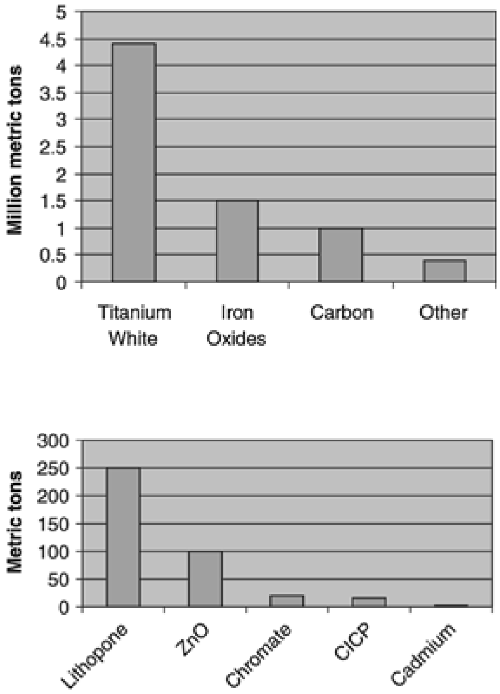

Fig. 1. Production volumes of key pigments.

4.1.2. Properties

Crystals of titanium dioxide can exist in one of the three crystal forms: rutile [1317-80-2], anatase [1317-70-0], and brookite [12188-41-9]. Both rutile and anatase crystallize in the tetragonal system, brookite in the rhombic system. Only anatase and rutile forms have good pigmentary properties.

Anatase is softer than rutile with a hardness of 5–5.5 Mohs. It is less weatherable and has a lower index of refraction of 2.49, and therefore provides less hiding. Anatase is primarily used in paper and fiber applications where lower abrasion is important. Anatase will transform rapidly to rutile at a temperature $> 700^\circ$C.

The higher temperature rutile form has both better weathering and a higher refractive index of 2.73. This makes it the primary white pigment for coating applications, the major user of inorganic pigments. Most rutile pigments have a particle size $< 0.5\ \mu$. A well-dispersed rutile pigment with a 0.2–0.3 μ average particle size will result in a coating the highest coverage of commercial white pigments, about 38 m^2/g.

Titanium whites resist various atmospheric contaminants, such as sulfur dioxide, carbon dioxide, and hydrogen sulfide. Under normal conditions they are not readily reduced, oxidized, or attacked by weak inorganic and organic acids. Titanium dioxide dissolves slightly in bases, hydrofluoric acid and hot sulfuric acid. Being chemically inert, as well as environmentally preferred, allows titanium dioxide to be the preferred white in most all paint, paper, and plastics applications.

4.1.3. Production

Since titanium is the seventh most common metallic element in the earth's crust, titanium minerals are plentiful in Nature (22). The most common mineral–raw materials used for the production of titanium dioxide pigments are shown in Table 1.

Table 1. Mineral Raw Materials for the Production of TiO_2 White

Mineral/raw material	Main composition	Yield % TiO_2
ilmenite	$FeO—TiO_2$	35–65
leucoxene	$Fe_2O_3—TiO_2$ (+TiO_2)	60–90
rutile	TiO_2	90–98
anatase	TiO_2	80–90
titanium Slag	TiO_2 (Fe)	70–85
rutile (synthetic)	TiO_2	85–96

Ilmenite is more abundant than rutile. Its world's supplies are estimated to meet the requirements of the industry for the next 150 years. The largest sources of ilmenite are in Australia, Canada, South Africa, Russia, and the United States. Large, unexplored sources of this mineral also exist in China. At this time ~9 million metric tons of ilmenite is mined annually. Long term atmospheric effects will weather ilmenite into leucoxene [1358-95-8], which contains most of its iron as Fe^{3+}. The majority of the world's supply of rutile comes from the beach sands of Australia, Florida, India, Brazil, and South Africa. The total worldwide supply is estimated to be ~50 million metric tons, with about a half million tons mined a year.

Titanium slag and synthetic rutile are also used as raw materials in the production of titanium whites. Titanium slag results from a metallurgical process during which iron is removed from ilmenite by reduction with coke in an electric arc furnace at 1200–1600°C. Under these conditions, iron oxide is reduced to metal, melts, and separates from the formed titanium slag. Titanium slag contains 70–75% of TiO_2 and only 5–8% of iron.

Synthetic rutile raw material is produced from ilmenite by reducing its iron oxides and leaching out the metallic iron with hydrochloric or sulfuric acids. In both processes, the objective is to increase the amount of TiO_2 in the raw materials.

Titanium white pigments are commercially produced either by the older sulfate process (SP), or by the chloride processes (CP). The advantages of the sulfate process are low capital investment and low energy consumption. The disadvantage is the formation of a large amount of by-products: 3–4 tons of ferrous sulfate heptahydrate [7782-63-0] $FeSO_4·7H_2O$ and 8 tons of diluted sulfuric acid for each ton of titanium dioxide pigment. Difficulties in finding an effective use for these by-products led to the commercialization of the chloride process. In the past 20 years the chloride process has overtaken the sulfate process as the most common production method. While the sulfate process is still widely used in developing markets, it is rapidly being eliminated where environmental costs are high. North American production in 2003 showed only 119 out of 1772 metric tons of titanium dioxide produced by the sulfate process (23). The chloride process is simple, but requires more expensive raw materials and a higher capital investment. For certain applications, CP pigments are needed (automotive top coats, coil-coatings and PVC). These applications, however, represent only ~10% of world demand. For the balance, good quality SP and CP pigments are virtually interchangeable. Further details of both processes are discussed below.

4.1.3.1. Sulfate Process. The flow chart of the sulfate process is presented in Figure 2.

Titanium-bearing raw materials, ilmenite or titanium slag, are beneficiated before their digestion in sulfuric acid. The beneficiation consists of the milling, screening, and drying of raw materials to ~40 μ particles. To prevent formation of hydrogen during the digestion process, any metallic iron must be magnetically separated at this point. Digestion of the ground raw materials is carried out using a concentrated sulfuric acid. The reaction is started by adding water or oleum to the reactor. During the addition of sulfuric acid, heat is generated that raises the temperature in the reactor to between 170 and 220°C, and starts the ilmenite decomposition.

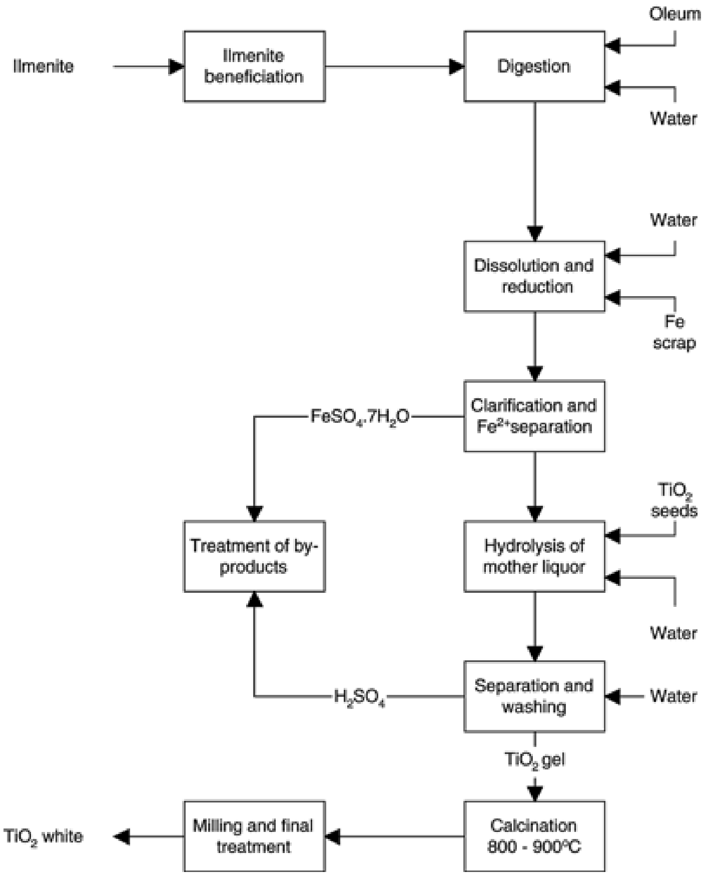

Fig. 2. Flow chart of sulfate process for the production of the pigment titanium white.

This decomposition usually lasts ~12 h and can be described by the following:

$$FeTiO_3 + 2\,H_2SO_4 \rightarrow TiOSO_4 + FeSO_4 + 2H_2O$$

Under normal conditions, 95–97% of TiO_2 from ilmenite is solubilized. Most of the iron in the solution is in the Fe^{2+} oxidation state. Any Fe^{3+} present in the solution must be reduced to Fe^{2+} since iron can only be removed by crystallization in its divalent form. The reduction is usually done by adding some scrap iron during the digestion step.

The cake produced by the digestion is extracted with cold water and possibly with some diluted acids from the subsequent processes. During the cake dissolution, it is necessary to maintain the temperature close to 65°C – the temperature of iron sulfate maximum solubility. To prevent the reoxidation of the Fe^{2+} ions during processing a small amount of Ti^{3+} is prepared in the system by the Ti^{4+} reduction. The titanium extract, which is a solution of titanium oxo-sulfate, iron sulfate, and sulfuric acid, is filtered off. Coagulation agents are usually added to the extract to facilitate the separation of insoluble sludge.

The main impurity of the filtrate is iron(II) sulfate, which can be crystallized as the heptahydrate, $FeSO_4 \cdot 7H_2O$, by cooling the solution to a temperature $< 15°C$. This process is most often carried out in vacuum crystallizers. The crystals of iron sulfate are separated by centrifugation or filtration. To prevent premature hydrolysis of titanium dioxide, the temperature of the above processes should not exceed 70°C.

The concentrated mother liqueur contains a large amount of sulfuric acid in a free form and as titanium oxy-sulfate and some metal impurity sulfates. To yield the purest form of hydrated TiO_2, the hydrolysis is carried out by adding crystallizing seeds to the filtrate and heating the mixture close to its boiling temperature (∼109°C). The crystal structure of the seeds (anatase or rutile) and their physical properties will affect the pigmentary characteristics of the final product.

Chemically, the hydrolysis step can be described by a simple reaction:

$$TiOSO_4+(n+1)H_2O \rightarrow TiO_2{\cdot}nH_2O+H_2SO_4$$

Whereas the hydrolysate, $TiO_2{\cdot}nH_2O$, does not have any pigmentary properties, its physical characteristics, such as particle size, will eventually affects its value as a pigment. For that reason, the conditions of the hydrolysis step have to be carefully controlled.

To produce the anatase titanium dioxide pigment, the crystallization has to be initiated by anatase microcrystalline seeds. These can be prepared by neutralizing a small portion of the mother liqueur, eg, by NaOH addition and heating the formed suspension to 80–90°C. The formed microcrystals have a particle size of ∼1 nm and an anatase crystal structure. Adding these microcrystals to the original mother liqueur (in a concentration of ∼0.5–1.0% as related to TiO_2) and hydrolyzing the mixture for 3–6 h will yield the pigment with the anatase crystal structure.

To produce the rutile titanium dioxide pigment, hydrolysis of the mother liqueur has to be carried out in the presence of a specially prepared hydrosol as a seeding agent. This hydrosol is made by the neutralization of a portion of the mother liqueur in the presence of hydrochloric or other monohydric acid. Because of the large amount of the hydrosol must be added to the mixture (∼6% concentration), the hydrolysis reaction only takes ∼1 h.

Since free sulfuric acid is present, the hydrolysate has to be quickly separated from the mother liqueur to prevent its possible dissolution. The separation and subsequent water washing is usually carried out by rotary vacuum filters. Even after a good washing of the gel, ∼10% of H_2SO_4 (in relation to the weight of TiO_2) remains in the cake. This remainder is removed during the following calcination step. The hydrolysate is usually doped with small quantities of various chemicals to improve the pigmentary properties of the final product.

The calcination of the washed cake of the hydrated gel of TiO_2 is carried out in rotary kilns similar to those used for producing cement. The kilns are directly heated with gas or oil. An excess of air in the kilns is required to prevent the possible reduction of TiO_2 to its lower oxides. The presence of such oxides, even in small quantities, will give the final product a bluish-gray shade.

During calcination, water is removed at temperatures between 200 and 300°C; sulfur trioxide is removed at temperatures between 480 and 800°C. At about 480°C, the crystals of TiO_2 are being formed and they continue growing with the increasing temperature. To prepare the anatase pigment, the final calcination temperature of the hydrolysate prepared in the presence of anatase seeds should reach ∼800–850°C.

To produce the titanium white rutile pigment, the hydrated TiO_2 gel prepared in the presence of rutile seeds is calcined at temperatures of 900–930°C. This temperature is quite important as pigments with a particle size of 200–400 nm are produced at these temperatures. When the calcination is carried out at temperatures $>$ 950°C, the particles of TiO_2 become considerably larger and they will not have optimum pigmentary properties.

The calcined TiO_2 exits the rotary kiln in the form of various aggregates and agglomerates. It must be milled to attain its optimum pigmentary properties. The milling can be wet or dry and can be combined with air classification to produce the pigment with its optimal particle size distribution. During the wet milling, soluble salts present in the pigment can be removed.

4.1.3.2. Chloride Process. The flow chart of the chloride process is presented in Fig. 3.

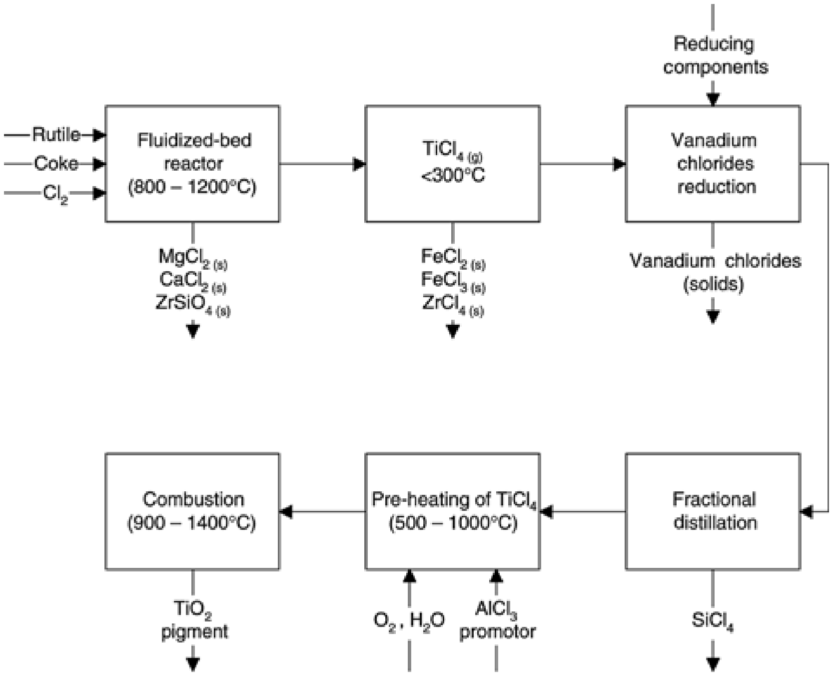

Fig. 3. The chloride process.

In the chloride process, finely ground rutile reacts with chlorine in the presence of calcined petroleum coke. At a temperature between 800 and 1200°C, the following reaction occurs:

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

Today, the chlorination is mostly carried out in fluidized-bed reactors. While the reaction is slightly exothermic, the heat generated during the reaction is not sufficient to maintain it. For that reason, a small amount of oxygen is added to the mixture to react with the coke and to create the necessary amount of heat. To prevent any formation of HCl, all reactants entering the reactor must be completely dry. At the bottom of the chlorination furnace, chlorides of metal impurities present in the titanium source (eg, magnesium, calcium, and zircon) accumulate.

Impurities that form volatile chlorides leave as gases at the top of the furnace together with $TiCl_4$. By cooling those gases, most impurities, with the exception of vanadium and silicon chlorides can be separated from titanium tetrachloride. Vanadium chlorides can be reduced to lower oxidation state chlorides that are solids; highly volatile $SiCl_4$ can be removed from $TiCl_4$ by fractional distillation.

High purity $TiCl_4$ is preheated, mixed with hot oxygen (sometimes also with a small amount of water) and combusted at 900–1400°C to TiO_2.

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

Factors, such as reaction temperature, excess of oxygen, water addition, addition of other minor reactants (eg, $AlCl_3$ to promote the formation of rutile), mixing conditions inside the reactor, and many others influence the quality of TiO_2 pigment. In general, titanium white pigments produced by the chloride process exhibit better lightness than those produced by the sulfate process.

For many applications, the individual particles of titanium dioxide pigment have to be encapsulated by the shell of an inorganic oxide, eg, SiO_2, and/or coated with an organic surfactant. These coatings are fulfilling two functions: They prevent a possible reaction between the highly reactive surface of TiO_2 and the matrix it is dispersed in, and improve their dispersability in those matrices. Any reaction between pigments and the matrix can result in poor lightfastness and weathering of the pigmented article. Poor pigment dispersability can have immediate economic impacts.

The deposition of inorganic coatings on the surface of pigment particles can be carried out either from a gaseous phase or by precipitation from an aqueous solution. Particles can also be partially coated by absorbing coating agents during milling operations.

4.1.4. Use

Titanium dioxide is mainly used in the production of paints and lacquers (∼50%), plastics (∼20%), and paper (∼20%). Other applications include the pigmentation of printing inks, rubber, textiles, leather, synthetic fibers, glass enamel, white cement, roofing granules, and cosmetics.

Nonpigmentary applications are in the production of glass, ceramics, electroceramics, catalysts, and as raw materials to form mixed-metal oxide pigments.

4.2. Zinc Oxide

By volume, zinc oxide is the second most significant white pigment. It is known as zinc white, Chinese white, or flowers of zinc. Its pigmentary properties are good, providing good coverage. It has a good lightfastness and is well miscible with other pigments.

Zinc oxide pigments have a lower index of refraction (2.95–2.10) than both anatase and rutile titanium dioxide whites. It has a lower Mohs hardness (4–4.5) and may be used where abrasion is critical.

The chemical properties of zinc white are considerably worse than those of titanium white. Zinc oxide dissolves in many inorganic acids and bases. While it is not attacked by water, it reacts with SO_2 and CO_2 to form sulfates and carbonates, respectively. As zinc white pigments are slightly basic, they react readily in paints with the acidic film-forming agents. This property causes the thickening of ZnO containing paints and facilitates their hardening. If these properties are not desirable, another pigment must be used. With the increasing popularity of titanium dioxide as a white pigment, the use of zinc oxide has been decreasing.

4.2.1. History

Historically, ZnO is an older pigment than TiO_2. In France, the industrial production of zinc oxide started in 1840. In the French process, zinc white was produced by the direct combustion of zinc vapors. Around 1850, the New Jersey Zinc Company in the United States started producing zinc oxide by a two step process (American process). Almost 99% of zinc oxide is produced by one of the two dry processes.

The direct American process is basically a metallurgical operation. Zinc oxide ores are reduced with coal in a rotary kiln at temperatures of 1000–1200°C to zinc metal. At these temperatures the produced zinc metal evaporates and is oxidized with air to ZnO in the upper part of the kiln.

$$\mathrm{ZnO\ (ore)+C \rightarrow Zn_{(g)}+CO}$$

$$\mathrm{Zn_{(g)}+0.5O_2 \rightarrow ZnO}$$

Because of the limited availability of high quality zinc oxide ores and the lower quality of produced zinc oxide (it can contain oxides of Pb, Cd, etc) this production process has limited applications.

In the indirect French process, metallurgically refined zinc metal is boiled and the generated vapors are combusted with air to zinc oxide. As metallic zinc is the starting material of this process, the process is more expensive than the American one. Today, however, it is the preferred production method because it yields a purer product. Volatile metals, such as lead and cadmium, are again the main impurities that can be found in zinc white. Complex purification methods, such as fractional distillation, have been devised to reduce the amount of these impurities to acceptable levels.

Different types of furnaces (rotary, muffle) can be used for producing zinc vapors. In most cases, these furnaces are heated with gas. The oxidation of zinc vapors is carried out with preheated air in specially designed chambers:

$$Zn_{(g)}+0.5O_2\rightarrow ZnO$$

Because the oxidation reaction is highly exothermic, the temperature in the combustion chamber reaches 1200°C and microcrystals of zinc oxide are formed. By controlling the reaction conditions in the combustion chamber, zinc oxide with an optimal particle size (400–700 nm) can be produced. In combustion chambers, an excess of air (30–50%) must be maintained to prevent an undesirable reaction of zinc vapors and zinc oxide, with combustion by-products:

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

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

$$2Zn+CO_2\rightarrow 2ZnO+C$$

Formed zinc oxide microcrystals are collected in a series of sedimentation chambers. The largest particles are collected in the first chamber together with nonoxidized zinc, cadmium, and lead oxide. Finer fractions settle in the subsequent chambers. The grades of the produced zinc oxide are determined by its purity, particle size, and shape.

4.2.2. Use

While zinc oxide was originally used as a pigment, at present its most important application is to aid in vulcanizing synthetic and natural rubber. Up to 5% of ZnO can be present in rubber products. Paint and coating industries are not using anymore zinc white as their main white pigment, but it is used as an additive to improve anticorrosion properties, mildew resistance and durability of external coatings. Zinc oxide is also used as a chemical in the production of many mixed metal oxide pigments, particularly spinels.

4.3. Zinc Sulfide

While zinc sulfide is mainly important as a component of the composite white pigment *lithopone*, it also has a limited use as a single pigment. Under the commercial name *Sachtolith*, pure ZnS is produced by Sachtleben Chemie in Germany. Properties of ZnS are reported in the Lithopone section where they are compared with properties of $BaSO_4$, the second component of lithopone.

Zinc sulfide has, after titanium white, the second highest refractive index of all the white pigments. Its chemical and thermal resistances are, however, inferior to those of TiO_2. As a pigment it has a pure, white color shade, it reflects uv radiation, and, because its particles are spherical, the oil number of the pigment is quite low. The sphericity of the particles, as well as their low hardness of 3 Mohs, contribute to the low abrasivity of this pigment. This property reduces machinery damage during extrusion of plastics and fibers and therefore in some application it is preferred over titanium white pigments.

4.3.1. Production

Zinc sulfide production started in the United States and in Europe in the 1920s. In the early 1950s, zinc sulfide, like most white pigments popular at that time, was slowly replaced by the more superior titanium white. Zinc sulfide can be prepared by a process similar to the one used to manufacture lithopone. In the first step, barium sulfide is reacted with sodium sulfate to produce sodium sulfide solution:

$$BaS+Na_2SO_4 \rightarrow Na_2S+BaSO_4$$

In the following step, sodium sulfide is reacted with zinc salts to produce the final product:

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

Most of the heavy metal impurities present in zinc salt solutions must be removed before the precipitation reaction, or they will form insoluble colored sulfides and reduce the whiteness of the zinc sulfide pigment. This end is usually achieved by the addition of zinc metal that will reduce most heavy metal ions to their metallic form. The brightness of zinc sulfide can be improved by the addition of a small amount of cobalt salts ($\sim$0.04Co/100Zn) (24). Barium sulfate formed in the first step is isolated and can be used as an extender.

Zinc sulfide can also be prepared by the direct reaction of barium sulfide with zinc chloride solution:

$$BaS+ZnCl_2 \rightarrow ZnS+BaCl_2$$

Commercially, zinc sulfide is available in the standard untreated grade and in several grades with particles treated by surfactants to improve their dispersability in either aqueous or organic media.

4.3.2. Use

Zinc sulfide is used in applications where white color shade and low abrasivity are required. In printing inks and paints, it also contributes to their stability and good rheological and printing properties. For those reasons, zinc sulfide is mainly utilized for coloring plastics, synthetic fibers, and in the preparation of special coatings, greases and lubricating oils. When used to color sealing compounds, it also slows down their aging and helps to preserve their elasticity.

4.4. Lithopone

Lithopone is a mixture of ZnS and $BaSO_4$. The pigmentary properties of the mixture are determined by zinc sulfide, and therefore lithopone pigments are characterized by the amount of ZnS present in the mixture. While the amount of ZnS in commercial lithopones varies from 15 to 60%, the most common is a 30% lithopone pigment, containing 28–30% of ZnS and 70–72% of $BaSO_4$. It has an average index of refraction between that of zinc sulfide (2.37) and barium sulfate (1.64). Its hardness is similar to that of zinc sulfide.

4.4.1. Production

Commercial production of lithopone started in the first one-half of the nineteenth century, and continued to grow until the middle of this century when titanium dioxide started to dominate the white, inorganic pigment market.

Lithopone is prepared by combining barium sulfide and zinc sulfate solutions at 50–60°C:

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

Both zinc sulfide and barium sulfate are insoluble in water. To improve the stability of lithopone, a small amount of a cobalt salt is added to the precipitated mixture. The mixture has to be filtered off, dried, and calcined. The calcination is carried out in rotary calciners at temperatures between 600 and 700°C. During calcination, the particle size of zinc sulfide grows from its original size ($\sim 0.1\ \mu m$), to the pigmentary-optimal size of $0.4–0.6\ \mu m$.

Hot lithopone leaving the calciner has to be cooled quickly to prevent the oxidation of ZnS to ZnO. Rapid cooling is accomplished by its suspension in water that may contain a small amount of sulfuric acid to remove any traces of undesirable zinc oxide. The suspension is then wet milled, filtered off, and dried to the commercial product.

The barium sulfide needed for the reaction is prepared by the reduction of barite, $BaSO_4$, with petroleum coke in a rotary furnace:

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

The fused product contains ~60–85% of barium sulfide, unreacted barium sulfate, and impurities present in barite and ash. The soluble barium sulfide is extracted from the mixture with water and separated from the insoluble impurities by filtration.

The other component of the lithopone precipitation reaction, zinc sulfate, is prepared by the dissolution of various zinc containing raw materials in sulfuric acid:

$$Zn+H_2SO_4 \rightarrow ZnSO_4+H_2$$

The amount of impurities present in the zinc sulfate solution is determined by the local source of zinc-containing material used in the above reaction. To get a good quality Lithopone, the impurities must be removed from the solution.

Pure solutions of zinc sulfate can only be used for the preparation of lithopone with a low percentage of zinc sulfide (up to 30%). Additional zinc compound must be added for the preparation of lithopone with a higher concentration of ZnS. Most often that compound is zinc chloride. One can either use a mixture of sulfuric and hydrochloric acid for the dissolution of zinc-containing raw materials, or directly mix separately prepared solutions of zinc sulfate and zinc chloride. The precipitation of 60% of the lithopone can be approximated by the following reaction:

$$2ZnSO_4+5ZnCl_2+7BaS \rightarrow 7ZnS+2BaSO_4+BaCl_2$$

During this reaction, some barium ions remain in the solution as chlorides and can be utilized for the preparation of other barium compounds.

4.4.2. Use

Lithopones are used in water-based paints because of their excellent alkali resistance; in paper manufacturing as a filler and opacifying pigment; and in rubber and plastics as a whitener and reinforcing agent.

4.5. Lead Whites

Basic lead carbonate, sulfate, silicosulfate, and dibasic lead phosphate are commonly referred to as lead whites. Usage is limited because of environmental restrictions placed on the use of lead-containing compounds.

5. Colored Pigments

5.1. Iron Oxide Pigments

The worldwide consumption of iron oxide pigments represents ~40% of the total production of colored, inorganic pigments. Iron oxides can be produced by the beneficiation of naturally occurring materials or synthetically from iron salts. Natural iron oxide pigments account for only ~30% of the total iron oxide production. Some of the natural iron compounds are the oldest pigments known to mankind. Chemically, they are oxides or oxide–hydroxides compounds of iron(III). The following oxides and oxide–hydroxides have acceptable pigmentary properties and are components of natural and synthetic iron oxide pigments: yellow goethite [1310-14-1] α-FeO(OH); orange lepidocrocite [12022-37-6] γ - FeO(OH); red hematite [1317-60-8] α - Fe_2O_3; and brown maghemite [12134-66-6] γ - Fe_2O_3.

Black magnetite, a binary iron oxide ($FeO.Fe_2O_3$) with a spinel structure, has not gained wide acceptance as a pigment because of its poor tinting strength. Orange Lepidocrocite, often referred to as yellow iron oxide, and red hematite or red iron oxide are the most common grades. These two oxides are also important raw materials for the production of many mixed-metal oxide pigments.

In general, all iron pigments are characterized by low chroma and excellent lightfastness; they are nontoxic, nonbleeding, and inexpensive. They do not react with weak acids and alkalis, and if they are not contaminated with manganese, they will not react with organic solvents. However, properties vary from one oxide to another.

5.1.1. Natural Iron Oxides

The earth's crust contains ~7 wt % iron oxides, but only a few deposits are rich enough in iron to be suitable for mining pigmentary-quality iron oxides. Deposits that are a suitable source of natural iron oxide pigments are usually hydrated aluminum silicates that contain various amounts and forms of iron oxide. Most of these are contaminated with oxides of aluminum, manganese, magnesium, and in some cases, carbon and other organic compounds. After a mechanical beneficiation, and in some cases calcination, iron oxides are supplied to the market as red, ocher, sienna, and umber natural pigments. The hue of the natural iron oxide pigments is determined by their raw material composition and processing. Material composition varies from one geographic location to another as does the quality of iron pigments. In some cases, iron oxide pigments have a name that reflects the mine location, for example Persian red comes from the Ormuz Island in the Persian Gulf.

About 60% of the natural iron oxide pigments are used to color cement and other building materials, and ~30% is consumed in the production of paints. For coloring plastics and rubber, synthetic iron oxide pigments are preferred. The main advantage of the natural iron oxide pigments, as compared to the synthetic ones, is their low cost. However, their quality is inferior, and in most cases, they are consumed in close proximity to the mines. As colorants, they are ~50% weaker than synthetically produced iron oxides.

5.1.2. Synthetic Iron Oxides

Iron oxide pigments have been prepared synthetically since the end of the seventeenth century. The first synthetic red iron oxide was obtained as a by-product of the production of sulfuric acid from iron sulfate containing slate. Later, iron oxide pigments were produced directly by the thermal decomposition of iron sulfates. Today, ~63% of all iron oxide pigments consumed are prepared synthetically.

Advantages of synthetic iron oxides over their natural counterparts include their chemical purity, more uniform particle size and size distribution, and in the case of precipitated oxides, the ability to prepare them in predispersed vehicle systems by flushing techniques. The popularity of browns, yellows, and earth-tone colors, and environmental regulations that are limiting the use of heavy metal toxic pigments, are helping to increase the sale of iron oxides worldwide. In Europe, iron oxide pigments dominate construction materials (ceramics, cement, roofing granules). In the United States, it is mainly the paint and coating material sectors that are consuming the largest quantities of these pigments. Other areas of synthetic iron oxide applications are plastics, paper, and magnetic recording tapes.

5.1.2.1. Iron Oxide Reds. From a chemical point of view, red iron oxides are based on the structure of hematite, α-Fe_2O_3, and they can be prepared in various shades, from orange through pure red to violet. Different shades are controlled primarily by the oxide's particle size, shape, and surface properties.

Production. Four methods are commercially used in the preparation of iron oxide reds, two stage calcination of $FeSO_4.7H_2O$, precipitation from an aqueous solution, thermal dehydration of yellow goethite, α-FeO(OH), and oxidation of synthetic black oxide, Fe_3O_4.

The final product of all the above processes is iron(III) oxide, α-Fe_2O_3, but its properties are determined by the method of preparation. Thermal dehydration of goethite yields a pigment with the lowest density (4.5 g/cm^3), the highest density pigment is one prepared by two-stage calcination (5.2 g/cm^3). The particle size varies from 0.3 to 4 μm, while the refractive index varies from 2.94 to 3.22. A large variance in oil absorptions results from the variety of particle shapes associated with these iron oxides. Hiding power for the group is 120–200 m^2/kg.

The largest volume of synthetic red iron oxide is produced by the two-step calcination of iron(II) sulfate. In the first step, the iron(II) sulfate heptahydrate is dehydrated to a monohydrate:

$$FeSO_4{\cdot}7H_2O \rightarrow FeSO_4{\cdot}H_2O + 6\,H_2O$$

The second step involves thermal decomposition of the monohydrate product at a temperature above 650°C in the absence of air (25):

$$6FeSO_4{\cdot}H_2O \rightarrow 2Fe_2O_3 + Fe_2(SO_4)_3 + 6H_2O + 3SO_2$$

$$Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3SO_3$$

or in the presence of air:

$$6FeSO_4{\cdot}H_2O + 3/2O_2 \rightarrow 3Fe_2O_3 + 6SO_3 + 6\,H_2O$$

By-products of these reactions are reclaimed and recycled. The color depends on the size of the particle formed, which is controlled by regulating the calcination time and temperature. The calcined product is ground, washed, and classified.

Wet preparation of red iron oxides can involve either a hydrothermal process or a direct precipitation and growth of iron oxide particles on specially prepared nucleating seeds of Fe_2O_3. In the hydrothermal process, iron(II) salt is chemically oxidized to iron(III) salt, which is further treated by alkalis to precipitate a hydrated iron(III) oxide gel. The gel can be dehydrated under pressure at a temperature of ~150°C to anhydrous hematite.

In the direct precipitation process, the seeds of iron(III) oxide are added to an iron salt solution, most often iron(II) sulfate, which is subsequently oxidized by air. The released sulfuric acid is removed by the addition of metallic iron with which it reacts to iron(II) sulfate. The overall reaction shows that ferrous sulfate is not consumed during the process. Actually, it only helps to oxidize metallic iron to ferric oxide:

$$2FeSO_4+2Fe+3/2O_2\rightarrow Fe_2O_3+2FeSO_4$$

The reaction conditions are critical, as hydrated iron oxide, $Fe_2O_3{\cdot}H_2O$, can also precipitate. The particles are either spherical or rhombohedral, depending on the nucleating material.

Ferrite reds can also be prepared by calcining synthetic yellow iron oxide and the process parallels the production of reds from natural yellow oxides. Red iron oxide pigments can also be produced by the oxidation of the ferrous oxide component, FeO, of the binary black iron oxide, $FeO.Fe_2O_3$, at 370°C. The original cubic shape of the black iron oxide is retained. A Venetian red iron oxide is prepared by calcining a mixture of iron sulfate and lime. The final product typically contains 40 wt% Fe_2O_3, 60 wt% $CaSO_4$. The color range of Venetian red is not as wide as that of the other iron oxides and is limited to light shades.

Synthetic red iron oxides are prepared in a variety of grades from light reds to dark reds and they are sold under a variety of names, eg, Indian red, Turkey red, and Venetian red.

Use. Synthetic red iron oxide can be used in most products requiring red pigmentation. It is thermally and chemically stable, and because it absorbs uv radiation, it is added to plastics, paints, and paper to prevent their decomposition by uv radiation. Most red and brown materials are pigmented by the synthetic iron oxides. Calcined iron oxide (copperas red) is particularly suitable for coloring rubber. Pigments prepared by the oxidation of synthetic black Fe_3O_4 are very pure and are used as an additive to pharmaceutical and cosmetic products.

5.1.2.2. Iron Oxide Yellows. From a chemical point of view, synthetic iron oxide yellows, also known as iron gelbs, are based on the iron(III) oxide hydroxide, α-FeO(OH), known as goethite. Their color varies from light yellows to dark buffs and is primarily determined by particle size, which is usually between 0.1 and 0.8 μm. The density of iron gelbs is 4.05 g/cm^3, the refractive index is between 2.3 and 2.4, and an oil absorption between 30 and 60 g/100 g. They are stable in air and water and they weather well. Because of their resistance to alkalis, they are used by the building industry to color cement. Thermally, iron oxide yellows are stable up to 177°C; above this temperature they dehydrate to iron(III) oxide:

$$2\,FeO(OH)\rightarrow Fe_2O_3+H_2O$$

Production. Three commercial processes are used for the production of iron yellows (the Penniman) Zoph process, the precipitation process, and the Laux process.

The Penniman-Zoph process involves the preparation of seeds or nucleating particles by the alkali precipitation of ferrous sulfate. The reaction is carried out at a low temperature with an excess of ferrous ions; the hydroxide is then oxidized to the seeds of hydrated ferric oxide:

$$FeSO_4+2\,NaOH\rightarrow Fe(OH)_2+Na_2SO_4$$

$$4Fe(OH)_2+O_2\rightarrow Fe_2O_3{\cdot}H_2O+4H_2SO_4$$

The seeds are transferred to tanks containing scrap iron and a ferrous sulfate solution, and the mixture is heated to a temperature between 70 and 90°C. While the seeds circulate over the scrap iron, air is bubbled through the medium causing the seeds to grow. The process can be described by the following reactions:

$$4\,\mathrm{FeSO_4}+6\,\mathrm{H_2O}+\mathrm{O_2}\rightarrow 4\,\mathrm{FeO(OH)}+4\mathrm{H_2SO_4}$$

$$4\,\mathrm{H_2SO_4}+8\,\mathrm{FeSO_4}+2\mathrm{O_2}\rightarrow 4\,\mathrm{Fe_2(SO_4)_3}+4\mathrm{H_2O}$$

$$4\,\mathrm{Fe_2(SO_4)_3}+4\,\mathrm{Fe}\rightarrow 12\,\mathrm{FeSO_4}$$

The overall reaction can be summarized as,

$$4\,\mathrm{Fe}+3\,\mathrm{O_2}+2\,\mathrm{H_2O}\rightarrow 4\,\mathrm{FeO(OH)}$$

indicating that in this process it is actually the metallic iron that is consumed in the production of yellow gelbs, and ferrous sulfate is the intermediate that is replenished by the reaction of formed sulfuric acid with the scrap iron. Variables that affect production and determine the shade of yellow are: the temperature of the reaction, the circulation rate of oxygen, the circulation rate of the ferrous sulfate solution, and the size and shape of the seed particles. As the reaction continues over several days, larger particles develop, which are deeper and redder. The reaction is stopped at the desired hue and the precipitate is washed free of soluble salts, dried carefully, ground, and bagged.

Iron oxide yellows can also be produced by the direct hydrolysis of various ferric solutions with alkalis [eg, NaOH, $Ca(OH)_2$ and NH_3]. To make this process economical, ferric solutions are prepared by the oxidation of ferrous salts (eg, ferrous chloride and sulfate) that are available as waste from metallurgical operations. The produced precipitate is washed, separated by sedimentation, and dried at ~120°C. Pigments prepared by this method have lower coverage, and because of their high surface area, they have a high oil absorption.

The Laux process is a modification of the Bechamp reaction that was discovered in 1854. It has been used for the reduction of nitrobenzene to aniline with metallic iron:

$$\mathrm{C_6H_5NO_2}+2\,\mathrm{Fe}+2\,\mathrm{H_2O}\rightarrow \mathrm{C_6H_5NH_2}+2\,\mathrm{FeO(OH)}$$

Originally, iron oxides were the by-products of this reduction process and did not have any pigmentary properties. Laux of Bayer AG (26) discovered that when the reduction is carried out in the presence of aluminum or ferrous chlorides high quality iron pigments can be produced. At the end of the reduction process, aniline is distilled off, and the pigments are separated from the unreacted iron, washed, dried, and ground or micronized. Depending on the reaction conditions, red α-Fe_2O_3, or yellow α-FeO(OH) pigments can be produced by this process.

Use. Yellow iron oxides strongly absorb radiation in the blue and uv spectral regions. For that reason, they are particularly useful in protecting polymers in plastics and paints from degradation caused by sun exposure. Iron gelbs are the preferred yellow pigments in coloring plastics and paints.

5.1.2.3. Iron Blacks. Chemically, iron blacks are based on the binary iron oxide, $FeO.Fe_2O_3$. Although the majority is produced in the cubical form, they can also be produced in acicular form. Most of the black iron oxide pigments contain iron(III) oxide impurities, giving them a higher ratio of iron(III) than would be expected from the theoretical formula. Iron blacks have a density of 4.95–5.18 g/cm^3, a refractive index of 2.42, and an oil absorption of 18–28 g/100 g. In most cases, their particle size is between 0.1–0.8 μm. They provide high coverage and have good weather and alkali resistance. They are thermally stable up to 110°C when the ferrous component oxidizes to ferric oxide, which can end up (depending on the temperature and conditions) as a brown γ-modification ($> 180°C$) or a black α-modification ($> 350°C$).

Production. Iron blacks can be produced by one of two processes. The major process used worldwide for the production of black iron oxide pigments is a modified Laux process (the aniline process). If the nitrobenzene reduction to aniline is carried out in the presence of aluminum chloride, iron gelbs are formed. By substituting aluminum chloride with ferrous chloride, black binary iron oxides, $FeO.Fe_2O_3$, are formed.

In the second process, iron black pigments are prepared by a partial oxidation of the precipitated ferrous salts. The most common raw material is iron(II) chloride waste from metallurgical operations, which is treated with a stoichiometric amount of calcium hydroxide. The iron oxide suspension formed is partially air oxidized at room temperature until the ferrous to ferric ratio is 1:1. At that time, additional calcium hydroxide is added, and the oxidation is completed at about 90°C, resulting in a final 1:2 ferrous to ferric ratio. The overall reaction can be expressed as

$$2\,Fe(OH)_2+O_2 \rightarrow Fe_2O_3+2H_2O$$

$$Fe(OH)_2+Fe_2O_3 \rightarrow FeO\cdot Fe_2O_3+H_2O$$

After oxidation, the precipitate is washed, filtered off on a rotary filter, and the separated paste is dried at ~100°C. The final particle size of the product is achieved by dry milling. The product has a black color with various brown or blue shades.

Use. Synthetic iron blacks are used in paints because of their favorable particle size distribution, ease of dispersion, and their relative inertness towards iron and steel when compared to other pigments. Their oil absorption number is low, and paints prepared with them have a low viscosity and good coverage. They are also used for coloring construction materials, cosmetic products, and as an additive to animal feed.

5.1.2.4. Iron Browns. Iron browns have a density between 4.70 and 4.95 g/cm^3, a refractive index ~3.0, an average particle size of 0.1–0.8 μm, and an oil absorption number around 25 g/100 g. They are often prepared by blending red, yellow, and black synthetic iron oxides to the desired shade. The most effective mixing can be achieved by blending iron oxide pastes, rather than dry powders. After mixing, the paste has to be dried at temperatures ~100°C, as higher temperatures might result in the decomposition of the temperature-sensitive iron yellows and blacks. Iron browns can also be prepared directly by heating hydrated ferric oxides in the presence of phosphoric acid, or alkali phosphates, under atmospheric or increased pressure. The products of precipitation processes (ie, the yellows, blacks, and browns) can also be calcined to reds and browns.

Use. Iron browns have excellent pigmentary properties. They are used for the surface treatment of leather, for the production of wood stains and floor paints, and for coloring cement, plastics, rubber and cardboard.

5.1.3. Micaceous Iron Oxide (MIO) Pigment

The majority of micaceous iron oxide consumed today comes from natural sources, but several methods have been developed for the production of synthetic MIO. Most of them are based on thermal or hydrothermal processes under special conditions. An example of the thermal process is the reaction of ferric chloride with iron at 500–1,000°C in an oxidizing atmosphere (27).

5.2. Complex Inorganic Color Pigments

Based on the crystal structure, the Color Pigments Manufacturers' Association (CPMA), (formerly Dry Color Manufacturers' Association, DCMA) has classified 53 key inorganic pigments into fourteen categories. In 1991, in its third catalogue edition (28), the CPMA has decided to call these inorganic colorants *complex inorganic color pigments*. The Association felt that the original name, (*MMO*) *pigments*, did not accurately describe the chemical nature of all the classified pigments. In particular, several single oxides (eg, Cr_2O_3, and Fe_2O_3) and metal salts [eg, $Co_3(PO_4)_2$, and $CoLiPO_4$] that were included in the CPMA classification are not mixed metal oxides.

The name complex inorganic colored pigments is used because these pigments are solid solutions or compounds consisting of two or more metal oxides. Each pigment has a defined crystal structure that is determined by the host lattice. Other oxide(s) interdiffuse at high temperatures into the host lattice structure forming either a solid-state solution or a new compound. The CICP pigments belong to a significant, but by volume, a small category of inorganic pigments. Most of them contain metal cations balanced by oxygen anions with structures similar to naturally occurring minerals. Structurally, CICP pigments belong to one of the 14 structure types, the most common ones are rutile and spinel. Their commercial significance is in their thermal, chemical, and light stability, combined with their low toxicity. When they are employed for coloring glass enamels and ceramics, they are sometimes referred to as *colors* or *stains*; when used to color paints and plastics, they are known as pigments.

The color of CICP pigments results from the incorporation of cations of transition metals, so-called *chromophores*, into the structure of stable *host oxides*. The host can be a single oxide (eg, SnO_2, TiO_2), or a mixed oxide (eg, $ZrSiO_4$, $MgAl_2O_4$). Most of the host oxides can be found as minerals in Nature, and when pure, they are usually colorless. It is the stability of these oxide host lattices that gives these pigments high thermal stability and resistance towards the corrosiveness of mediums in which they are dispersed (e.g. molten glass in glazes and enamels). The refractive index of the host oxide also affects the hiding power of the produced pigment. Typical host oxides are baddelleyite [12036-23-6], ZrO_2; Zircon, $ZrSiO_4$; cassiterite, SnO_2; Sphene, $CaSnSiO_5$, spinels, $MgAl_2O_4$, $TiZn_2O_4$, corundum/hematite, Al_2O_3, Fe_2O_3; and rutile, TiO_2. Typical chromophores are transition-metal ions, such as Fe, Cr, Mn, Ni, Co, Cu, and V.

When the host is a mixed oxide, the incorporation of the chromophore is best achieved during its high temperature formation from single oxides:

$$ZrO_2+SiO_2 \rightarrow ZrSiO_4$$

$$CaO+SiO_2+SnO_2 \rightarrow CaSnSiO_5$$

When the host is a single oxide, incorporation is best achieved during a high temperature phase transition of the host lattice, such as when TiO_2 transforms from anatase to rutile, or during its formation from carbonates or other salts.

The crystal defects of the host lattice structure aid in the incorporation of chromophores. By increasing those defects, reactants can diffuse more easily through the product layers and the pigment is formed faster. The presence of mineralizers can also positively affect the solid-state reaction (29). A mineralizer is a compound that facilitates crystal growth during solid-state reactions by providing a local environment that makes the movement of reactants through the solids' mixture easier.

The color of the resultant pigment is caused by the created ligand field which surrounds the chromophore. An example of this is the pink to blue color change in cobalt containing oxide crystals as the bonding changes from octahedral to tetrahedral as discussed by Weyl and co-worker (30).

5.2.1. Spinel Pigments

Pigments with a spinel structure are widely used as ceramic colorants for glazes, and also by the paint and plastic industries. They produce a wide range of colors containing browns, yellows, greens, blues and blacks, and many are thermally stable up to 1400°C. Spinel compounds have a common chemical formula AB_2O_4; structurally they have a cubic symmetry and are derived from magnesium aluminate, $MgAl_2O_4$, a naturally occurring mineral. Common MMO compounds with the spinel structure include the following chemistries: $Zn(Fe,Cr)_2O_4$ browns, $CoAl_2O_4$ blue, $Co(Al,Cr)_2O_4$ blue greens, Co_2TiO_4 green and $CuCr_2O_4$, and $(Ni,Mn,Co)(Cr,Fe)_2O_4$ blacks.

Most spinels contain small quantities of other metal oxides, *modifiers*, to change their color shade without affecting the crystal structure. More than half of the spinel pigments reported by the CPMA are dark (brown and black).

5.2.2. Rutile Pigments

Structurally, all rutile pigments are derived from the most stable titanium dioxide structure: rutile. The crystal structure of rutile is very common for AX_2 type compounds, such as the oxides of four-valent metals, (eg, Ti, V, Nb, Mo, W, Mn, Ru, Ge, Sn, Pb, Te) and halides of divalent elements (eg, fluorides of Mg, Mn, Fe, Co, Ni, Zn).

Rutile pigments, prepared by dissolving chromophoric oxides in an oxidation state different from 4+ in the rutile crystal lattice, are described by Hund (31,32). To maintain the proper charge balance of the lattice, additional charge-compensating cations of different metal oxides also have to be dissolved in the rutile structure. Examples of such combinations are presented below:

$$Ni^{2+}+Sb^{5+} \text{ in 1:2 ratio as } NiO+Sb_2O_5$$

$$Cr^{3+}+Sb^{5+} \text{ in 1:1 ratio as } Cr_2O_3+Sb_2O_5$$

and

$$Cr^{3+}+W^{6+} \text{ in 2:1 ratio as } Cr_2O_3+WO_3.$$

Many pigments with such substitutions have been commercialized. The most important are Ti—Ni—Sb yellow Ti—Mn—Sb brown and Ti—Cr—Sb buff. Rutile types of pigments can be prepared by the simple calcination of mixed starting oxides. For example, the Cr—Sb—Ti yellow pigment (33) can be produced by mixing chromium and antimony oxides (10–20% by weight) with titanium dioxide (80–90% by weight). The anatase form of TiO_2 is the preferred starting material as it changes to rutile (at temperatures ~900°C) that is defective and highly reactive. The recommended calcination temperature is 1040°C.

Rutile pigments are used to color plastics, paints and enamels (firing temperature 750–850°C); some are stable enough to be used to color ceramic glazes (firing temperature 950–1000°C). They are used in high volume paint and plastics applications for exterior weathering due to their high durability and their ability to reflect ir radiation and minimize surface temperature. There are 13 classifications of rutile pigments by the CPMA.

5.2.3. Zircon Pigments

Zircon pigments are almost exclusively used in ceramic applications and are relatively new compared to other complex inorganic color pigments. Blue zircon pigment was discovered in 1948 (34), yellow in the early 1950s, and pink in the 1960s (35,36). The earliest studies describing the effects of reaction conditions on the properties of zircon pigments were published in 1962 (37). Several more recent publications describe today's understanding of the reactions occurring during the formation of zircon pigments (38,39,40,41,42).

Because zircon is stable up to 1600°C, and is resistant to attack by silicate melts, zircon pigments are used in a wide range of ceramic glazes. At high temperatures, they begin to loose their strength, due to a combination of dissolution and chromaphore migration out of the crystal (43).

Zircon pigments are derived from the tetragonal zirconium silicate, $ZrSiO_4$, which is also used as an opacifier in glazes and porcelain enamels. In pigments, zirconium silicate serves as the host lattice for various chromophores, such as vanadium, praseodymium, iron, etc. Zirconium silicate crystals are usually formed in situ during pigment preparation by a high temperature reaction of ZrO_2 and SiO_2:

$$ZrO_2 + SiO_2 \rightarrow ZrSiO_4$$

To facilitate this reaction, mineralizers such as alkali halides are added to the mixture. In rare instances, zircon pigments are prepared directly from the zircon mineral, $ZrSiO_4$. Based on the mechanism of color formation, zircon pigments can be divided into two categories, substitution-defect pigments and inclusion pigments. Defect pigments have more brilliant colors than inclusion pigments, but only a few are known. The blue Zr—Si—V and yellow Zr—Si—Pr pigments are probably the best known of this type. An example of an inclusion pigment is the pink coral pigment formed by surrounding fine particles of Fe_2O_3 by the zirconium silicate lattice. The pigment is essentially a mixture of phases and can be described as $(ZrSiO_4)_{1-x}\cdot(Fe_2O_3)_x$.

Inclusion of cadmium sulfoselenide into a zircon lattice results in red and orange pigments that are stable enough to be used in coloring glazes. These pigments are also a mixture of phases and can be described by the formula: $(ZrSiO_4)_{1-x}\cdot[Cd(S_{1-y}Se_y)]_x$.

5.2.4. Bismuth Vanadate

The use of lead chromate pigments has been slowly phased out of many applications. Thus a search for more environmentally acceptable relatively inexpensive yellow pigments having excellent coloristic properties has been ongoing.

The use of bismuth vanadate [14059-33-7], $BiVO_4$, as a nontoxic, yellow pigment with good hiding strength and lightfastness was patented by DuPont in 1978 (44). Because of the high cost of bismuth, the pigment could not compete with the inexpensive lead chromate, and for years $BiVO_4$ has only been a laboratory curiosity. That situation has changed as the result of environmental pressures, and at this time many pigment producers, including Ciba, BASF, and Cappelle in Europe and Dainichiseika in Japan are marketing this pigment primarily for plastic and paint applications.

Bismuth vanadate can be produced by chemical precipitation, as well as by high temperature calcination methods. In the wet process, the acidic solution of bismuth nitrate, $Bi(NO_3)_3$, is mixed with the alkaline solution of sodium vanadate, Na_3VO_4. The formed gel is filtered off on a filter pressed, washed, and converted to a crystalline form by calcination at low temperatures of 200–500°C for 1 h (45,46). Multiple phase pigments can be prepared by the coprecipitation of bismuth vanadate with compounds of molybdenum, tungsten, or niobium (47). If needed, the product can be milled to remove any agglomerates and optimize its particle size.

In the calcination process, a mixture of corresponding oxides and an optional modifier (eg, molybdic acid) are milled together to achieve a homogenous mixture. The mixture is calcined at 750–950°C and milled to a desired particle size. Wet milling in an alkaline medium is recommended to remove any unreacted vanadium salts that are believed to degrade the pigmentary properties of bismuth vanadate (48).

For most applications, bismuth vanadate is not thermally or chemically stable enough, and it has to be encapsulated with a dense, amorphous shell of silica (49,50). It is recommended that bismuth vanadate be granulated to improve its handling and eliminate any dusting problems.

5.3. Chromium (III) Pigments

There are two green pigments based on chromium in the 3+ oxidation state. The first one is chromium oxide, Cr_2O_3, and the second is hydrated chromium oxide, $Cr_2O_3 \cdot xH_2O$. Their worldwide production is ~50 thousand metric tons. Major producers are Bayer in Germany, Elementis in the United Kingdom and Nipon Denko in Japan. Production is China is growing rapidly.

5.3.1. Chromium (III) Green Pigment

Chromium oxide green is characterized by outstanding lightfastness with excellent resistance to acids, alkalis, and high temperatures. Because it weathers well, chromium oxide green is applied as a colorant for roofing granules, cement, concrete, and outdoor industrial coatings. It is also used in ceramic applications. Because they can withstand vulcanization conditions and do not degrade, chromium pigments are also used for rubber pigmentation. One unique feature of chromium oxide green is that it reflects ir radiation similarly like chlorophyll. Therefore, it is used extensively in formulating camouflage coatings for military applications. One drawback for some applications is its abrasiveness.

5.3.2. Hydrated Chromium (III) Green Pigment

Hydrated chromium oxide has a brilliant green color and is referred to as Gingnet's green. It exhibits a limited hue range, is semitransparent with a low opacity, but provides excellent lightfastness and alkali resistance. Water of hydration limits its heat resistance to application temperatures no $> 260°C$; thus, the pigment is unsuitable for ceramic use. Transparency permits the formulation of polychromatic finishes. Its consumption has diminished since the introduction of phthalocyanine green in the 1940s.

5.4. Ultramarine Pigments

Ultramarines are derived from lazurite [1302-85-8] (Lapis lazuli), a semiprecious stone, which was the natural source of ultramarine blue for hundreds of years. Ultramarines can be prepared in many shades. Examples of commercially significant ones are ultramarine blue, ultramarine violet and ultramarine pink. The ultramarine pigment with a green shade can also be prepared but it is not commercially available. The first German Patent issued in 1877 was for the manufacture of ultramarine red (51).

Chemically, ultramarines are complex sodium aluminates with a zeolite structure. The basic lattice can be approximated by the formula $Na_6Al_6Si_6O_{24}$ with entrapped sodium ions and ionic sulfur groups that causes the pigment's color. The composition of ultramarine blue varies within certain ranges: Na_2O, 19–23 wt %; Al_2O_3, 23–29 wt %; SiO_2, 37–50 wt %; S, 8–14 wt %.

Ultramarine blue is prepared from intimate mixtures of china clay, sodium carbonate, sulfur, silica, sodium sulfate, and a carbonaceous reducing agent, e.g., charcoal, pitch, or rosin.

The largest use of ultramarine blue is for use in plastics, and it is also used in printing inks, textiles, artist colors, cosmetics, and laundry bluing.

5.5. Cyanide Iron Blues

Cyanide iron blue, also known as Prussian blue, is one of the oldest industrially produced, inorganic pigments. Chemically, cyanide iron blues are based on the $\{Fe^{2+}[Fe^{3+}(CN)_6]\}^-$ anion, with the charge balanced by sodium, potassium or ammonium cations. Modern iron blues are ammonium salts. Iron blue pigments were usually named according to their place of production or their original developer. For those reasons they became known as Berlin or Prussian blue, Milori blue, Paris blue, Chinese blue, Toning blue, or Turnbull blue.

Cyanide iron blues can be prepared by several methods. The most common one is the indirect, two-step process. In the first step, a white precipitate (Berlin white), is produced by the reaction of sodium, potassium,

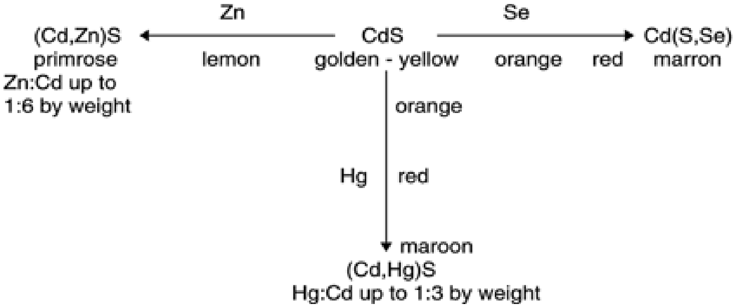

Fig. 4. Color and composition correlation of cadmium.

or ammonium ferrocyanide with ferrous sulfate:

$$Fe^{2+}SO_4 + M_4^+[Fe^{2+}(CN)_6] \rightarrow M_2^+Fe^{2+}[Fe^{2+}(CN)_6]$$

The precipitate is digested with hot sulfuric and following digestion, is oxidized with sodium chlorate or sodium bichromate to iron blue, $M^+\{Fe^{2+}[Fe^{3+}(CN)_6]\}^-$. After oxidation, the iron blue is filtered, washed, dried, and packaged.

Iron blues are mainly used by the printing industry for coloring printing inks.

5.6. Cadmium Pigments

Historically, cadmium pigments have been very important, providing a range of clean, bright shades of yellow, orange, red, and maroon colors. Unfortunately, their bright and durable color comes at the expense of environmental concerns associated with the production and use of Cd, Se, and Hg containing compounds.

Cadmium pigments are prepared by either precipitation or a combination of precipitation and calcination. During calcination between 500 and 700°C, Cd and S components may escape, requiring both care for the formulation and to mitigate the toxic volatiles. The pigment color is determined by the ratio of Cd (and Zn, or Hg, if present) to S and Se in the product and can be changed all the way from primrose to maroon. The mercury substitution for cadmium yields (Cd,Hg)S pigments with red and maroon shades similar to those obtained with the selenium substitution. The Cadmium Association provides a simple diagram showing the color and composition correlation (Fig. 4.)

Cadmium pigments are primarily used in engineering plastics, where organic pigments cannot withstand the processing temperatures. Cadmium pigment usage is relatively stable since color formulators have already replaced cadmium pigments wherever feasible. The number of producers has been decreasing over the past 10 years. At this time there is only one major producer of cadmium pigments in the United States (52). Over the past 10 years production has been near 2000 metric tons/year. Major producers of cadmium pigments in the United States are Millennium Chemicals. In Europe, they are Johnson Matthey Colors Ltd., and James M. Brown, Ltd. in the United Kingdom, General Quimica in Spain and SLMC in France. Dainichiseika and Mitsubishi are two producers of cadmium pigments in Japan.

5.7. Lead Chromate Pigments

Lead chromate [7758-97-6], $PbCrO_4$ occurs in Nature as the orange-red mineral crocoite [14654-05-8]. Synthetically prepared lead chromate [7446-14-2], $PbSO_4$, or lead molybdate [10190-55-3], $PbMoO_4$, are known to have excellent pigmentary properties. Some lead chromate pigments can also contain basic lead chromate, lead carbonate, and lead phosphate. The usage of these pigments has been steadily decreasing because of environmental regulations restricting the production and the use of lead-containing products. The various hues of the lead chrome yellows, chrome oranges, and molybdate oranges depend on the interrelationship of three factors: chemical composition, crystal structure, and particle size.

Lead chromates are prepared by precipitation techniques from soluble salts in aqueous media. The raw material list includes a number of different lead compounds, eg, litharge, lead nitrate, basic lead acetate, basic lead carbonate, as well as acids, alkalis, sodium bichromate, and sodium chromate. The typical reaction can be represented by the following equation:

$$2\,Pb(NO_3)_2 + Na_2Cr_2O_7 + H_2O \rightarrow 2\,PbCrO_4 + 2\,NaNO_3 + 2\,HNO_3$$

Insoluble lead chromate can be chemically treated where applicable, then filtered, washed, dried, and ground.

Most lead chromates are surface treated with various inorganic and/or organic compounds. End treatments enhance the working and performance properties of the pigment, eg, wetting, texture, heat stability, and lightfastness. Compounds used for these purposes include hydrous oxides, silicates and phosphates of elements, eg, aluminum, titanium, zirconium, rare earths, tin, or antimony compounds, and organics, eg, fatty acids (53,54). Traditional use of these pigments in traffic paint formulations and automotive finishes has been decreasing as the result of environmental regulations. Less toxic, inorganic metal-oxide yellow pigments, such as titanium-nickel yellow, praseodymium yellow, bismuth vanadate, and their combinations with organic pigments, are being used increasingly as a replacement for lead chromate pigments.

6. Black Pigments

Black pigments can be divided into two basic groups. The first group is represented by carbon blacks, which will be described in this section. Many other inorganic black such as spinel and rutile blacks, are discussed in the colored pigment category.

6.1. Carbon Black

Carbon black is one of the oldest pigments known to mankind. It was used by prehistoric man for painting pictures on cave walls and was commercially produced by the Chinese as early as 3000 BC.

While $> 90\%$ of carbon blacks are used in the manufacture of rubber tires, their nonrubber applications in the coloring of plastics, paints, and printing inks have been significant. For these applications, special carbon blacks have evolved to meet specific user requirements.

Commercial carbon blacks are produced with sizes from 5 nm to 500 μm and can be controlled by the process conditions and feedstock.

Two processes, partial oxidation and thermal decomposition, are used for the production of carbon blacks. These processes can be represented by the following reactions:

$$C_xH_y + 0.5\,O_2 \rightarrow x\,C + 0.5\,H_2O$$

$$C_xH_y \rightarrow x\,C + 0.5\,H_2$$

Large quantities of carbon blacks, called furnace blacks, are produced by this process in which a highly viscous, heavy aromatic feedstock from petroleum refining is atomized and dispersed into combustion gases of a secondary fuel that is burned in an excess of air. By controlling the air excess and by the temperature quenching of the product, the partial oxidation of feedstocks can be carried out. The product passes through heaters, where the combustion air is preheated, and it is quenched again at 270°C prior to the collection of carbon blacks in glass bag filters. The carbon blacks are ground or micropulverized and pelletized by dry or wet methods to provide a low dusting or non-dusting product. Dry pelletization is used for the production of pigmentary grade products.

Thermal decomposition of hydrocarbons is carried out in the absence of oxygen and at a high temperature required to break the carbon–hydrogen bonds.

$$C_xH_y \rightarrow x\,C + 0.5\,H_2$$

When natural gas is used as a feedstock to produce thermal blacks, the reaction is endothermic. In order to maintain it, the reactor has to be kept at ~1300°C. When acetylene is used as the feedstock to produce *acetylene blacks*, the reaction is exothermic, and can be run at a temperature between 800 and 1000°C.

The production process of the feedstock is sometimes reflected in the name of the product such as lamp black, acetylene black, bone black, furnace black, or thermal black. The reason for the variety of processes used to produce carbon blacks is that here exists an unique link between the manufacturing process and the performance features of carbon black.

Environmentally, carbon blacks are relatively stable and unreactive. There is no evidence that they are toxic to humans or animals. Because they are fine and light, dusting problems occur without careful housekeeping. Most of the carbon blacks used today are pelletized. This not only reduces dusting problems, but because of the higher bulk density, pelletization also lowers the cost of shipping.

7. Extenders and Opacifiers

Extender pigments are low cost, generally colorless or white pigments with a refractive index < 1.7. Sometimes these pigments are also referred to as fillers. Many extenders are derived from natural sources and they display many diverse properties. They are added to various formulations to improve their technical and application properties and to reduce their costs. Like pigments, extenders are dispersed in media in which they do not dissolve, but compared to pigments they do not have any significant coloristic properties. They are sometimes referred to as fillers, bulking agents, viscosity modifiers, or reinforcing agents.

In coating applications, extender pigments control gloss, viscosity, texture, suspension, and durability, and they enhance the opacity of white hiding pigments, eg, TiO_2. In plastic applications, extenders influence numerous properties of the resin including melt viscosity, thermal conductivity and electrical properties, tensile strength, and moisture resistance.

With few exceptions, extender pigments can be classified as commodity chemicals. They are manufactured in large quantities with less sophisticated production methods than most pigments. While the majority of pigments are prepared synthetically, extender pigments are mainly manufactured by the beneficiation of natural minerals. Based on chemical composition, extender pigments are carbonate, sulfate, silica- and silicate-based compounds.

Opacifiers are fine inorganic powders, usually white, that are used to reduce the transparency of ceramic glazes and porcelain enamels. The coating becomes opaque because the particles of the opacifier scatter and reflect the incident light. When inorganic pigments are combined with white opacifiers, pastel colors are obtained.

To achieve the maximum coating opacity the opacifier particle size should be between 0.2 and 0.3 μm. A good opacifier should not be soluble in the vitreous system, should have the refractive index substantially different from the refractive index of the system, and should be inexpensive, easily milled to a submicron particle size, and thermally stable at the film's firing temperature.

Commercially, the most important opacifiers for glazes are ZrO_2, $ZrSiO_4$, and SnO_2. Because of its low solubility in most molten glazes ($< 1\%$), and its relatively high refractive index, SnO_2 is the most effective opacifier of the group. It is usually added in 4–8 wt% to the glaze, but because it is very expensive, its commercial use is limited. Zirconia is less expensive and it has a higher refractive index than tin oxide, but it can be used as an opacifier only in low temperature glazes; at higher temperatures it reacts with SiO_2 present in the glaze and forms zircon, $ZrSiO_4$. Since zircon is less expensive, it is added directly to the glazes fired at temperatures $> 1000°C$. In most glaze mixtures the zircon concentration is between 8 and 10%. Because of its solubility in the molten glazes [$\sim$5% at 1200°C (55)], most glaze coatings contain two zircons, one that did not dissolve during the firing process, and the other one that dissolved in the molten glaze, but recrystallized on cooling. In porcelain enamels and some glazes that are fired at temperatures considerably $< 1000°C$, titania in anatase form is usually the preferred opacifier.

8. Miscellaneous Pigments

8.1. Anticorrosion Pigments

Anticorrosion pigments are designed to help a coating protect against corrosion of a metal substrate. In order to do this, they block the corrosion process, by either slowing molecular or ionic migration through the coating, or passivating these species before they attack the metal. As the result of environmental regulations, the use of heavy metal-containing anticorrosion pigments based on chromate have been declining steadily, being replaced with pigments based on phosphates and molybdates.

8.2. Luminescent Pigments

Luminescence is the ability of matter to emit light after it absorbs energy. Materials that have luminescent properties are known as phosphors, or luminescent pigments. If the light emission ceases shortly after the excitation source is removed ($< 10^{-8}$ s), the process is called *fluorescence*. The process with longer decay times is referred to as *phosphorescence*.

Semiconducting sulfides are fluorescent pigments and can be represented by the formula: nZnS.(1-n)CdS:A, where A stands for the activator, and $n = 0.15$–1. The activators are typically Cu^+, Ag^+, Mn^{2+} added in 0.003–1 wt% concentrations. Phosphorescence pigments can be expressed by the general formula: nZnS.(1-n)CdS:Cu, where $n = 0.78$–1.0 and the amount of the Cu^+ activator is only a few hundredths of a percent. Other phosphorescent sulfide pigments are nCaS(1-n)SrS:Bi, Cur, where $n = 0$–1 and Bi = 0.04wt% and Cu = 0.01 wt%.

Phosphorescent pigments are used in military applications, plastics, and paints. Zinc sulfide doped with Ag^+ (blue) cations, or with Cu^+ (green) cations are important pigments for the production of color television screens.

Zinc and calcium silicates, and calcium tungstate doped with activators such as Mn, Pb, Sn, and Eu are just a few examples of a large number of known ionically bonded luminescent pigments. Halide phosphates of the general formula $3Ca(PO_4)_2 \cdot CaX_2$, where X = F or Cl, with the Sb^{3+} and Mn^{2+} activators are extensively used in fluorescent lamps. Yttrium vanadate doped with europium, $YVO_4:Eu^{3+}$ is used as red phosphors in color television tubes and a single-crystal Al_2O_3 doped with about 0.05 wt% of Cr^{3+} is the basis of the ruby laser. The basis of the neodymium laser is yttrium aluminum garnet (YAG), $Y_3Al_5O_{12}$, activated with Nd^{3+}.

8.3. Metal Effect Pigments

Some metals, when prepared as small flakes, impart a special metallic appearance to the coatings and plastics in which they are dispersed. Metals most often used in these applications are aluminum (aluminum bronzes), copper and copper–zinc alloys (gold bronzes), and in smaller amounts zinc, tin, nickel, gold, silver, and stainless steel. Metallic pigments were first produced in the Middle Ages when gold leaf was made by hand beating. This was eventually replaced by stamping machines. Metal-effect pigments are now usually produced in ball mills using dry milling and wet milling.

8.4. Nacreous Pigments

Nacreous, ie, pearlescent, pigments are used for creating special decorative effects typical of natural pearls. Nacreous pigments are fine, thin plate-like transparent particles with a high refractive index. Because of these physical characteristics, when dispersed in a transparent film, they produce a "silky" appearance. When flakes have the right thickness, these pigments can also produce interference colors. These colors result from the interference of two light reflections, one from the upper and the other from the lower surface of a thin film.

Important requirements for achieving pearl essence effects include a platelike particle shape of pigment coupled with a high refractive index. Manufacture of the most popular nacreous pigments involves coating mica with 50–300 nm films of TiO_2, Fe_2O_3, or Cr_2O_3. The mica, which alone does not have a high enough refractive index for creating nacreous luster, provides the required transparent platelet base, and metal oxide films provide the desired high refractive index. Because of the controlled thickness of the inorganic oxide films, coated mica can also behave as an interference pigment, and some interesting color shades can be achieved by a combination coating of two oxide films, with TiO_2 being the one adjacent to mica. Mica flake dimensions are important, with the preferred thickness being 0.3–0.6 μm and the preferred length being 5–110 μm.

A large number of mica pigment grades were optimized for particular applications, such as industrial grades for plastics, coatings and printing inks, cosmetic grades for cosmetic use, and exterior grades modified to have good weather resistance (eg, rutile-coated mica) for outside applications. Mica-coated pigments are produced by The Mearl division of the Englehard Corporation, E. Merck and BASF (Germany), Kemira OY (Finland), and Tayco (Japan).

8.5. Transparent Pigments

Pigments having chemical composition corresponding to colored or white opaque pigments can, under certain circumstances, appear as transparent in a media. This happens when the particle size of these pigments becomes very small (2–15 nm), and if their refractive index is comparable to the refractive index of the media in which they are dispersed. Because of the very small particle size, the preparation of these pigments is much more complicated than the preparation of their nontransparent analogues. Their large surface area makes their dispersion difficult and they have a strong tendency to agglomerate.

Transparent iron oxide pigments have excellent weatherbility, lightfastness, and chemical resistance comparable to opaque iron oxides. They are produced by BASF (Germany) and Johnson Mathey (U.K.).

Two blue pigments can be prepared in transparent form: cyanide iron blue, and cobalt aluminum blue. Transparent cyanide iron blue is prepared by a precipitation reaction similar to the one used for the preparation of the opaque pigment, but considerably lower concentrations of solutions are used. It is produced by Degussa (Germany), Manox (U.K.) and Dainichiseika (Japan).

Transparent cobalt aluminum blue is prepared by the precipitation of diluted solutions of cobalt and aluminum with alkalis. The formed precipitate of hydroxides is washed, filtered off, dried and calcined at $\sim$1000°C. Transparent Titanium Dioxide having a primary particle size of 15–30 nm also exhibits transparency. In general, TiO_2 does not absorb light well in the visible region, and because of its small particle size it diffuses light very slightly and does not exhibit its white pigment characteristics anymore. It is used in the production of metallic paints, transparent plastic films (56) and in cosmetics. Pigments with the anatase structure are prepared by burning $TiCl_4$ in the presence of water vapors (flame hydrolysis) at a temperature $< 700°C$. Rutile transparent pigments can be prepared by a sol–gel process or by precipitation in the presence of protective colloids. Transparent TiO_2 is produced by DuPont, Kemira (Finland), Degussa, BASF (Germany), and Teikoku Kako Co. (Japan).

9. Environmental Aspects

Some inorganic pigments contain heavy metals. Thus production, use, and disposal are becoming more and more regulated. In the United States there are several federal regulations that control the use and disposal of heavy metals. Those relevant to the inorganic pigments industry are mentioned herein(57).

The Resource Conservation and Recovery Act (RCRA) controls the disposal of hazardous waste. The SARA Title III governs the toxic inventory and emission reporting, the Clean Water Act (CWA) sets the limits for metals that can be present in water discharge, and the Clear Air Act Amendments of 1990 controls the abatements of all materials in the air.

The Occupational Safety and Health Administration (OSHA) regulates the exposure to chemicals in the workplace. From the point of view of the inorganic pigments industry, the limits established for lead and cadmium exposure are particularly important. A comprehensive lead standard adopted by OSHA in 1978 has been very successful.

OSHA has enacted the permissible levels for all cadmium compounds, including fumes and dust, to be a maximum of 5 ppm per cubic meter of air over an 8-h exposure period. The permissible levels for the cadmium pigment producers are set up slightly higher. However, compliance with these higher levels might be difficult and as even tighter regulations are anticipated, it is becoming questionable whether the U.S. cadmium pigment producers will be able to manufacture these pigments at competitive prices. About 80% of cadmium produced pigments are used to color plastics. Research directed toward finding suitable substitutes is ongoing.

The situation of the lead containing inorganic pigments (lead chromates and lead molybdates) in the United States is similar. These pigments are primarily used for painting traffic signs, automobiles and producing industrial paints. As the result of various regulations usage has been declining ~5–7% a year since the 1970s (58). This trend is likely to continue even though more environmentally acceptable products are being developed. In these newer products, the lead bioavailability is lowered through pigment encapsulation. Table 2 lists those metals regulated by federal law that are or might be present in inorganic pigments.

Products packaging constitutes about one-third of the municipal solid waste and is usually decorated with various colors, some of them containing heavy metals. As landfill construction and placement became more complicated, the cost of garbage disposal escalated. For example, between 1984 and 1988, the fee for depositing trash in landfills in the northeast United States quadrupled. As a result, the Coalition of Northeast Governors (CONEG) developed a model state legislation to regulate cadmium, hexavalent chromium, lead and mercury in packaging to a gradually decreasing content, not leachability, of 100 ppm of all four metals combined in four years after its adoption. This legislation had a significant effect on the inorganic pigments industry that has relied heavily on the bright red and orange colors of cadmium- and lead-containing pigments. As of 1998, 18 states have enacted this legislation with some limited variations.

Two voluntary incentives that are being adopted by many U.S. chemical companies are 33–50 reduction in toxic releases and Responsible Care. Using 1988 as a baseline, Responsible Care companies have reduced emissions of core chemicals 70% while increasing production 25% during the same period. While most of this decrease was in air emissions, it shows the efforts made by the chemical industry to reduce the impact on the environment. The chemicals that are on the Environmental Protection Agency (EPA) list and that are relevant to the inorganic pigments industry are cadmium, chromium, lead, nickel, and their compounds (59).

Responsible Care is the incentive sponsored by the Chemical Manufacturers Associations. Any company that wants to be a member of CMA must embrace the philosophy of continuous improvements of health, safety and environmental efforts and an open communication to public about products, and their production. Under this philosophy one has to consider the total impact of any product on the environment, from the extraction of

Table 2. Metals Present in Inorganic Pigments

Element	RCRA	SARA	OSHA	CWA	CAA
Al				Y	
Ag	Y	Y			
As	Y	Y		Y	Y
Ba	Y	Y		Y	
Be		Y		Y	
Cd	Y	Y	Y	Y	Y
Co		Y		Y	Y
Cr	Y	Y		Y	Y
Cu		Y		Y	
Hg	Y	Y		Y	Y
Mn		Y			Y
Mo				Y	
Ni		Y		Y	
Pb	Y	Y	Y	Y	Y
Sb	Y	Y		Y	
Se	Y	Y		Y	
Ti				Y	
Tl		Y			
Zn				Y	

raw materials, their beneficiation, transportation, production of final product, and disposal of the product at the end of its useful life, must be taken into consideration.

Most lead- and cadmium-containing inorganic pigments have very low solubilities in body fluids, therefore the toxicity of these materials is extremely low. Additional encapsulation of these pigments into a silica or zircon matrix as practiced by some companies decreases solubility further, making these metals even more environmentally inert. Treated pigments are environmentally inert only from the narrow view of immediate application. There is often, however, a weak link in the whole life cycle of the product that can result in a release of a toxic element. Usually that weak link is either at the beginning or the end of the cycle. For example, fly ash particles created by the incineration of product colored with cadmium- or lead-containing inorganic pigments can contain soluble heavy metals that could potentially be leached into the ground water. Mining and beneficiation of heavy metals can also create environmentally hazardous by-products. Even though these potential hazards can be minimized by applying proper industrial practices, the trend to reduce the use of inorganic pigments containing lead and cadmium is expected to continue.

Inorganic pigments contribute to the enjoyment, beauty, and functionality of the objects we bring into the world. To insure that their benefits far outweigh their liabilities, research efforts are directed toward the development of environmentally acceptable pigments that do not release any toxic materials into the environment during their production, use, or disposal.

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