The Science of Pigments: Evolution, Structure, Optical Metrics and Sustainability Challenges

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Abstract

Pigments are the foundation of human creativity and discovery which bring color to our art, vibrancy to our world, and functionality to industries ranging from coatings and inks to rubber and plastics. Across the ages, pigment science has evolved from natural mineral and plant sources through early synthetic inventions to modern high-performance organic and inorganic systems. Understanding pigment behavior requires analyzing both chemical structure and optical properties, including standard colorimetric parameters such as CIELAB and **ΔE**. At the same time, present challenges over toxicity, environmental discharge, and sustainability are driving new directions in pigment development, design and regulation. This article reviews the historical development, chemical classifications, structure & property relationships, colorimetric foundations, and environmental/health aspects of pigments, highlighting recent breakthroughs and future challenges.

Introduction

Color is one of the instantaneous and powerful aspects of visual experience. In human societies, colored surfaces, paintings, textiles, prints, plastics & rubber products, toys, serve aesthetic, communicative and functional roles. At the chemical level, pigments are insoluble colorants that scatter or absorb light in selective regions of the visible spectrum, imparting hue to a substrate without dissolving in it.

Chemistry, materials science, optics, and environmental engineering are all combined in the multidisciplinary field of pigment science. In recent decades, the expansion of synthetic organic pigments, especially high-performance product categories have transformed many industries, while regulatory and ecological pressures have stimulated a shift toward safer, more sustainable options.

This article traces the development of pigment technology, investigates at chemical classes and optical metrics, explains how crystalline and molecular structure control pigment behavior, and discusses health and environmental concerns in the production and use of pigments.

Dyes vs Pigments

Despite frequently being grouped together, dyes and pigments exhibit significant differences.

The main areas of difference between dyes and pigments are their solubility and pigmentation techniques. Because dyes are soluble in water or other solvents, they can color materials by absorbing molecules throughout the medium. Pigments, on the other hand, are insoluble particles that use light scattering and surface absorption to produce color. While pigments usually stay more stable within a system, dyes can migrate, bleed, or leach due to their solubility. When it comes to optical performance, dyes offer brighter transparency and finer detail, particularly in applications such as textiles and printing inks, while pigments typically offer greater opacity, hiding power, and durability. But sometimes it's difficult to differentiate the difference between dyes & pigments, like azo pigments which are made from dye chemistry while more recent hybrid or functional pigments might contain soluble components. This interplay between soluble and particulate colorants is increasingly leveraged in advanced formulations to achieve specific optical and functional properties (Alegbe et al., 2024).

Historical Development of Pigments

Natural Origins

In art, ceramics, and decoration, ancient people uses organic materials (plants, insects) and naturally occurring minerals (such as carbon black, ochres, iron oxides, and ultramarine from lapis lazuli) as pigments. Some ancient pigments have remained stable over centuries, as evidenced by their durability (such as Egyptian blue and specific mineral oxides).Early Synthetic Pigments

The first synthetic pigments developed in the 18th and 19th centuries. Prussian blue (iron ferrocyanide complex), which was created around 1706 was one significant example. Another is the creation of lead chromate, also known as "chrome yellow," in the early 1800s and its use in paints for artists (chrome yellow is actually lead chromate, $PbCrO_4$). Compared to nature alone, these provided richer and more distinct hues.

Industrial Revolution and Synthetic Pigment Expansion

Industrialization led to the production of pigments on an immense scale. Synthetic organics originated when coal-tar chemistry expanded. Pigments like carbon black, titanium dioxide, cadmium pigments, and other synthetic organic types started to be produced in massive quantities. Another competitive advantage was the capacity to design pigments with certain qualities (particle size, fastness, and hue).

Modern Advances

In the late 20th and early 21st centuries, advanced high-performance pigments (HPPs) became prominent. These include derivatives from diketopyrrolopyrrole (DPP), perylene, isoindolinone, and other classes offering exceptional weathering resistance and chromatic purity. There is also growing interest in organic–inorganic hybrid pigments (e.g. dyes immobilized on coatings or layered hosts) to improve stability (Marzec et al., 2019). Meanwhile, computational and machine learning methods are beginning to assist design of pigments with desired optical and stability properties (Mao et al., 2025).

Chemical Classification and Properties

Pigments are commonly classified into inorganic, organic and Chrome pigment classes, with further subdivisions by chemical family.

Inorganic Pigments

Inorganic pigments are mineral-based compounds primarily composed of metal oxides, hydroxides, sulfides, or mixed oxides. They exhibit high thermal and chemical stability, excellent opacity, and strong light-scattering properties due to their refractive indices and crystalline structures (Buxbaum and Pfaff, 2005; Eastaugh et al., 2008). Unlike organic pigments, their coloration arises from electronic transitions within metal ions rather than extended conjugated π-systems, which generally results in less vibrant hues and a muted color appearance (Herbst and Hunger, 2004; Pfaff, 2008). The reduced chromatic intensity is attributed to the limited light absorption bands of transition-metal compounds compared with the broader and more intense absorption of organic chromophores (Hunger, 2003).

Examples

- Titanium Dioxide (Pigment White 6): Exhibits a high refractive index, brilliant whiteness, and excellent hiding power; widely used in paints, plastics, and cosmetics (Faust and Aly, 1998).
- Iron Oxides (Pigment Red 101, Yellow 42, Black 11): Provide red, yellow, and brown hues with outstanding weather and UV resistance; frequently applied in construction materials and protective coatings (Sharma et al., 2015).
- Chromium(III) Oxide (Pigment Green 17): Chemically inert and heat-resistant, suitable for ceramics and industrial paints (Pfaff, 2008).
- Cadmium Sulfide (Yellow 37): Brilliant yellow with high thermal stability; use restricted due to toxicity concerns (Hunger, 2003).
- Cobalt Aluminate (Pigment Blue 28): A stable, intense blue pigment employed in automotive and architectural coatings (Pfaff and Reynders, 2017).

Inorganic pigments remain vital components in coatings, plastics, rubber and construction materials for their durability and opacity, although increasing environmental regulations promote the adoption of safer, eco-friendly alternatives (Sharma et al., 2015).

Chrome (lead chromate–based) pigments represent a historically significant group of inorganic colorants, widely utilized for their vivid hues and exceptional opacity in paints, plastics, and artists' materials during the 19th and early 20th centuries (Herbst and Hunger, 2004). The most common forms include Chrome Yellow (Lead Chromate, $PbCrO_4$; CI Pigment Yellow 34), Molybdate Orange (Lead Chromate molybdate sulfate; CI Pigment Red 104), and Chrome Green (a mixture of Lead Chromate and Chromium (III) Oxide; CI Pigment Green 15) (Pfaff, 2008; Buxbaum and Pfaff, 2005). These pigments were once valued for their intense coloration, high covering power and good weather resistance.

However, chrome pigments associated significant environmental and health hazards due to the presence of lead (Pb) and hexavalent chromium (Cr^{6+}) compounds. Lead is a potent neurotoxin that can cause developmental and neurological disorders while hexavalent chromium is a recognized carcinogen and environmental contaminant that bioaccumulates in ecosystems (IARC, 2012; Singh et al., 2019). As a result, the production and use of these pigments have been strictly regulated or banned in most regions, triggering substitution with safer organic or mixed-metal oxide alternatives (Hunger, 2003).

Organic Pigments

Organic pigments are made up of carbon-based chromophoric structures, typically featuring conjugated π-electron systems. Unlike dyes, they are intentionally rendered insoluble either through molecular modification (such as substitution or extended conjugation) or by incorporation into host matrices. The organic class offers a broader chromatic palette, including vivid reds, blues, and greens, along with greater structural tunability. However, these advantages often come with compromises in thermal and photochemical stability. The principal categories are outlined below

1. Azo Pigments

Azo pigments are the largest class of synthetic organic pigments. They contain one or more azo groups (–N=N–) linking aromatic rings. They exhibit colors ranging from yellow through red to brown. Subtypes include monoazo, disazo, naphthol, benzimidazolone, and metal-complex azo pigments. They are widely used because of affordability and versatility. However, some degrade under heat to produce aromatic amines, potentially carcinogenic (e.g. diarylide yellows degrade to 3,3′-dichlorobenzidine) or even form inadvertent PCBs (iPCBs) in pigment manufacture (Nestler, 2019).

Subtypes:

- Monoazo Pigments
  - Example: Pigment Yellow 1, Pigment Red 3, Pigment Red 112
  - Widely used for Printing inks, plastics, coatings
- Disazo Pigments
  - Example: Pigment Yellow 12, Pigment Yellow 14
  - High tinting strength, moderate lightfastness
- Naphthol AS Pigments
  - Example: Pigment Red 57:1, Pigment Red 170
  - Brilliant reds used in plastics, paints, inks
- **β-Naphthol (Bon** Arylide) Pigments
  - Example: Pigment Yellow 74
  - Widely used for its bright yellow hue
- Benzimidazolone Pigments
  - Example: Pigment Yellow 151, Pigment Orange 36, Pigment Red 176
  - Excellent light and solvent fastness, good for high-performance coatings
- Metal Complex Azo Pigments (Chelated Azo)
  - Example: Pigment Brown 23
  - Contain coordination with metals (Ni, Cu, Cr) for improved fastness

2. Phthalocyanine Pigments

Phthalocyanines are copper-based macrocyclic pigments known for their vivid blue (PB15) and green (PG7) hues. Their planar structure and metal coordination provide exceptional stability, lightfastness, and color strength, making them ideal for high-performance applications such as coatings, plastics, and printing inks (Savastano, 2020).

Examples:

- Pigment Blue 15, 15:1, 15:2,15:3,15:4 (Copper Phthalocyanine Blue)
- Pigment Green 7, 36 (Chlorinated Phthalocyanines)

3. Quinacridone Pigments

Quinacridones are valued for their vivid red-to-violet hues and excellent lightfastness. They are widely used in high-end paints and automotive coatings.

Examples: Pigment Violet 19, Pigment Red 122, Pigment Red 202

4. Anthraquinone Pigments

Anthraquinone pigments produced red, violet and blue shades with excellent lightfastness, weather resistance, and strong chroma, making them ideal for automotive finishes, industrial coatings and plastic applications.

Examples: Pigment Red 177, Pigment Violet 43

5. Diketopyrrolopyrrole (DPP) Pigments

DPP pigments are among the most powerful modern pigments, providing brilliant red-orange hues with very high chroma, exceptional lightfastness, thermal stability, and durability, making them suitable for automotive coatings, plastics, rubber and high-performance paints.

Examples: Pigment Red 254, Pigment Orange 73

6. Perylene and Perinones

These pigments produce deep red and orange tones characterized by high durability and vivid coloration resulting from their extended conjugated molecular structures, which enable strong light absorption. They exhibit excellent weather resistance and outstanding color brilliance, maintaining stability under prolonged exposure to sunlight and environmental conditions. Because of these properties, they are widely applied in exterior coatings, automotive paints, and high-performance rubber/plastic applications.

Examples: Pigment Red 179, Pigment Orange 43, Pigment Violet 29, Pigment Red 194

7. Isoindolinone and Isoindoline Pigments

These pigments produce bright yellow and orange tones with good chroma and solvent resistance, making them suitable for coatings, printing inks, and plastics.

Examples: Pigment Yellow 109, Pigment Yellow 139, Pigment Orange 61

8. Indanthrone and Related Pigments

These pigments are deep, stable blues with excellent heat and light stability, making them ideal for automotive and industrial coatings as well as plastics.

Examples: Pigment Blue 60 (Indanthrone Blue)

9. Condensation and High-Performance Pigments (HPPs)

This group includes quinophthalone and other specialized, condensation-derived pigments. They are designed for extreme applications (UV, chemical resistance).

Example:

- o Quinophthalone (Pigment Yellow 138)
- o DPP, Isoindolinone, and Perylene derivatives

10. Other Notable Classes

Other useful pigment classes include thioindigo, acridone, dioxazine, and others. Some pigments are hybrids or composites combining organic chromophores with inorganic supports for added stability (Randhawa et al., 2024).

- Thioindigo Pigments (e.g., Pigment Red 88, Pigment Violet 38)
- Acridone Pigments (e.g., Pigment Violet 23)
- Azomethine Pigments (e.g., Pigment Yellow 150)

Structure–Property Relationships

The performance of a pigment including its hue, chroma, lightfastness, chemical stability, dispersibility and hiding power is closely linked to its molecular and crystalline structure.

Conjugation and chromophore design play a critical role as the position, extent, and substituents on conjugated π systems determine absorption maxima. Electron-donating or electron-withdrawing groups can shift both hue and intensity, enabling fine-tuning of color properties (Fryer, 1997).

Polymorphism is another important factor. many pigments exist in multiple crystal forms, and variations in crystal packing can alter absorption and scattering behavior due to subtle electronic or intermolecular interactions (Fryer, 1997).

Particle size and morphology strongly influence scattering properties and hiding power. Particles that are too small relative to the wavelength of light may reduce opacity, while overly large particles can lead to settling or surface roughness.

Aggregation and crystallinity affect pigment stability and color strength. Highly crystalline pigments with well-defined domains typically exhibit strong absorption and resistance to photodegradation, whereas amorphous or disordered forms degrade more readily (Marzec et al., 2019).

Intermolecular interactions and stabilization, including hydrogen bonding, π–π stacking, coordination to metal centers, or embedding in inert matrices (e.g., inorganic hosts), further protect pigments against photochemical and thermal attack (Marzec et al., 2019). Hybrid or composite approaches, such as immobilizing organic chromophores on inorganic hosts or layered materials, enhance thermal and photochemical stability and solvent resistance without compromising hue.

Finally, electronic structure and optical transitions govern absorption wavelengths and intensities. The energies of frontier molecular orbitals (HOMO and LUMO) and electron delocalization determine color properties, and computational methods increasingly enable the prediction of pigment colors from first principles (Tomczak et al., 2013).

Understanding these structure & property relationships enables rational design of pigments with tailored hue, strength, and durability.

Colorimetric Parameters of Pigments

A major challenge in pigment science is repeatable & reproducible color assessment. To achieve this, the *CIE 1976 (Lab) color space** which commonly known as CIELAB together with the color difference (ΔE) metrics serves as the international standard for color evaluation and quality control (CIE, 1978; Hunt and Pointer, 2011).

CIE 1976 (L*ab**) Color Space – CIELAB

The CIELAB color space, developed by the International Commission on Illumination (CIE) in 1976, represents color numerically using three parameters: L* for lightness, a* for the red–green axis, and b* for the yellow–blue axis. The system was designed to be *approximately perceptually uniform*, meaning that equal changes in coordinate values correspond to similar perceptual differences (CIE, 1978).

CIELAB describes color in three coordinates:

- L* (lightness) from 0 (black) to 100 (white)
- a* (red–green axis)
- b* (yellow–blue axis)

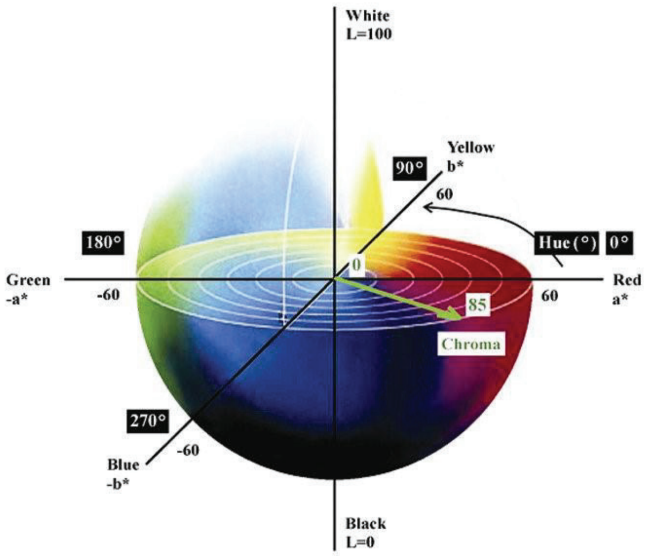

*Image 01: The three-dimensional CIE L*a*b* color space*

Conversion from CIE XYZ tristimulus values (X, Y, Z) to L*, a*, b* involves non-linear transformations based on a standard white reference point, typically illuminant D65, and functions designed to reflect human visual nonlinearity (Fairchild, 2013). Once these coordinates are obtained, chroma ($C^* = \sqrt{(a^2 + b^2)}$) and *hue angle* (*$h° = arctan(b/a)$*)** can be calculated to describe color intensity and tone.

Color Difference (ΔE)

The color difference (ΔE) quantifies the perceived difference between two colors in the CIELAB space. The original CIE76 formula defines this as the Euclidean distance between two color points (Robertson, 1977)

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

Although simple, ΔE* has perceptual limitations, particularly for low-chroma or near-neutral colors. To address this, subsequent refinements introduced weighting factors and perceptual corrections:

In industrial practice, ΔE is widely used for color tolerance assessment. Typical thresholds as follows.

- $\Delta E \leq 1$:The color difference is nearly imperceptible to the human eye
- $\Delta E \leq 2$:The difference is slight and noticeable under controlled lighting conditions.
- $\Delta E \leq 3$:The difference is clearly noticeable and outside of industry standards (Sharma, 2017)

Overall, the CIELAB color system and ΔE metrics provide a robust quantitative framework for assessing pigment color, ensuring consistency and precision across formulation, production, and quality control processes.

Environmental and Health Considerations

Due to the extensive and worldwide usage of pigments, there are serious environmental and health consequences associated with the manufacturing process, use, and disposal. These concerns have driven stricter regulatory frameworks and extensive research toward developing safer and more sustainable alternatives.

Toxic Metals and Substitution Efforts

Many traditional inorganic pigments, such as lead chromates and cadmium sulfides, incorporate heavy metals that are toxic, carcinogenic, and bioaccumulative (Tomczak et al., 2013). Lead chromate pigments (e.g., Chrome Yellow, $PbCrO_4$) contain both lead and hexavalent chromium, making them highly hazardous and subject to severe restrictions or bans in most jurisdictions (European Chemicals Agency, 2023). Similarly, cadmium-based pigments (e.g., Cadmium Yellow, CdS) are restricted under the European Union's REACH Regulation due to their persistence and toxicity (ECHA, 2023).

These regulatory pressures have accelerated the substitution of hazardous pigments with environmental friendly alternatives, including organic pigments, rare-earth oxides, and non-toxic metal-based pigments (Randhawa et al., 2024). Additionally, manufacturing processes for certain azo and diarylide pigments can inadvertently generate toxic by-products, including inadvertent polychlorinated biphenyls (iPCBs) and 3,3′-dichlorobenzidine, a known human carcinogen (Shin et al., 2010; Washington State Department of Ecology, 2015).

Environmental Legislation

Regulatory measures governing pigment and dye industries have become increasingly stringent. In the United States, the Environmental Protection Agency (EPA) designates certain pigment production wastes particularly from azo, anthraquinone, and triaromatic pigment classes as hazardous under the K181 listing (US EPA, 2005). In the European Union, the REACH framework enforces restrictions on substances with proven toxicity or environmental persistence, including azo colorants capable of degrading into banned aromatic amines (European Commission, 2020).

Within the textile and dyeing sectors, effluent discharge regulations impose limits on chemical oxygen demand (COD), biological oxygen demand (BOD), total dissolved solids (TDS) and heavy metal content. These measures aim to mitigate water pollution and ecological damage (Shindhal et al., 2020). Studies indicate that regulatory enforcement has significantly improved wastewater quality while encouraging cleaner technologies and process optimization (Ghaly et al., 2014).

Effluent and Waste Management

Pigment and dye manufacturing often generate heavily colored effluents containing organic compounds, metal ions, and prolonged intermediates. Conventional treatment technologies such as coagulation, flocculation, adsorption, biological degradation, and advanced oxidation are widely used but can be limited by the complexity and toxicity of pigment effluents (Al-Tohamy et al., 2022). As a result, industries are moving toward zero-liquid discharge (ZLD) and closed-loop recycling systems to minimize wastewater generation and maximize resource recovery.

Solid wastes, particularly pigment sludge can concentrate toxic metals and organic residues, necessitating safe disposal or stabilization through solidification or encapsulation (Savastano, 2020). Increasingly, hybrid approaches combining chemical, biological, and photocatalytic treatments are being adopted to achieve higher degradation efficiency and lower environmental impact.

Shift to Sustainable Manufacturing

In response to regulatory and community pressures, pigment manufacturers are transitioning toward sustainable production models. Key strategies include:

- Development of bio-derived or renewable pigments from microbial or plant-based sources.
- Implementation of green synthesis routes using non-toxic reagents, minimal solvents and energy-efficient conditions.
- Recycling and reclamation of pigment residues and process intermediates.
- Encapsulation and immobilization techniques to reduce pigment leachability and enhance environmental safety.
- Conducting lifecycle assessments (LCA) to evaluate and minimize environmental impact.
- Ensuring supply chain transparency to prevent contamination with iPCBs or restricted substances (Nestler, 2019).

Recent innovations in pigment chemistry emphasize non-toxic metal centers, safer chromophore design and hybrid nanostructures that combine color performance with reduced environmental burden (Randhawa et al., 2024). As consumer and regulatory expectations for sustainability grow, pigment producers increasingly invest in eco-friendly formulations, renewable raw materials and closed-loop manufacturing systems (Savastano, 2020).

Conclusion

Pigments are both ancient and cutting-edge: roots in natural minerals and organic extracts and modern versions in high-performance molecular systems. Their chemical diversity ranging from inorganic oxides to advanced organic classes which provides a rich palette for applications across art, coatings, inks, plastics, rubber and beyond. Understanding pigment performance demands a firm grasp of structure & property relationships and strict quantification via colorimetric systems like CIELAB and ΔE. Yet as we continue to push pigment capability, we must equally attend to the environmental and health repercussions of pigment manufacture, use and disposal. The future of pigment science lies in balancing optical excellence with ecological responsibility: designing stable, safe & sustainable pigments for a colorful yet healthy world.

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