



Review article

Phthalein Dyes: Chemistry and Characteristics

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ARTICLE INFO

ABSTRACT

Keywords:

Dyes,
Phthalein dyes,
pH indicator,
Phenolphthalein,
toxicity

Article History:

Received: 03-02-2024
Accepted: 15-04-2024
Published: 02-05-2024

Cite this article:

Yusuf, M. (2024). Phthalein Dyes: Chemistry and Characteristics. *Jabirian Journal of Biointerface Research in Pharmaceutics and Applied Chemistry*, 1(3), 01–05. <https://doi.org/10.55559/jjbrpac.v1i3.215>

Phthalein dyes, a distinguished class of synthetic organic compounds, have garnered recognition for their multifaceted utility as both pH indicators and coloring agents in a wide array of industrial and laboratory contexts. This comprehensive review endeavors to delve into the nuanced chemistry and defining attributes of phthalein dyes, providing insights into their structural intricacies and expansive applications. Furthermore, the review expounds upon the paramount significance of phthalein dyes across diverse domains, elucidating their foundational chemistry and versatile properties that underpin their indispensable role in contemporary scientific and industrial pursuits. Moreover, in light of growing concerns about their toxicity and associated health implications, this review advocates for the exploration and adoption of safer alternatives, thereby emphasizing the imperative for continued research and innovation in this domain.

1. Introduction

Phenolphthalein, a member of the phthalein family, shares structural similarities with triphenylmethane dyes, and its versatility extends across various industries, from therapeutics to construction and commercial sectors (Hassanien et al. 2022; Yusuf et al. 2012; Sabnis 2018; Khan et al., 2024). Historically valued for its role as a pH indicator and its use in laxatives and other pharmaceutical preparations, phenolphthalein has found applications in concrete curing, textile manufacturing, and even as a component in certain photographic developers. However, recent years have witnessed a concerning trend where phenolphthalein has been exploited illicitly, serving as an inexpensive and readily available adulterant due to its lack of taste and low detection threshold when used in small doses (Yusuf et al. 2019; Sabnis 2018). The clandestine use of phenolphthalein as an adulterant poses significant risks across multiple domains. The pharmaceutical industry's unauthorized addition to medications can compromise patient safety, leading to adverse effects or therapeutic inefficacy (Yusuf et al. 2015; Yusuf 2023; Sabnis 2018). In construction, the incorporation of phenolphthalein into concrete mixes can undermine the structural integrity of buildings, potentially resulting in costly repairs or safety hazards. Moreover, its presence in commercial products, such as food and beverages, raises concerns regarding consumer health and regulatory compliance. Despite regulatory measures to curb its illicit use, phenolphthalein continues to present challenges due to its accessibility and inconspicuous nature. Efforts to mitigate its misuse require collaborative action from regulatory bodies, law enforcement agencies, and stakeholders across relevant

industries. Furthermore, public awareness campaigns regarding the dangers associated with phenolphthalein adulteration are crucial for safeguarding public health and ensuring the integrity of products in the market. By addressing these issues proactively, society can mitigate the risks posed by the illicit use of phenolphthalein and uphold safety standards across diverse sectors (Yusuf et al. 2017; Sabnis 2018). Phthalein dyes represent a captivating realm within the domain of synthetic organic compounds, renowned for their multifaceted roles as pH indicators and coloring agents across diverse industries. Characterized by their intricate chemical structures and remarkable color-changing properties in response to varying pH levels, these compounds have garnered substantial attention and utility in both scientific research and practical applications. At the heart of phthalein dyes lies their distinctive molecular architecture, typically centered around the phthalic anhydride moiety with appended aromatic rings bearing functional groups such as hydroxyl or amino groups. This structural arrangement confers upon them the ability to undergo reversible color transformations, making them indispensable tools for pH determination and titration endpoints in analytical chemistry. The intricate interplay between chromophores within these molecules dictates their absorption spectra, resulting in vivid color transitions across a defined pH range, a feature that underpins their pivotal role in chemical analyses (Rahmat et al. 2023; Yeow et al., 2021; Yusuf et al., 2017; Yusuf 2018).

Beyond their chemical makeup, the characteristics of phthalein dyes extend to their practical applications and industrial significance. From their widespread use as pH indicators in laboratory settings to their incorporation as vibrant

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<https://doi.org/10.55559/jjbrpac.v1i3.215>

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coloring agents in textiles, cosmetics, and biological staining techniques, phthalein dyes epitomize versatility and adaptability. Their water solubility, chemical stability, and structural variability further amplify their appeal, rendering them indispensable across a spectrum of fields. This review aims to illuminate the diverse facets of phthalein dyes, offering insights into their chemistry, properties, and manifold applications, while also highlighting avenues for future exploration and innovation in this intriguing realm of organic chemistry.

2. Chemistry

Phthalein dyes are characterized by their distinctive molecular structure, typically consisting of a central phthalic acid core with various substituents attached to the aromatic rings. The phthalic acid core comprises two benzene rings connected by a carboxylic acid group (-COOH) in the ortho position. The substituents attached to the benzene rings can

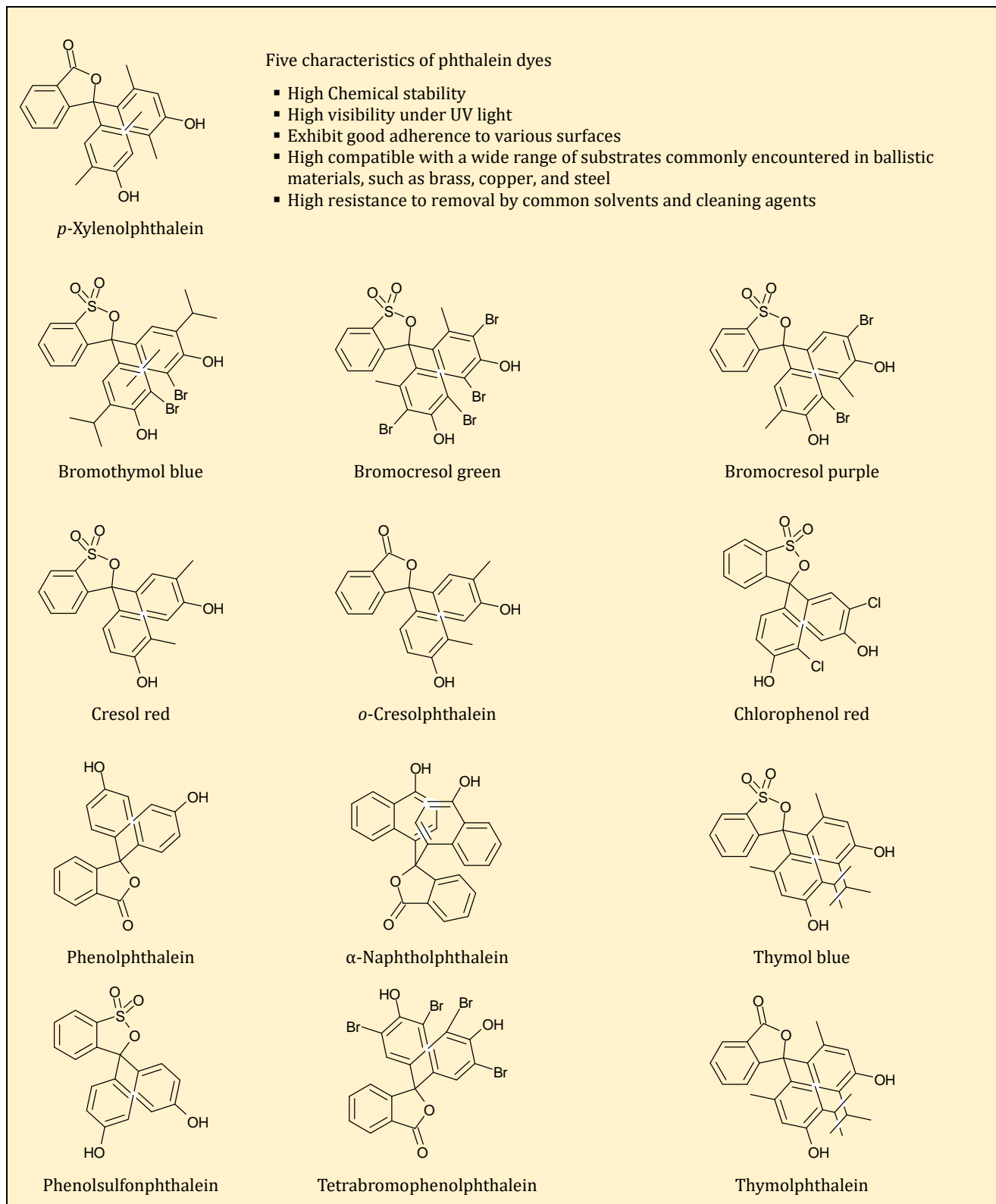


Fig. 1: The chemical structure of common phthalein dyes.

vary, leading to a wide range of phthalein dye derivatives with diverse chemical and physical properties. The molecular structure of phthalein dyes plays a crucial role in determining their color, solubility, stability, and reactivity. The presence of electron-donating or electron-withdrawing groups on the benzene rings can influence the electronic distribution within the molecule, affecting its color intensity and hue. Additionally, the positioning of substituents relative to the phthalic acid core can impact the dye's solubility in different solvents and its affinity for specific substrates.

The structural versatility of phthalein dyes allows for the synthesis of custom-designed molecules tailored to specific applications, making them highly adaptable to various industrial processes. The chemical structure of common phthalein dyes is depicted in Fig. 1.

3. Synthesis Strategies

Synthesis methods for phthalein dyes typically involve the condensation reaction between phthalic anhydride (or phthalic acid) and phenols or aromatic amines. The reaction is often catalyzed by strong acids or bases to facilitate the formation of the dye molecule. Various modification reactions, such as alkylation, acylation, or sulfonation, can be employed to introduce different functional groups onto the benzene rings, thereby modulating the dye's properties. Common synthesis routes for phthalein dyes include (Sabnis 2018; Yeow et al., 2021):

Phthalic Anhydride with Phenols: This method involves the reaction of phthalic anhydride with phenols in the presence of an acid catalyst, leading to the formation of phthalein dyes (Fig. 2a).

Phthalic Anhydride with Aromatic Amines: Aromatic amines can also be used as reactants in the synthesis of phthalein dyes, resulting in amine-substituted derivatives (Fig. 2b).

Modification Reactions: After the formation of the phthalein core, various modification reactions can be employed to introduce additional functional groups, alter the dye's solubility, or enhance its performance in specific applications.

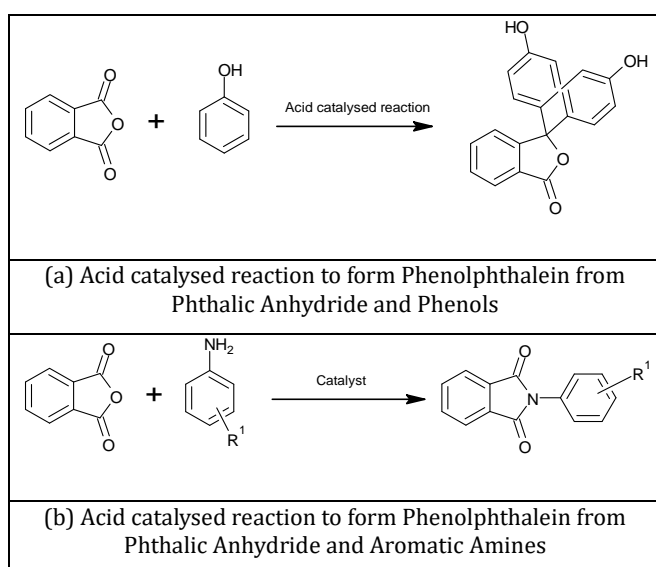


Fig. 2: Synthetic methods for phthalein dyes.

The choice of synthesis method depends on factors such as the desired dye structure, reactivity of the reactants, and scalability of the process for industrial production.

4. Properties of Phthalein Dyes

4.1 Color Characteristics

Phthalein dyes exhibit a wide range of colors, spanning from vibrant shades of red, blue, and green to more subtle hues. The color of a phthalein dye is primarily determined by its molecular structure, including the nature and positioning of substituents on the benzene rings. Electron-donating groups such as hydroxyl (-OH) or amino (-NH₂) substituents tend to impart deeper, more intense colors, while electron-withdrawing groups such as nitro (-NO₂) or carbonyl (-CO) substituents may lead to paler colors. Additionally, the presence of conjugated π -electron systems within the dye molecule contributes to its absorption of visible light, resulting in characteristic coloration. Phthalein dyes can exhibit significant color changes in response to changes in pH or solvent polarity, making them useful as pH indicators or solvatochromic dyes.

4.2 Solubility and Stability

The solubility of phthalein dyes in different solvents depends on their molecular structure and the presence of polar or non-polar functional groups. Generally, phthalein dyes are soluble in organic solvents such as alcohols, ketones, and aromatic hydrocarbons, facilitating their application in various dyeing processes. The stability of phthalein dyes refers to their resistance to degradation or fading over time when exposed to environmental factors such as light, heat, and chemicals. Phthalein dyes are known for their good light fastness, meaning they retain their color intensity when exposed to sunlight or artificial light sources. However, prolonged exposure to harsh conditions or incompatible chemicals may lead to color fading or degradation of the dye molecule.

4.3 Light Fastness and Wash Fastness

Light fastness and wash fastness are important properties of phthalein dyes, particularly in textile dyeing applications where color retention and durability are critical. Light fastness refers to the ability of the dye to resist fading or color change when exposed to light, while wash fastness refers to its resistance to removal or bleeding during laundering or wet treatments. Phthalein dyes are generally known for their excellent light fastness and wash fastness, attributed to their strong molecular interactions with textile fibers and resistance to environmental factors. However, the performance of phthalein dyes in terms of fastness properties may vary depending on factors such as dye concentration, dyeing method, fiber type, and post-treatment processes.

4.4 Chemical Properties

Phthalein dyes exhibit a range of chemical properties that contribute to their suitability for different applications:

Reactivity: Phthalein dyes contain reactive groups that enable them to bind strongly to substrates through covalent or non-covalent interactions. This reactivity is crucial for achieving durable coloration in textiles and other materials.

pH Sensitivity: The color of phthalein dyes can be influenced by changes in pH, with some dyes exhibiting pH-dependent color transitions. This property is exploited in pH indicators, where

the dye changes color in response to changes in acidity or alkalinity.

Thermal Stability: Phthalein dyes generally exhibit good thermal stability, making them suitable for high-temperature dyeing processes without significant degradation.

Solubility: The solubility of phthalein dyes in different solvents can vary depending on their molecular structure and functional groups. This property is important for formulating dye solutions and achieving uniform dye penetration in substrates.

5. Industrial applications

Phthalein dyes, renowned for their versatile chemical properties and vivid coloration, find extensive utilization across a myriad of industrial domains. Delving into the intricate tapestry of industrial applications, the following comprehensive overview elaborates on the diverse roles played by Phthalein dyes (Yusuf 2023; Yusuf and Haji 2023; Sabnis 2018; Yeow et al., 2021):

Textile Industry: Within the textile realm, Phthalein dyes reign supreme as indispensable agents for imparting rich hues to both natural and synthetic fibers. Their exceptional color vibrancy, coupled with remarkable lightfastness and washfastness attributes, renders them pivotal in the creation of enduring and aesthetically pleasing textiles. From haute couture garments to resilient upholstery fabrics and sumptuous carpets, Phthalein dyes infuse the textile landscape with an endless spectrum of captivating colors and enduring brilliance.

Printing Industry: In the realm of printing, Phthalein dyes emerge as veritable stalwarts, serving as linchpins in ink formulations tailored for diverse printing methodologies. Whether employed in offset, gravure, or flexographic processes, these dyes deliver unparalleled color intensity, stability, and substrate compatibility, facilitating the production of crisp and vibrant prints across a plethora of materials ranging from paper and cardboard to plastics and films.

Plastics and Polymers: Phthalein dyes leave an indelible mark on the realm of plastics and polymers, offering an expansive palette of shades and tones for coloring a wide array of plastic materials. Their compatibility spans a gamut of polymers including polyethylene, polypropylene, PVC, and polystyrene, empowering manufacturers to craft a cornucopia of colorful and visually striking plastic products encompassing everything from toys and packaging materials to consumer goods.

Paints and Coatings: In the arena of paints, coatings, and varnishes, Phthalein dyes wield their influence as indispensable constituents, augmenting color formulations with their superb dispersibility, stability, and resistance to fading. Whether adorning architectural facades, automotive finishes, or industrial surfaces, these dyes enhance not only the visual allure but also the longevity and durability of painted substrates, thereby leaving an enduring mark on myriad applications.

Forensic Tracing and Marking: Phthalein dyes cast their illuminating glow within the realm of forensic science, particularly in ballistic investigations where their fluorescence

under ultraviolet (UV) light, chemical robustness, and tenacity against removal prove invaluable. From marking bullets and casings for traceability in criminal investigations to aiding in the identification and tracking of firearms used in illicit activities, Phthalein dyes serve as silent sentinels in the pursuit of justice.

Biomedical Applications: Venturing into the realm of biomedical sciences, Phthalein dyes emerge as potent tools for illuminating the intricate tapestry of biological phenomena. Leveraged as fluorescent probes in biomedical research and diagnostics, these dyes facilitate the labeling and visualization of biological molecules, cells, and tissues, thereby catalyzing breakthroughs in drug discovery, molecular biology, and medical imaging sectors.

Therefore, Phthalein dyes stand as veritable titans across a kaleidoscope of industrial frontiers, imbuing products and processes with a vibrant spectrum of colors, functionalities, and traceability, thus underscoring their indispensability in the modern industrial landscape.

6. Toxicity and Health Hazards

While phthalein dyes are widely used in various industries, concerns have been raised regarding their potential toxicity and health hazards. Some phthalein dyes may contain aromatic amines or other chemical moieties that pose health risks, particularly if they come into direct contact with the skin or are ingested. Additionally, certain dye intermediates or by-products formed during the synthesis of phthalein dyes may be carcinogenic or mutagenic. Regulatory agencies such as the European Union's REACH (Registration, Evaluation, Authorization, and Restriction of Chemicals) have established strict guidelines and restrictions on the use of certain phthalein dyes and related substances to protect human health and the environment. Manufacturers and industries are required to comply with these regulations and ensure the safe handling, use, and disposal of phthalein dyes to minimize potential risks (Yusuf 2019; Yusuf et al. 2023a & 2023b).

In response to concerns regarding potential carcinogenicity, the US Food and Drug Administration (USFDA) enacted a ban on the use of phthalein dyes in certain applications (Jasińska et al., 2019). Despite their once-prominent role in various industries, including pharmaceuticals and cosmetics, their association with adverse health effects prompted regulatory action. Among the primary signs of toxicity following ingestion is a laxative effect, indicating their disruptive impact on gastrointestinal functions. However, the repercussions of phthalein dye exposure extend beyond immediate gastrointestinal distress, often manifesting as delayed symptoms encompassing a spectrum of health complications. The adverse effects of phthalein dyes are not limited to the gastrointestinal system; they can also precipitate a range of systemic disorders. From gastrointestinal and blood disorders to pulmonary edema, liver dysfunction, and impaired kidney function, the toxicological profile of these compounds underscores the gravity of their ingestion (Jasińska et al., 2019; Yusuf 2018). While addressing immediate symptoms such as fluid and electrolyte imbalances, supportive measures are crucial for restoring hepatic and renal functions compromised by toxic exposure. This multifaceted approach aims to mitigate the acute and potentially long-term consequences of phthalein dye toxicity, safeguarding patient well-being amidst the challenges posed by their deleterious effects. Therefore, understanding the properties of phthalein dyes, including their molecular structure, synthesis methods, chemical properties, and potential health hazards, is

essential for informed decision-making in industrial applications and regulatory compliance. Further research and development efforts are needed to address challenges related to toxicity, environmental impact, and sustainability in the use of phthalein dyes.

7. Conclusion

The regulatory measures implemented by the US Food and Drug Administration (USFDA) reflect the gravity of concerns surrounding the use of phthalein dyes due to their potential carcinogenicity and associated health risks. Despite their historical significance in various industries, including pharmaceuticals and cosmetics, the ban underscores the imperative of prioritizing consumer safety and public health. In view of the above discussion, safer alternatives might be a situational option. Moving forward, sustained efforts in research, regulation, and public awareness are essential to mitigate the risks posed by phthalein dyes, ensuring the safety and well-being of individuals and communities worldwide.

Funding

None.

Conflict of Interest

None.

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