The Chemistry of Colorants

Dyes & Pigments

28 June 2018
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_Dyes & Pigments_

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1. (Brief) History of colorants
2. Classifications
3. Physical chemistry
4. Types of dyes and pigments
5. Eight modern research examples
6. Why you might care/current industry
History of dyes and pigments

- Dyes have been derived from plants, animals, and minerals
  - *Indigoid dye* represents the arguably oldest natural dye
    - From plant *Indigofera tinctoria*
    - Used in India for ~4000 years
  - *Woad* was another source of blue in Europe
    - From *Isatis tinctoria*
    - Used in Bronze Age Europe (2500-800 BC)
  - *Tyrian purple* produced the royal color
    - From shell fish Purpura and Murex
    - Made in Tyre and Sidon since 800 BC
    - Produced an awful smell
    - Only source of purple for thousands of years

Many natural dyes have a low chemical affinity to textiles. It was a multistep process to prepare fibers:

1. A mordant (metal salt) is used to impregnate the fibers
   - Metal ion complexes with functional groups
   - Often Al, Fe, Sn, Cr, Cu
   - Commonly used were potash alum $[\text{KAl(SO}_4\text{)}_2 \cdot 12\text{H}_2\text{O}]$ and iron sulfate $[\text{FeSO}_4 \cdot 7\text{H}_2\text{O}]$ and $(\text{SnCl}_2)$
   - Treatment of fabric occurred often in metal vats or with iron nails present
2. The dye was introduced to coordinate with the metal-impregnated fabric

J.N. Chakraborty, in Handbook of Textile and Industrial Dyeing, 2011
Moving away from natural sources

• First two synthetic pigments developed:

1. White lead, basic lead carbonate $[2\text{PbCO}_3\cdot\text{Pb(OH)}_2]$  
   • Described first by Theophrastus of Eresos (~300 BC)  
   • Created by combining lead and acetic acid in the presence of $\text{CO}_2$

2. Blue Frit, Egyptian Blue $[\text{CaCuSi}_4\text{O}_{10}]$  
   • First evidenced in Egypt (~3000 BC)  
   • Created by heating together quartz sand, copper, calcium carbonate, and alkali from ash up to 800-1,000 °C

$$\text{Cu}_2\text{CO}_3(\text{OH})_2 + 8\ \text{SiO}_2 + 2\ \text{CaCO}_3 \rightarrow 2\ \text{CaCuSi}_4\text{O}_{10} + 3\ \text{CO}_2 + \text{H}_2\text{O}$$

Moving into Modernity

• Prussian Blue
  • First truly modern synthetic pigment arising as a result of a deliberately conducted chemical reactions
  • Produced by Diesbach in Berlin in 1704 trying to produce a lake pigment (metal coordinated natural pigment)
  • Created originally by mixing potash, iron sulfate, and blood
  • Cyanide in Greek means “dark blue”
By the early 19th century, synthetic blue colorants existed:
- French ultramarine
  - Synthesized - 1826
  - \( \text{Al}_6\text{Na}_8\text{O}_{24}\text{S}_3\text{Si}_6 \)
- Cobalt blue
  - Synthesized - 1802 (Thenard)
  - \( \text{CoAl}_2\text{O}_4 \)
- Cerulean blue
  - Discovered 1789 (Hopfner)
  - \( \text{CoO}_3\text{Sn} \)
- Phthalo blue (CuPc)
  - Discovered 1927

Soon in the 20th century, reddish-purples, blues, violets, greens, and red dyes started replacing more expensive natural dyes.

Dyes and Pigments

Dyes

Pigments

Acid red 52

**Dyes**

Dyes are required to solvate during the application process; they often also have some affinity for the material being colored. Selectively absorb light due to specific chemical nature of dye.

**Pigments**

Pigments are specific colorants composed of particles insoluble in the application medium; they are colored, colorless, or fluorescent and can be organic or inorganic, finely divided solids. Selectively absorb and/or scatter light due to pigment & material.

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Dyes and Pigments

Colorants

Organic (~15%)

Dyes (75%)

Inorganic (~85%)

Pigments (25%)

Pigments

The Chemical Physics of Colorants

• Industrial value of dyes depends on *wavelength* and *intensity* of the absorption band as a function of dye concentration.

\[ A = \log_{10} \frac{I_o}{I} = \varepsilon l c \]

Technically important dyes display extinction coefficients in excess of \(10^4 - 10^5 \text{ M}^{-1} \text{ cm}^{-1}\)

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The Chemical Physics of Colorants

• Chromophores absorb light within the UV or visible range
  • *Examples*: C=C, C≡C, C=O, C≡N, N=N, NO₂

• Different transitions can occur with chromophores
  • $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$

• Auxochromes are covalently saturated groups that change the wavelength or intensity of the absorption maximum
  • *Examples*: NH₂, OH, SH, halogens
  • Tend to increase wavelength and intensity through conjugation resonance

• Conjugated chromophores tend to increase wavelength and intensity
  • Create an additional set of HOMO/LUMO pairs and increase conjugation area
  • Energy difference between HOMO & LUMO is lowered leading to a bathochromic shift
The Chemical Physics of Colorants

• Chromogens are chemical compounds that are colored or could be made colored by the attachment of a suitable substituent (increases the conjugated system size)

• Solvent yellow 7 (4-Hydroxyazobenzene) as an example:

![Chemical structure of Solvent yellow 7]

• Colorants possess several important traits
  • Absorbs light in the visible spectrum (400-700 nm)
  • Have at least one chromophore
  • Have a conjugated system
  • Exhibit resonance of electroms

Hossain I (2014). Investigation into cotton knit dyeing with reactive dyes to achieve right first time (RFT) shade. Master Thesis. Daffodil International University, Bangladesh
The Chemical Physics of Colorants

• General rules for adjusting color:

  • Adding electron-donating groups gives a bathochromic effect

  • Electron-donating and electron-accepting groups in conjugation provide an intense bathochromic effect

  • Increasing the number of electron-attracting groups conjugated with electron-donor groups has a bathochromic effect

  • The electron donating group are enhanced by adding alkyl groups to the N-atom

Common Classes of Colorants

• Dyes:
  • Acid Dyes
  • Anthraquinone Dyes
  • Azo Dyes
  • Basic Dyes
  • Direct Dyes
  • Disperse Dyes
  • Indigoid Dyes
  • Nitro and Nitroso Dyes
  • Phthalocyanine Dyes
  • Reactive Dyes
  • Sulfur Dyes
  • Vat Dyes

• Pigments:
  • Inorganic Pigments
  • Organic Pigments
Common Classes of Colorants

• Dyes:
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  • Vat Dyes

• Pigments:
  • Inorganic Pigments
  • Organic Pigments
Acid Dyes

• Generally comprised of organic sulfonic acids

• Commercially available as sodium salts; excellent water solubility

• Contains azo, anthraquinone, triphenylmethane, nitro, and nitroso chromophoric groups

• Used to dye many types of fiber:
  • Cotton
  • Polyester
  • Rayon
  • Wool
  • Silk

Anthraquinone Dyes

• Based around an anthraquinone central structure

• Some of the oldest types of dyes (found >4000 years ago)
• Good brightness and fastness
• Most synthetic substitution occurs at the α-position with sulfonation or nitration
• For β-substituted dyes, synthesis usually starts from phthalic anhydride or benzene derivatives

Disperse red 60
Reactive blue 19

Azo Dyes

• Most common and most widely used; >60% of the dyes

\[
\text{A} - \text{N}=\text{N} - \text{B}
\]

• Often contain two aromatic groups in A & B, but must have at least one
• Exist in the trans form
• “A” often contains electron-accepting substituents while “B” contains electron-donating substituents

Acid red 2

Disperse yellow 7

Basic Dyes

• Also called cationic dyes due to the presence of a positive charge, often caused by an ammonium cation

• Being water soluble, they were originally used for paper, silk and wool

• Generally low color fastness
  • Forms covalent bonds with acrylic fibers negating this issue
Direct Dyes

• Water-soluble and easily applied to cellulose
  • Anionic; forms bonds with cellulosic fibers
  • No mordant required
  • Applied from aqueous mixture containing an electrolyte

• Generally have high molecular masses
  • Promotes dye aggregation
  • Promotes substantively to the fiber

• Also called substantive dye

Direct blue 1

Direct black 22

Disperse Dyes

• Often contain azo, anthraquinone, and nitro groups

• Water-insoluble dyes with affinity for hydrophobic fibers
  • Nylon
  • Cellulose
  • Acrylic

Disperse yellow 26  Disperse red 9

Indigoid Dyes

• All based on the organic compound—indigo

\[
\text{H} = \begin{array}{c}
\text{N} \\
\text{C} \end{array} 
\]

• Obtained from natural sources for \(~5000\) years until the 19\(^{th}\) century
• One of the first natural molecules synthesized
• Pflegers’s method is used to create most of the high quality indigo

\[
\text{NaOH} \quad \text{KOH} \quad \text{NaNH}_2 \quad \text{-H}_2\text{O} \quad \text{O}_2 \quad \text{-H}_2\text{O}
\]

\[
\begin{align*}
\text{pH} & \quad \text{Below 11.4} & \quad \text{Above 13.0}
\end{align*}
\]

Ünlü M (2008) Indigo dyeing wastewater treatment by the membrane based filtration process, Master Thesis, Middle East Technical University, Ankara, Turkey
Nitro and Nitroso Dyes

• Minor commercial importance

• Of interest for their small molecular structure

• Used in acid form to dye natural fibers such as silk or wool

Disperse yellow 1

Picric Acid

Acid yellow 24

Phthalocyanine Dyes

• A class of macrocyclic compounds possessing a highly conjugated electron system with intense near-IR absorption

• They have a number of unique properties:
  • Increased stability
  • Diverse coordination properties
  • Architectural flexibility

• Often intense color in 650-750 nm range

• Coordinates with metals such as Cu, Fe, Si, Ge, As

Reactive Dyes

• Differ from other dyes because their molecules react to form covalent bonds with functional groups on the fibers

• Have exceptional qualities:
  • High wet-fastness
  • Brilliant
  • Large range of hues

• Usually contain –NH–, –CO–, or –SO₂– as linking group

Reactive Red 198

Sulfur Dyes

• Almost always used for dyeing cellulosic fibers

• Insoluble in water
  • Reduced to the water-soluble leuco (white/reduced) form
  • Applied using sodium sulfide solution
  • Dye formed via oxidation while impregnated in the fiber

• Often they don’t have well defined structures or compositions due to oligomerization & di/poly-sulfide links

Springer RM (1997) Chemistry and Applications of Leuco Dyes
Vat Dyes

• Water-insoluble pigments
  • Called dyes because in alkaline solution, reduction occurs forming a water-insoluble leuco form

• Held to cellulose via van der Waals forces and hydrogen bonding

• Oxidizes on drying to become water-insoluble again leading to high color fastness

• Lack of industry knowledge and basics for application techniques have led to a decrease of usage

Vat yellow 4
Vat blue 1 / Indigo
Vat brown 45
Inorganic Pigments

• Broken into four categories:
  1. White
  2. Black
  3. Colored
  4. Miscellaneous
    • Metal effect
      • Flakes/lamella-shaped particles of soft, ductile metals
      • Avoid issues of organic molecules hindering cold welding
    • Nacreous
      • Pearlescence due to multiple partial reflections
      • Fish-scales (guanine)
    • Transparent
      • Used in protection as a lacquer
      • Blocks UV light with small particles
    • Luminescent
      • Solid fine particulates
      • Reemit absorbed energy as light
      • Rely on fluorescence or phosphorescence

Buchel KH, Moretto H, Werner D (2015) Industrial Inorganic Chemistry
Organic Pigments

• Based on carbon chains and carbon rings
  • Can have metallic elements for stabilization
  • Must be insoluble at the time of application
  • Have a smaller average particle size than inorganic pigments

• Broken down into six main categories:
  1. Azo
  2. Triaryl carbonium
  3. Anthraquinone
  4. Dioxazine
  5. Polyclic
  6. Quinophthalone

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Pigment yellow 12
Pigment yellow 138
Pigment violet 23

BASF (2017) Pigments
YInMn Blue

• Discovered accidentally by Andrew Smith and Prof. Mas Subramanian at Oregon State University in 2009
  • Looking for multiferroics
  • Instead formed, at 2,000 °F upon mixing of YInO₃ and YMnO₃, a bright blue compound
• Prof. Subramanian recognized the potential use as a pigment
  • Had worked for DuPont Co.
  • Filed patent disclosure covering the pigment
• Notable features
  • Extremely vibrant, near-perfect blue
  • Extremely stable; does not fade (as does ultramarine/Prussian blue)
  • Non-toxic (as is cobalt blue)
  • Strong infrared radiation reflection (useful for energy-saving cool coatings)
• Crayola created the “Bluetiful” crayon, replacing Dandelion (2017)
• Being released as an acrylic paint by Matisse
• Can adjust color by changing ratios; YIn₀.₈Mn₀.₂O₃–optimal

C@ZrSiO$_4$

- Published 2016 by Weihui Jiang at Jingdezhen Ceramic Inst.
- A zircon-based black pigment consisting of \textit{in-situ} polycondensation
- After enameling on tiles at 1200 °C, C@ZrSiO$_4$ pigment appeared a promising candidate for high temp. ceramics
  - Smooth, clean, deep hue
  - High tinting ability
  - Absence of any surfactants

- 30m in air at 1200 °C
- No cracks or holes seen
- Inclusion of pigment has good thermal and chemical stability in the glaze at high temp.

Synthetic Development of Succinimide Dyes

- Published 2014 by Yousef Valizadeh
- Developed a one-pot reaction of *Meldrum’s acid*, alkyl isocyanide, and 4-(2-phenyldiazenyl)benzenamine

\[
A = \log_{10} \frac{I_o}{I} = \varepsilon l c
\]

<table>
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<tr>
<th>( \lambda_{\text{max}} ) (nm)</th>
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<th>346.7</th>
<th>344</th>
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<td>1.66</td>
<td>0.4</td>
<td>1.35</td>
<td>1.32</td>
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<td>( \varepsilon )</td>
<td>30,180</td>
<td>40,000</td>
<td>26,470</td>
<td>24,900</td>
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Tyrian purple
Theoretical/Computational Studies

• Yujun Zheng’s group at Shandong University study the most important component of modern deep red pigments—alkannin
• The group explores the mechanism of the double proton transfer

Model the energy

• Confirm importance TS1
• Suggest the stepwise excited state double proton transfer
Development of a New Chelating Dye

• Hongping Zhou in Anhui University in 2018 developed a copper sensitive dye for use in water samples and *in vivo* experiments.

![Chemical structure](image)

Huihui Zhang, Zeyue Wei, Ying Xia, Min Fang, Weiju Zhu, Xingyuan Yang, Fei Li, Yupeng Tian, Xuanjun Zhang, Hongping Zhou, Exploration research on synthesis and application of a new dye containing di-2-picylamine. Saa(2017), https://doi.org/10.1016/j.saa.2018.02.023
Photochromic Colorants

• Ben Zhong Tang at HKUST-Shenzhen Research Institute published in 2018 a multiphotochrome molecule

- Can “turn-on” or “turn-off” based on amount of water present in CH$_3$CN

- Could be doped into a polymer matrix to act as miroactuators and create a corresponding macroscopic behavior in the material

<table>
<thead>
<tr>
<th>Fraction of water (vol %)</th>
<th>0</th>
<th>50</th>
<th>70</th>
<th>80</th>
<th>99</th>
</tr>
</thead>
<tbody>
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<td>Dimerized</td>
<td>&lt;1%</td>
<td>&lt;4%</td>
<td>&lt;4%</td>
<td>90%</td>
<td>99%</td>
</tr>
<tr>
<td>Cyclized</td>
<td>99%</td>
<td>96%</td>
<td>96%</td>
<td>&lt;10%</td>
<td>&lt;1%</td>
</tr>
</tbody>
</table>
Vertically Aligned Nanotube Arrays

- Original development by Lehman in the UK for use in thermal detection applications in the infrared
- Spectrally flat over most visible wavelengths
  - Absorbs 99.965% of visible light
  - Vertical nanotubes are grown using chemical vapor deposition
  - Light doesn’t reflect out, but gets trapped in the tubes until absorption

"Vantablack, the world's darkest material, is unveiled by UK". South China Morning Post - World. 15 July 2014.
Kohei Mizuno, Juntaro Ishii, Hideo Kishida, Yuhei Hayamizu, Satoshi Yasuda, Don N. Futaba, Motoo Yumura, and Kenji Hata PNAS April 14, 2009. 106 (15) 6044-6047; https://doi.org/10.1073/pnas.0900155106
Near-Infrared-Transmitting Optical Filter

- Developed by Ayyappanpillai in 2017
- Visibly opaque but NIR-transparent materials are important for security systems and night-vision technology
  - DPP-Amide blocks 300-800 nm light by H-bonding and π-stacking
  - Transmits beyond 850 nm
Industrial Opportunities

• Typical Education Requirement
  • Ph.D. required for most research positions
  • Postdoctoral work required for most academic positions
    • Synthetic chemistry
    • Analytical chemistry
    • Organic chemistry
    • Polymer chemistry
    • Material chemistry

• Future Employment Trend
  • Steady growth in paints & varnishes
    • Accounts for 43% of pigment and 27% of plastic colorant demand
  • Niche markets expected to grow
    • Photochromic colorants
    • Medical dyes
    • Infrared dyes for security
    • Hair dyes
  • High-tech applications up-and-coming
    • Inkjet microfabrication
    • 3D printing

• Laboratories
  • Academic
  • Industrial
  • Government

• Salaries (2015)
  • Lab managers: $76,000 median
  • Pigment chemists: $65,400 median
  • Ink chemists: $60,200 median
  • (note: B.S. chemists earn $50 to $80K)
Industrial Opportunities

• Typical work
  • Develop applications for existing dyes and pigments
  • Examine health, environmental, and safety concerns of colorants
  • Design, create, and characterize novel products and formulations
  • Analyze historical artifacts and artwork for pigments and dyes used
  • Work in crime scene analytics determining dyes and pigments in evidence
  • Teach courses and train students

Professional Organizations

[ZnO]
Thank Your for Your Attention!

Great resources

