Lecture 5.1 – Classification of Dyes and Introduction to Key Dye Types

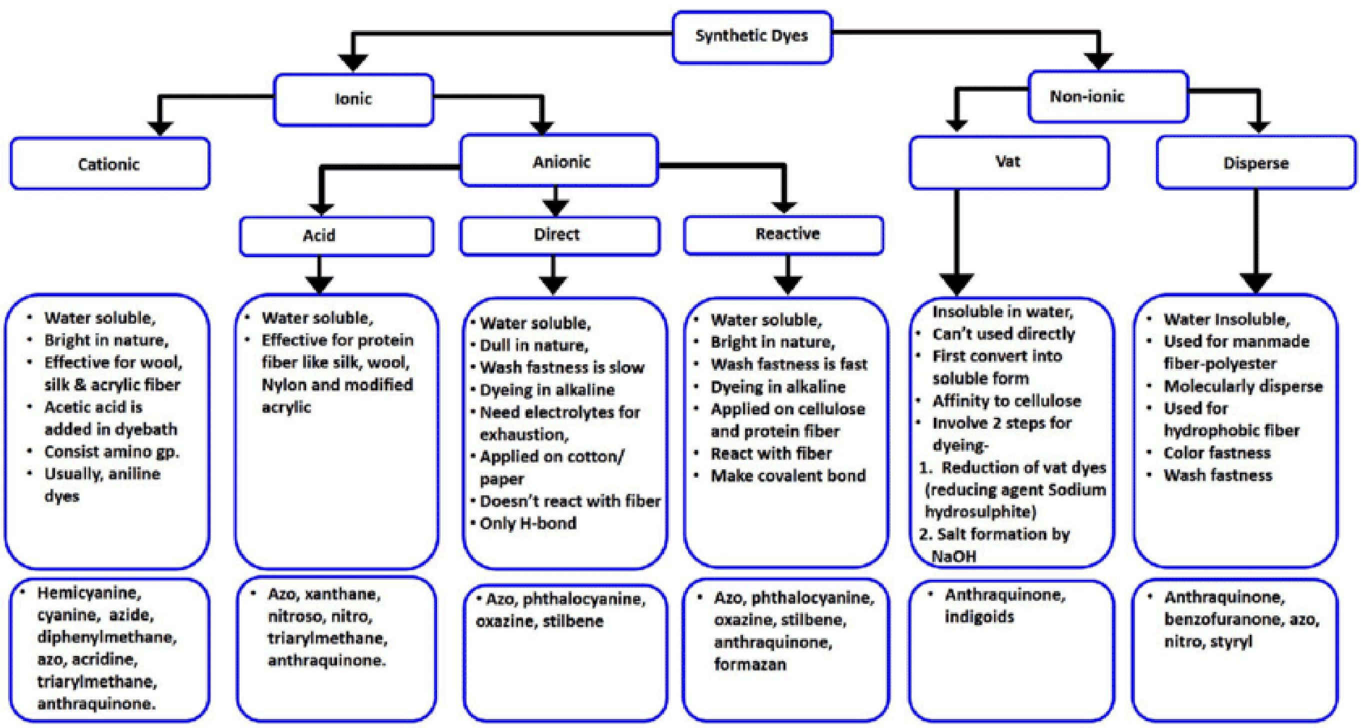
Learning Objectives

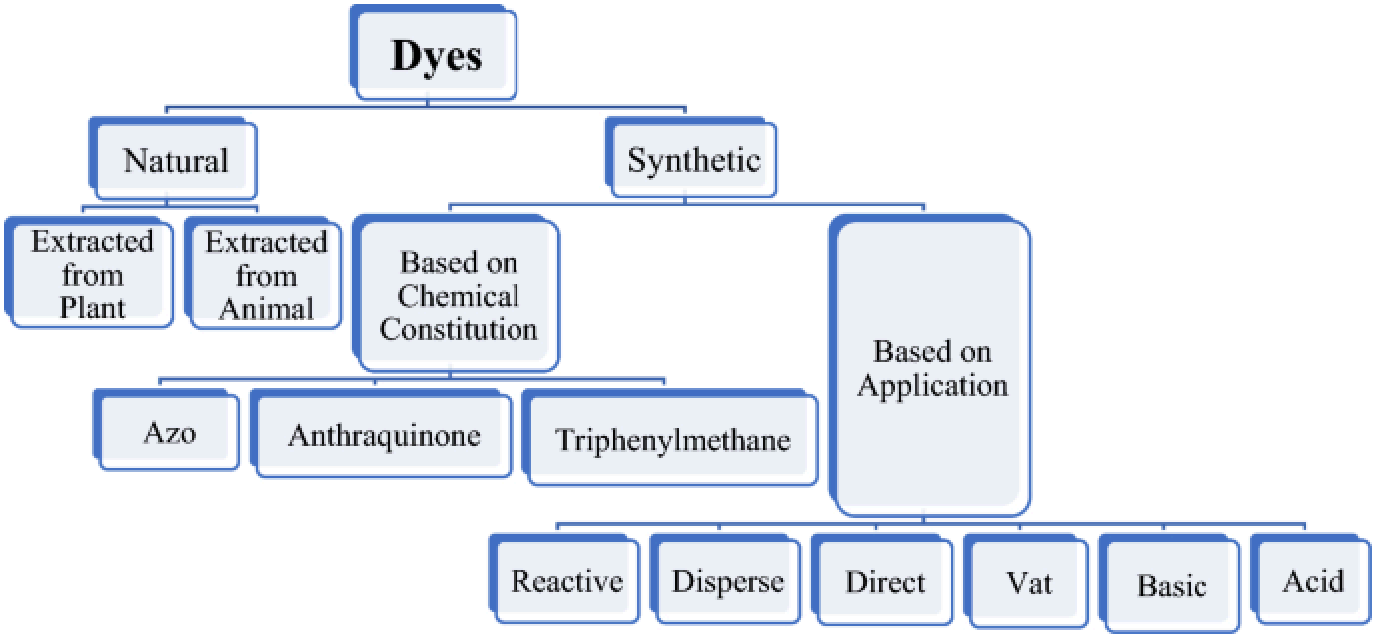
• Understand classification of dyes based on constitution and application.
• Gain knowledge about various types: Disperse, Reactive, Azo dyes.

1. Definition of Dye

A dye is a colored substance that has an affinity to the substrate to which it is being applied. Dyes are usually applied in an aqueous solution and may require a mordant to improve the fastness of the dye on the fiber.

2. Classification Based on Constitution

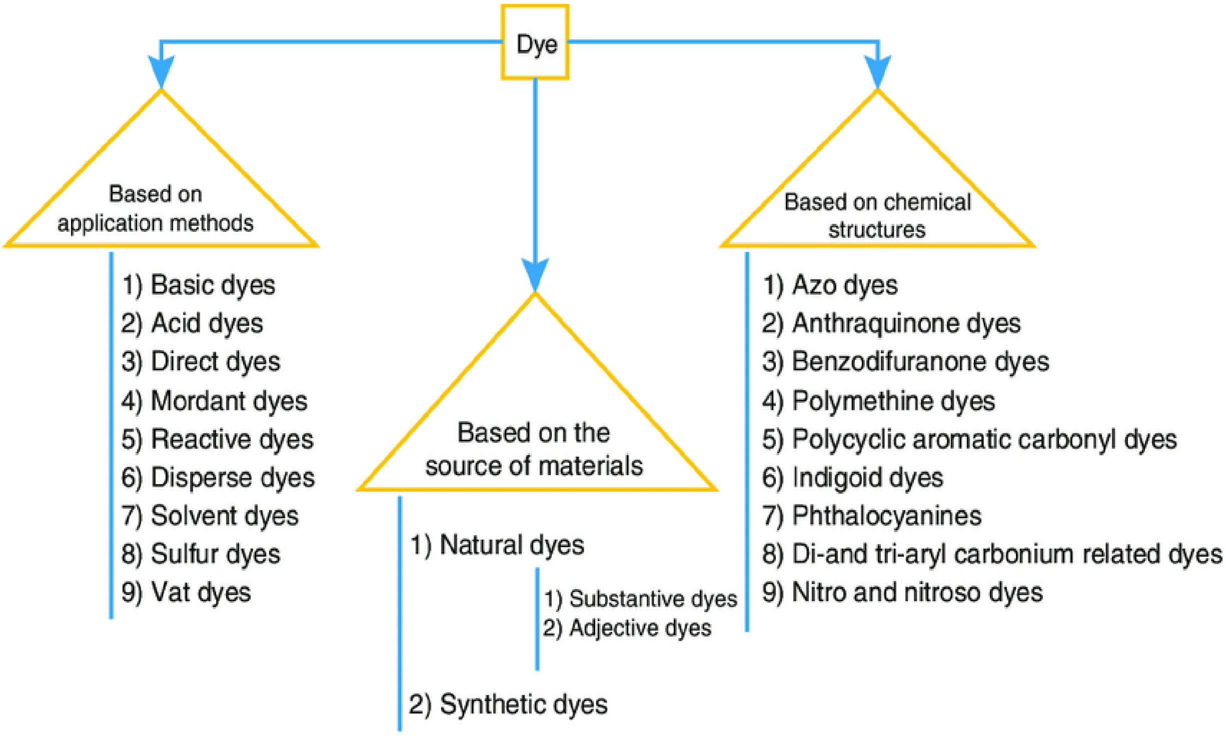




Dyes can be classified based on their chemical constitution as follows:

- Azo Dyes: Contain one or more azo (-N=N-) groups. These are the largest and most important class of synthetic dyes.
- Anthraquinone Dyes: Derived from anthraquinone; used in vat and disperse dyes.
- Nitro/Nitroso Dyes: Contain nitro or nitroso functional groups, typically used for wool and silk.

3. Classification Based on Application



Dyes may also be classified by their application method:

- Reactive Dyes: React chemically with the fiber to form a covalent bond. Used for cellulose fibers like cotton.
- Disperse Dyes: Non-ionic dyes used for synthetic fibers such as polyester and nylon.
- Vat Dyes: Water-insoluble dyes made soluble by reduction for application, then reoxidized to become water-insoluble again.
- Direct, Acid, Basic, and Mordant dyes are also included in this classification.

4. Introduction to Azo Dyes

Azo dyes are characterized by the presence of one or more azo (-N=N-) bonds. They are usually formed by diazotization of aromatic amines followed by coupling with phenols or aromatic amines.

Example Reaction (Formation of Methyl Orange):

5. Introduction to Disperse and Reactive Dyes

- Disperse Dyes:

◆ **Definition:**

Disperse dyes are **non-ionic**, **sparingly water-soluble dyes** that are mainly used for dyeing **hydrophobic synthetic fibers** like **polyester, cellulose acetate, and nylon**. They are applied from **aqueous dispersions**, hence the name *disperse* dyes.

History and Development:

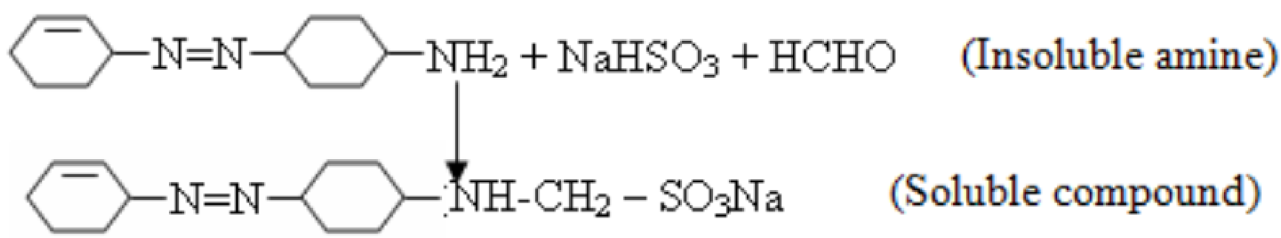
Disperse dyes were first developed in the **1920s** to dye **cellulose acetate fibers**, which could not be dyed with traditional water-soluble dyes due to their hydrophobic nature. The breakthrough came with the use of **fine suspensions** of these dyes and **dispersing agents**.

Chemical Nature:

- Typically **azo**, **anthraquinone**, or **nitro** compounds.
- They are **small**, **planar**, and **non-polar to moderately polar** molecules.
- They contain **no ionic groups** (no $–SO_3^-$ or $–NH_3^+$ groups).
- Often have **amino**, **nitro**, **hydroxyl**, or **cyano** substituents to control solubility and color tone.

Structure Example:

A typical disperse dye structure:



Application Mechanism:

1. **Dispersion**: Dye is ground into fine particles and mixed with dispersing agents (like lignin sulfonates).
2. **Dye bath preparation**: Disperse dye is added to water, creating a suspension.
3. **Diffusion**:
   - Under **high temperature (130°C in HT dyeing)** or **with carriers**, the synthetic fiber swells slightly.
   - The dye molecules **diffuse** into the **amorphous regions** of the fiber by **solid-solution** mechanism.

4. **Exhaustion and Fixation**: Dye molecules are absorbed and **physically entrapped** inside the fiber due to hydrophobic interactions and Van der Waals forces.

◆ **Key Properties:**

Property	Description
Solubility	Very low in water (hence used as dispersions)
Affinity	High for synthetic fibers like polyester
Lightfastness	Generally good, varies with structure
Washfastness	Good due to physical entrapment in fiber
Sublimation	Tendency to sublime at high temperatures (used in transfer printing)

◆ **Classification (Based on Energy Level):**

Disperse dyes are classified by **molecular size and sublimation fastness**:

Class	Features	Example Fibers
Low energy	Small, easily diffusing molecules; require carriers	Acetate, Nylon
Medium energy	Intermediate diffusion and temp.	Polyester blends
High energy	Large, thermally stable; HT dyeing needed	Polyester (PET)

◆ **Dyeing Methods:**

1. **High Temperature Dyeing (HT)** – at ~130°C under pressure.
2. **Carrier Dyeing** – using aromatic organic carriers to swell fiber at 100°C.
3. **Thermosol Dyeing** – pad-dry-heat set at ~200°C (used in continuous dyeing).
4. **Transfer Printing** – dye is sublimed from paper to fiber (sublimation printing).

◆ **Advantages:**

- Bright, vibrant shades
- Suitable for synthetic fibers
- Good wash and light fastness

- Compatible with various dyeing and printing methods

Limitations:

- Environmental concerns due to dispersing agents and carriers
- Sublimation at ironing temperatures (for low-energy dyes)
- Difficult to dye deep shades uniformly without HT dyeing

Environmental and Sustainability Aspects:

- Many disperse dyes and carriers can be **toxic or bio-accumulative**.
- Effluent treatment and development of **biodegradable dispersants** are areas of active research.
- Supercritical CO_2 dyeing is an emerging eco-friendly method.

Applications:

- **Polyester garments** (sarees, sportswear, T-shirts)
- **Blended fabrics** (polyester-cotton)
- **Home textiles** (curtains, upholstery)
- **Transfer printing** (for logos, graphics)

Example Dyes:

CI Disperse Name	Shade	Type
Disperse Yellow 3	Yellow	Monoazo
Disperse Red 11	Red	Anthraquinone
Disperse Blue 79	Blue	Anthraquinone

• Reactive Dyes: Contain reactive groups like chlorotriazine or vinyl sulfone which form covalent bonds with cellulose fibers.

◆ **Definition:**

Reactive dyes are **anionic, water-soluble dyes** that form **covalent bonds** with the **hydroxyl groups of cellulose** (cotton, rayon, linen) or **amino groups of protein fibers** (wool, silk) during dyeing. This **chemical reaction** ensures **excellent wash fastness**, making them one of the most permanent dye classes.

◆ **Historical Background:**

Introduced by **ICI (Imperial Chemical Industries)** in **1956** under the brand name *Procion*, reactive dyes revolutionized cellulose dyeing. They addressed the poor wash fastness of direct dyes.

◆ **Chemical Nature:**

A reactive dye typically consists of three key components:

1. **Chromophore** – Provides the color (e.g., azo, anthraquinone, phthalocyanine).
2. **Reactive group** – Forms covalent bond with fiber (e.g., chlorotriazine, vinyl sulfone).
3. **Bridging group/linker** – Connects chromophore to reactive group (e.g., ethylene, amino groups).

Example:

Procion Red MX-5B

- Chromophore: Azo
- Reactive group: Dichlorotriazine

◆ **Mechanism of Dyeing:**

1. **Adsorption** – Dye is attracted to the fiber surface (usually in alkaline pH).
2. **Diffusion** – Dye penetrates into the fiber matrix.
3. **Fixation** – **Nucleophilic substitution** or **addition reaction** forms **covalent bond**:
   - Cell-OH + Dye-X → Cell-O–Dye + HX

   (Where X = good leaving group, like Cl^- or SO_3^-)
4. **Washing-off** – Unreacted dye is removed using detergent and water.

🔹 **Types of Reactive Dyes (Based on Reactive Groups):**

Type	Reactive Group	Reaction Type	Temperature Range	Example Brand
Monochlorotriazine	–Cl	Nucleophilic substitution	30–40°C	Procion MX
Dichlorotriazine	$–Cl_2$	Nucleophilic substitution	40–60°C	Cibacron
Vinyl sulfone	$–CH=CH_2$ (from β-sulfatoethylsulfone)	Nucleophilic addition	60–80°C	Remazol
Mixed bifunctional	2 reactive groups	Dual reactivity	30–80°C	Drimarene, Cibacron C

🔹 **Advantages:**

- **Strong covalent bond → Excellent wash and light fastness**
- **Wide color range** and brightness
- Applicable by **cold pad-batch, exhaust, or continuous methods**
- Eco-friendly alternatives available

🔹 **Limitations:**

- High **salt (NaCl or Glauber's salt)** and **alkali (Na_2CO_3 or NaOH)** requirements
- Unfixed dye can cause **environmental pollution** if not treated properly
- Sensitive to **hydrolysis**, leading to reduced fixation efficiency

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🔹 **Dyeing Methods:**

1. **Exhaust Dyeing** (Common in yarn/fabric):
   - Temp: 30–80°C
   - Add salt to promote dye uptake, then alkali for fixation
2. **Cold Pad Batch** (Curing at room temp):
   - Efficient and low energy
   - Pad with dye-alkali solution → batch → wash

3. **Continuous Dyeing (Pad-Dry-Cure)**:
    - For large-scale operations
    - Short process time

🔹 **Applications:**

- **Cotton** (main use)
- **Viscose rayon**, **linen**
- With modification, even on **wool** and **silk**
- **Inkjet textile printing**
- **Reactive pigment printing** (new research area)

🔹 **Environmental Concerns:**

- Unfixed dye + salts = **high COD/BOD in effluent**
- **Biological treatment**, **membrane filtration**, and **advanced oxidation** are used for wastewater treatment
- Research ongoing in **low-salt** and **salt-free** dyeing technologies

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- **Structure Example:**

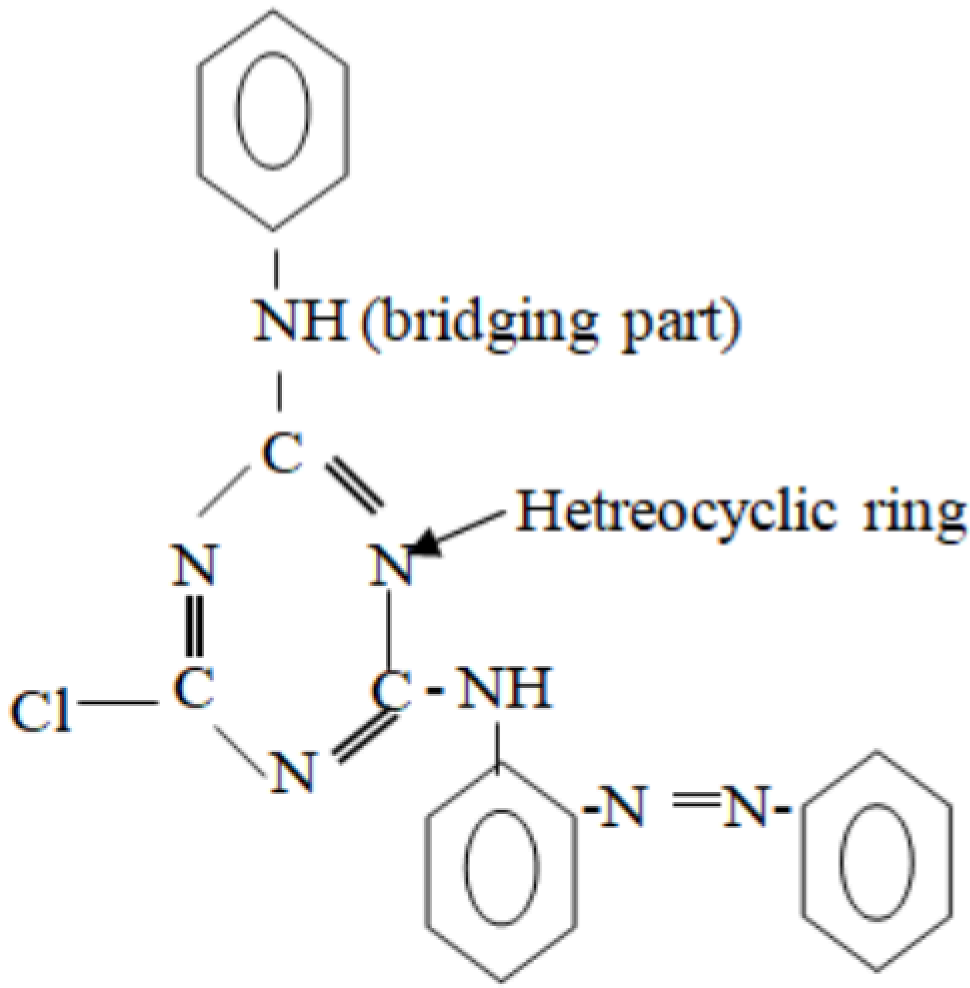

Fig: Chemical structure of reactive dyes

- **Comparison with Other Dyes:**

Property	Reactive Dyes	Direct Dyes	Vat Dyes
Bond Type	Covalent	Hydrogen bonding	Van der Waals
Wash Fastness	Excellent	Poor to moderate	Excellent

Property	Reactive Dyes	Direct Dyes	Vat Dyes
Cost	Moderate	Low	High
Application Ease	Moderate	Easy	Difficult

🔹 **Real-World Brands & Commercial Names:**

Brand	Manufacturer	Type
Procion MX	Dystar	Cold reactive dye
Remazol	Huntsman	Vinyl sulfone
Cibacron	Ciba	Monochlorotriazine
Drimarene K	Clariant	Bifunctional

References

1. Shreve's Chemical Process Industries, 5th Edition
2. Kirk-Othmer Encyclopedia of Chemical Technology
3. NPTEL Course: Industrial Chemistry – https://nptel.ac.in/courses/103103217

Assignment Questions

1. Classify the following dyes: Congo red, Indigo, Methyl orange.
2. Write the key difference between Disperse and Reactive dyes.
3. Draw the diazotization reaction for Azo dye formation.