

Natubhai V. Patel College of Pure & Applied Sciences
 B.Sc. Semester VI
 Industrial chemistry/Industrial chemistry (Vocational)
 US06ICH01/US06CICV01: Dyes and intermediates
 UNIT – 3

SYLLABUS

Introduction, classification and applications of Anthraquinone (VAT) dyes, Indigoid dyes. Disperse dye, Reactive dyes.

3.0 ANTHRAQUINONE DYES

3.0.1 Introduction

Anthraquinone, the **basic system** of these dyes, has a **faintly yellow colour**, It is **not itself a dye**. The **introduction of relatively simple electron donors** gives anthraquinone compounds which, according to the strength of the electron donors ($\text{OH} < \text{NH}_2 < \text{NR}_2 < \text{NHR}$) absorb in any desired region of the visible spectrum. Dyes based on anthraquinone and related polycyclic aromatic quinones are of great importance. In Anthraquinone dyes Quinonoid group and $\text{C}=\text{O}$ are chromophore.

3.0.2 Classification

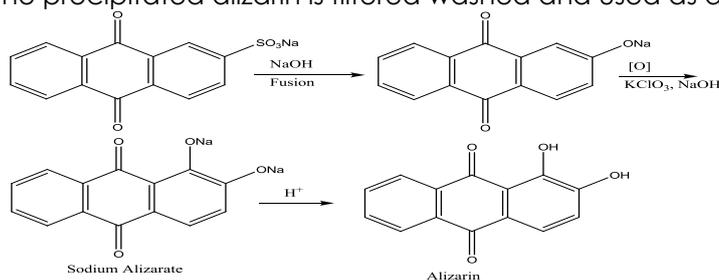
1. Anthraquinone Mordant dyes.
2. Anthraquinone Vat dyes.
3. Anthraquinone Acid dyes.
4. Anthraquinone Disperse dyes

3.0.2.1 Anthraquinone mordant dyes

These **contain** groups such as **hydroxyl or carboxyl group** which can combine with metal ions so as to form insoluble compounds called lakes. The colour of the lake depends upon the mordent i.e. the metal used. Some of the important anthraquinone mordant dyes are as follows.

1. Alizarin

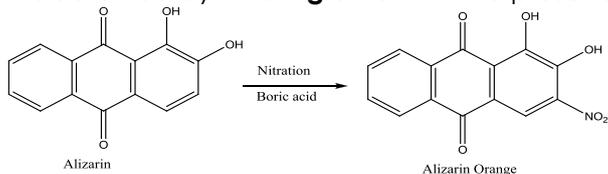
It is **1, 2-dihydroxyanthraquinone**. It is also known as **Mordant R-11**. It is obtained by heating under pressure, silver salt (sodium anthraquinone-2-sulphonate, so called because of its silvery crystals), caustic soda, potassium chlorate and water in a steel autoclave at about 180°C . The resulting melt is blown into water and acidified to decompose the sodium alizarate, the precipitated alizarin is filtered washed and used as a paste (2.0%).



Alizarin is a **red crystalline solid** insoluble in water but soluble in alcohol and alkali. It is a mordant dye and colour is mainly depends on the type of mordant.

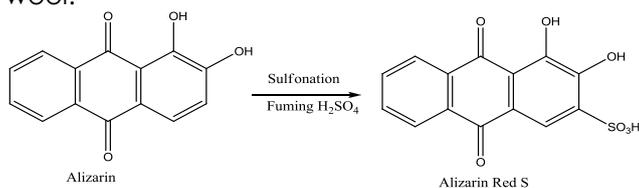
2. Alizarin Orange

It is obtained by **nitrating alizarin** in the presence of boric acid.



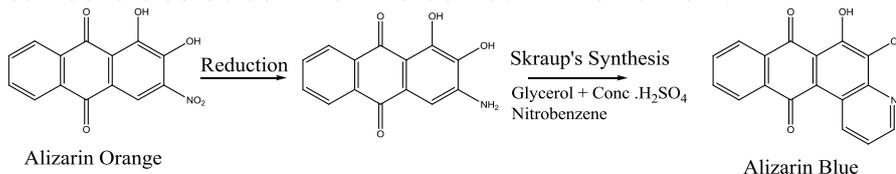
3. Alizarin Red-S

It is obtained by the **Sulfonation of alizarin** with fuming sulfuric acid. It is used for dyeing wool.



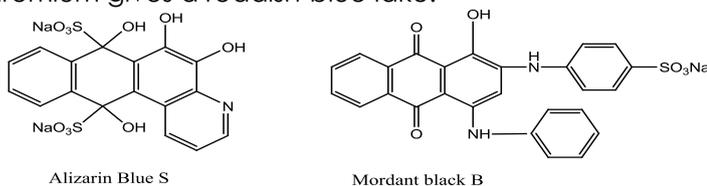
4. Alizarin Blue

It is obtained by **reducing alizarin orange** to 3-aminoalizarin followed by **Skrup's synthesis** of quinoline, i.e. by heating with glycerol, conc. H_2SO_4 and nitrobenzene. Alizarin blue dyes wool a blue colour when mordanted with Chromium.



5. Alizarin Blue-S

It is the **sodium bisulphite salt of Alizarin Blue**. It is soluble in water. It when mordanted with chromium gives a reddish-blue lake.



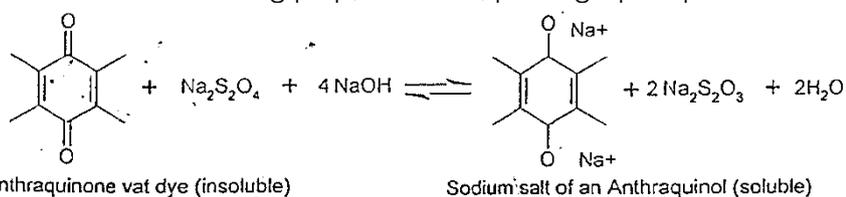
6. Mordant Black-B

It is made by **condensing aniline** with **1,2,4-trihydroxyanthraquinone** and **sulphonating the resulting base**. It is applied to wool with a chromium mordant and is quite fast to light and washing.

3.0.2.2 Anthraquinone vat dyes

Most of the **vat dyes** are **derivatives of Anthraquinone** or **related compounds**. These essentially contain grouping such as $-\text{CO}-\text{CH}=\text{CH}-\text{CO}-$ present as a quinonoid ring system or $-\text{CO}-(\text{CH}=\text{CH})_n-\text{CO}-$ where "n" is a suitable integral and $-(\text{CH}=\text{CH})_n$ part is involve either through the fused heterocyclic or through the, polycyclic system These have a high molecular weight and are insoluble in water. In order to **apply anthraquinone vat dyes** to the fabrics, these are first of all **converted into soluble form** by treating them with a **reducing agent** (sodium hyposulphite) in **alkaline medium**. Then the cloth is immersed in the vat soluble dye solution, kept there for some time and **finally exposed to air**.

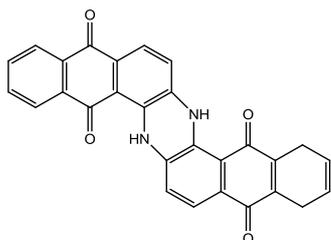
These dyes are mainly used for dyeing cotton, wool, nylon, silk, calico-printing etc. These are also used for colouring pulp, cements, photographic prints etc.



The important anthraquinone vat dyes are:

1. Indenthron blue / Indanthrone / Indanthrene / Vat Blue-4

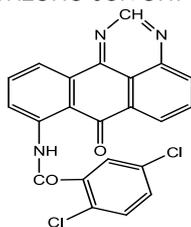
It is manufactured by fusing 2-amino anthraquinone with potassium hydroxide in the presence of potassium chlorate or potassium nitrate at 250°C .



Indanthrene blue

2. Indanthrone / Indenthrene Yellow-4GK

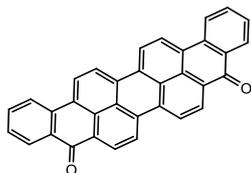
It is prepared by condensing **2,5-dichlorobenzoyl chloride** with **1,9-anthra pyrimidine**. The latter compound is obtained by condensing 1,5-diaminoanthraquinone with formamide in nitrobenzene solvent in the presence of copper compound.



Indanthrene Yellow 4GK

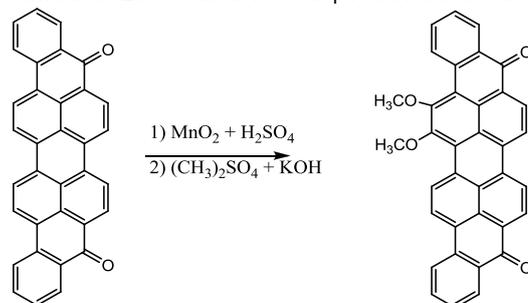
3. Manufactured from benzanthrone

Several important vat dyes have been manufactured from benzanthrone. Among these are **di-benzanthrone** (Vat Blue-20) and **Caledon Jade Green**.



Dibenzanthrone

Di-benzanthrone when **oxidized with manganese** by methylation with dimethyl sulfate in nitrobenzene and in the presence of alkali yields **Caledon Jade Green**.

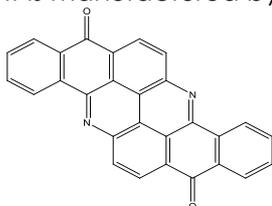


Dibenzanthrone

Caledon jade green

4. Flavanthrone / Flavanthrene / Indenthrene Yellow

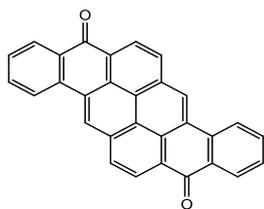
It is manufactured by **fusing 2-amino anthraquinone** with **caustic potash** at 350°C.



Flavanthrone

5. Pyranthrone / Pyranthrene / Indanthrene Golden Orange-G

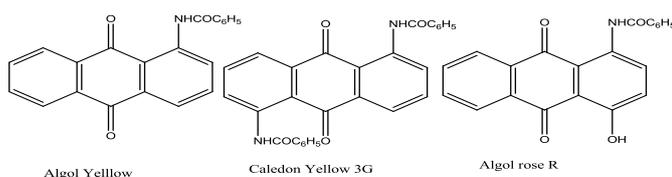
It is manufactured by **heating 1-chloro-2-methyl anthraquinone** with **copper powder** followed by **treatment** with **alcoholic KOH**. It is yellow dye and is very fast.



Pyrenthron

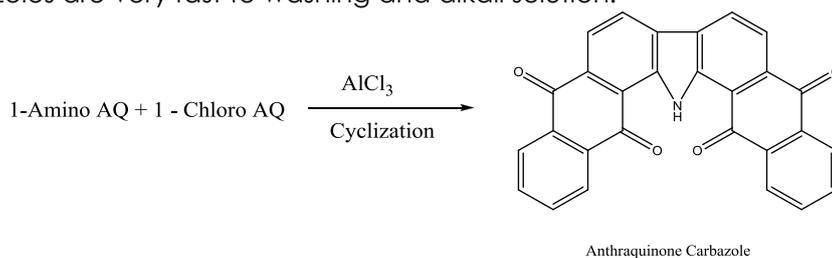
6. Algol dyes

There are many dyes belonging to this class but **Algol Yellow is important**. Chemically it is 1-benzoylamino anthraquinone which is prepared by heating the corresponding amino compound with benzoic acid



7. Anthraquinone Carbazoles

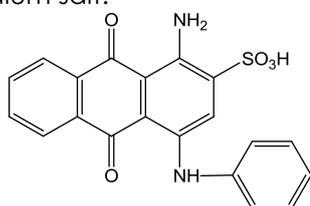
These are prepared by the **cyclization** of a **suitable dianthraquinoyl amine**. For example, a yellow coloured dye is obtained by condensation of (1-aminoanthraquinone with (1-chloroanthraquinone followed by cyclization with anhydrous AlCl_3 . Anthraquinone Carbazoles are very fast to washing and alkali solution.



3.0.2.3 Anthraquinone acid dyes

These dyes are **water soluble anthraquinone derivatives** which are used for dyeing wool, silk, nylon, leather and paper. These have **soluble sodium sulfate groups**. These are among the fastest of those dyes which are applied to wool from a sulfuric acid dye bath. However, they are **more expensive than** those of the **azo dyes**. An important example of anthraquinone acid dyes is Solway Ultrablue-B (Acid Blue-25).

It is prepared from 1-aminoanthraquinone which is sulfonated and brominated to give Bromamine acid. Condensation with aniline yields Solway Ultrablue-B which is isolated as the sodium salt.



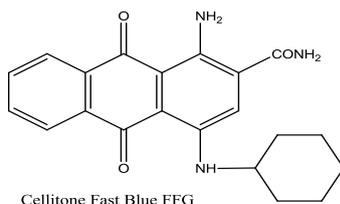
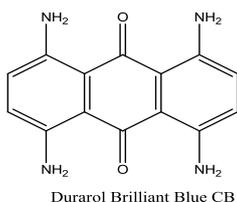
Solway ultrablue B

3.0.2.4 Anthraquinone disperse dyes

These are simple **insoluble derivatives of Anthraquinone**. These dyes are mainly used for dyeing of Acetate Polyester, Polyamide and synthetic fibers. These dyes are faster to light.

However, a **serious disadvantage** of most of these dyes is the **fading** and the **shade change** caused by **gas fumes**. This **disadvantage** has been **overcome by substituting** various **groups like** halogen, hydroxy, alkoxy, nitro and cyano groups in the **anthraquinone nucleus**.

Anthraquinone disperse dyes are more expensive than the insoluble azo dyes.



3.1 REACTIVE DYES

3.1.1 Introduction

It is a coloured organic compound which has a **suitable reactive group**, capable of forming **covalent bond** between **carbon of the dye molecule** and **N, O, SH or OH** group of **substrate**. Reactive dyes offer excellent fastness to washing since the dye becomes a part of the fiber by forming a covalent bond. In 1956 first reactive dye was introduced by ICI for the dyeing and printing of cellulose fibers. These reactive dyes were containing cyanuric chloride (2, 4, 6-trichlorotriazine) as a reactive system.

3.1.2 Application

They are applied to cellulosic fabric by a variety of dyeing process.

a) Batch dyeing process

In this process the **fibers** are **dyed** in a **batch containing salt**, a temperature is usually according to the reactivity of the dye concerned. Thus **Procion-M dyes** are applied from cold bath at 50-60°C and **Remazol dyes** at moderate temperature. Dyeing is completed within **half an hour** and at this stage **Na₂CO₃** is **added** to bring about fixation. This requires half to one hour in all case. Hydrolyzed dye is removed in final treatment with soap or detergent.

b) Semi continuous Process

This process is known as **hot bath processes**. The **fiber** to be dyed is **padded** with a **solution** of the **dye, alkali** and **wetting agent** at **20-30°C** and then allowed to stand until fixation is completed. The alkali used may be NaOH, Na₂CO₃ and NaHCO₃ for fixation. Finally remove unfixed dye by washing.

c) Continuous Process

It is carried out by **padding cloth** with a **neutral solution** of reactive dye, drying then passing it successively through a bath of caustic soda solution, a streamer, soap bath and dryer. In the case of dye of fairly low reactivity, the alkali may be applied with the dye. For light shade decomposition can be minimized by using NaHCO₃ in place of NaOH and the reaction time is reduced to a few minutes by the use of higher temperature.

3.1.3 Limitation of Reactive dyes

- Poor sublimation fastness.
- Lesser number of shades.
- Require more and skilled labors.
- More cost and technical knowledge is required.

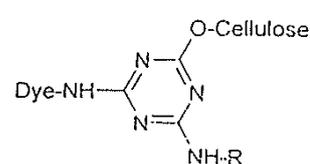
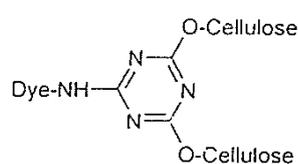
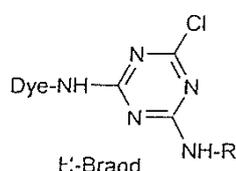
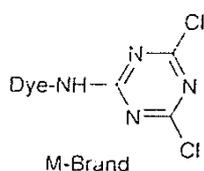
3.1.4 Classification of Reactive dyes

Reactive dyes are classified on the basis of types of reactive system present in to the dyes. **Reactive systems are mainly two types**

1. Nucleophilic substitution system (Mono and dichloro triazine, tri chloro pyrimidine etc.)
2. Nucleophilic addition system (vinyl Sulfone, acrylamide etc.)

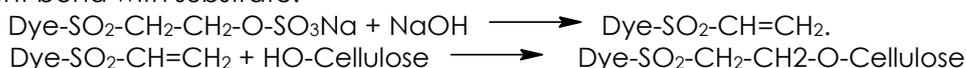
1. Procion dyes

This **class of dye** contains **Cyanuric-chloride** as a reactive system. In alkaline condition it is applied and become part of substrate. They are mainly **two types M-brand** (Cold Brand) and **H-brand** (Hot Brand), e.g. Procion Brilliant Red-M5B (Aniline → Cyanurated H-acid in alk.)



2. Remazole dyes

The **basic structure** of dye is Dye-SO₂-CH₂-CH₂-O-SO₃Na (Sodium sulfato of ethyl Sulfone). It is first marketed by F-Hoechst in 1953 for Wool and Nylon. The sodium sulfato of ethyl Sulfone group is hydrolyzed by alkali and give vinyl Sulfone group which formed covalent bond with substrate.



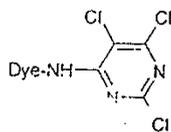
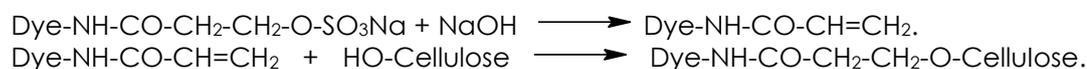
E.g. Remazole Brilliant Blue-R (Bromamine acid + m-amino phenyl sodium sulfato of ethyl Sulfone).

3. Trichloro pyrimidine dyes

These dyes are derived from **trichloro pyrimidine**. The chlorine group at 2, 5 and 6 are reactive site through it can form a bond with substrate. General formula of dye is

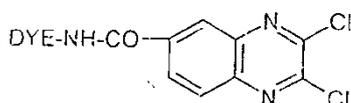
4. Acrylamide dyes

Structure which yield **acrylamide-group** on **treatment** with **alkali**. These dyes are Nucleophilic addition reactive system type dyes and principally used for wool and cellulose dyeing.



5. Quinoxaline derivative

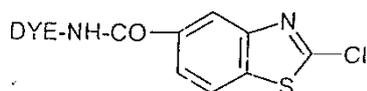
The general structure of this class is as under.



The reactive system is di-chloro quinoxaline. They are marketed as Leuafix by BAYER and Du-Pont.

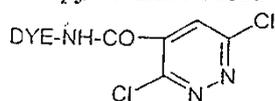
6. 2-Chloro Benzthiazole based reactive dyes

The reactive system of this class is **2-chloro benzthiazole**. The general formula is as under

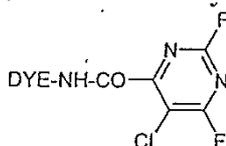


7. Chloropyridazine based reactive dyes

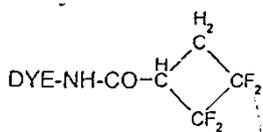
The general structure of dyes is as under and this class of dyes is marketed as Solidazole by BAYER and REATEX by Franc-Color.



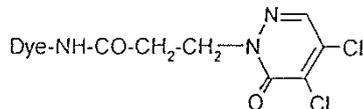
8. 2,6-difluoro-5-Chloro Pyrimidine based reactive dyes



9. Tetra fluoro butane based reactive dyes



10. 4, 5 dichloro-6-pyridazole based reactive dyes



11. Chloro acetyl or Bromo acetyl based reactive dyes

These classes of dyes are mainly **used** for the **Wool dyeing**. On which halogen acetyl group is reactive system and marketed by CIBA and SANDOZ.

Dye-CO-CH₂-X, Where X =-Cl OR-Br.

3.2 DISPERSE DYES

3.2.1 Introduction

Disperse dyes are **colored organic compounds**, which are only **very slightly soluble** in **water** and therefore, **dyeing** is carried out with **aqueous dispersion**. The disperse dyes have proved to be the **most successful type** of dye for the coloration of **cellulose acetate fibers** and are widely manufacturing in the form of powder or paste containing the requisite quantities of dispersing agent. It is **also used** on polyamide, poly-acrylonitriles, polyesters and cellulose triacetate.

Disperse dyes are essentially **low molecular weight derivatives** of azo, anthraquinone and other compounds. They **melt** at **above 150°C** and are **crystalline materials** which are ground with **dispersing agents** to produce **particles** of **0.5-4 μm** in **size** and which produce a stable dispersion in the dye bath. They are essentially **non-ionic** in **nature** and **contain** aromatic or aliphatic amino, mono and di-substituted amino and hydroxyl groups in their molecular structure. They have relatively low solubility in water under the dyeing conditions but it is at least 0.1 mg/liters.

3.2.2 Dispersion

Dispersion of disperse dyes can be achieved follows

- By using powerful dispersing agent.
- By attaching alkanol, carboxyl amide and other groups to the dye molecule,
- By using powerful dispersing agent. During the manufacturing, commercial disperse dyes are milled with a dispersing agent e.g. the sodium salt of a cresolnaphthalene sulphonic acid formaldehyde condensate plus a little sodium alkylnaphthalene sulphonate, thus enabling the particle size to be reduced to 2-4 μm, which is the maximum size for satisfactory dispersion.

3.2.3 Effect of dispersing agents

Certain dispersing agent are capable of **penetrating** cellulose acetate, but in view of the very small amounts involved it seems unlikely that the presence of dispersing agent within the fiber will have any appreciable effect on the rate of diffusion of the dye, although this would presumably not be the case if the effect of affinity or diffusion rate was appreciable.

Dispersing agents **increase** the **solubility** of the dye in the aq. phase, with **increasing temperature**, the **normal solubility** of the dye will **increase**, so that the effect of the dispersing agent in increasing the dyeing rate will be less marked. The dispersing agent also maintains a much more satisfactory dispersion thus penetrating the absorption of large particles of dye on to the surface of the fiber as well as assisting leveling by increasing solubility.

3.2.4 Leveling agent

Selected **non-ionic surface active agents** can also be used to increase the solubility of disperse dyes in water. The results in the **following benefits**, particularly when dyeing is carried out at temperature below the normal boiling point:

- Increased **rate of migration**, leveling and fiber penetration.
- Increased **rate of dyeing** of the relatively insoluble, more complex dyes. This is of advantage when disperse dyes of better than average wet fastness are applied to acetate and nylon.

- Less **tendency for** listing and ending in jig dyeing.

3.2.5 Classification

Disperse dyes can be classified according to their application on different fibers such as polyester, polyamide, polyacrylonitrile etc.

But chemically it can be classified into three well defined groups

- The **azo group** containing mostly monoazo derivatives.
- The **nitrodiphenylamine derivatives**.
- The **anthraquinone derivatives**.

Beside the simple anthraquinone, many derivatives having attached carboxylic or heterocyclic rings such as benzantraquinones, benzantrones, anthrapyridones, anthrapyrimidines, anthrapyrimidones are reported to be disperse dyes.

Almost all the classes contain amino or substituted amino groups, but no solubilising sulphonic acid groups.

Generally the anthraquinone derivatives are used for deeper shades like red, violet and blue. The less deep shades are obtainable from the azo series. However Duranol Brilliant yellow G3, ICI (3-methoxy benzanthrone) has been found to give yellow shade on cellulose acetate.

The shade of anthraquinone dyes for acetate depend upon the kind of auxochromes, their number and orientation, Auxochromes in the alpha position are more effective in shade changes, than those in the beta position. In general the effect of the auxochromes is additive. Introduction of substituent's such as halogen, hydroxyl, alkoxy, nitro, cyano, and other groups is reported to improve the fastness properties.

Strong salt forming groups and groups promoting water solubility generally decrease the affinity of dye.

Examples of Disperse dyes

- Disperse Yellow-3 (p-aminoacetanilide → p-Cresol).
- Disperse Black-1 (p-NA → α-naphthylamine).
- Disperse Yellow-9 (p-PDA + 1-chloro 2,4-dinitrobenzene).
- Disperse Yellow-11 (1, 4-diamino-2-methoxy AQ).
- Disperse Blue-1 (1, 4, 5,8-Tetra AQ).

3.3 INDIGOID DYE